The hard X-ray performance of pixelated CdTe-based detectors using Monte Carlo and ab initio simulations

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Abstract

The performance of pixelated semiconductor radiation detectors based on cadmium telluride (CdTe) were investigated using experimental, Monte Carlo and *ab initio* methods for their detection of hard X-rays while operating at room temperature.

To achieve the imaging, photon-counting and energy-resolving requirements of CdTe-based detector applications, pixelated detector designs are commonly used. Charge sharing and fluorescence interference as a result of pixelation, and distortions of the electric field profile, severely impact the performance in these detectors. Inhomogeneities and defects in the crystals due to on-going growth challenges of CdTe also limit performance.

The photon-counting and spectral performance of a novel high-flux capable CdZnTe (HF-CdZnTe) is measured at photon energies 6 to 140 keV and compared with a gold-standard CdTe detector. Factors contributing to the energy resolution of charge sharing events such as charge loss and fluorescence are quantified. A fully spectroscopic Monte Carlo (MC) detector model is developed and shown to accurately predict the rate of charge sharing in these detectors. By comparing experimental and MC simulated data, a number of quantities related to performance such as the size of the electron charge clouds, the strength of the electric field and the Zn concentration in the HF-CdZnTe material are estimated.

Using density functional theory (DFT), alloys of CdTe that are in early stages of development for radiation detection are studied from *ab initio*. The formation of the cadmium vacancy defect (V_{Cd}) in Cd_{1-x}Mn_xTe and Cd_{1-x}Mg_xTe crystals is studied and compared with the more well established Cd_{1-x}Zn_xTe system. The V_{Cd} formation energy as a function of alloy concentration x is calculated to help understand the defect concentrations and resistivity in these alloys. The effect the addition of Mn and Mg have on the physical properties of CdTe, including phase transitions of their lattices, are also determined.

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Chapter 1

Introduction

1.1 Motivation

Pixelated CdTe-based detectors can perform direct imaging and spectroscopic measurements of photons with hard X-ray energies while operating at room temperature. This has many useful applications such as in gamma-cameras for nuclear medicine, as the focal-plane detector in future hard X-ray, space-based telescopes or as the detectors for next-generation high-flux imaging at synchrotrons. Inevitably, there are a number of challenges which can strongly limit their performance including charge sharing between pixels, polarisation of the electric field and the growth of large volume, high-purity crystals with suitable resistivity and defect concentrations.

In this thesis we use experimental, Monte Carlo and *ab initio* methods to improve our understanding of some of the factors limiting the performance in pixelated CdTe-based detectors at hard X-ray energies. In particular, we focus on the performance of a novel high-flux capable CdZnTe material. Using *ab initio* simulations we study alloys of CdTe which have not yet received as much attention as CdZnTe, but have the potential to overcome some of the growth challenges which limit performance.

1.2 A brief history of X-ray detection using semiconductors

The first demonstration of a fully spectroscopic semiconductor detector can be attributed to van Heerden who in 1945, using cooled sliver chloride (AgCl) crystals, measured the energy of ionising radiation and charged particles [1]. In 1947, Hofstadter [2] expanded on this by showing that the thallous halides TlBr and TlI could also be used in such a detector. For the realisation of high performance spectroscopic capable detectors, good energy resolution and high counting efficiency are required. Although the first examples of solid-state detectors used compound semiconductors, material growth problems and low purity crystals meant poor counting efficiencies and large energy resolutions (~20%) limited their usefulness. Instead, the use of the elemental semiconductors silicon (Si) and germanium (Ge) for radiation detection, first demonstrated by McKay and McAfee in 1953 [3], became the dominant medium in semiconductor industry in the 1960s. Since, Si and Ge have set the laboratory standards on performance. Advances in crystal growing techniques over the past few decades, mean the fabrication of high-quality compounds is now possible. This has lead to a renewed and on-going interest in the use of compound semiconductors for radiation detectors. Their performance has evolved sufficiently that they increase the scope of possible applications for semiconductor detectors, while having become viable competitors to Si and Ge.

The emergence of practical solid-state radiation detectors based on semiconductors, with their compact size and direct detection, meant that detectors with a number of advantages over already existing detector technologies at the time became available. Compared to gas-filled detectors, semiconductor detector dimensions can be kept much smaller and more compact due to solid densities being some 1000 times greater than that for a gas. In comparison to scintillation detectors, which use a solid scintillating material and photomultiplier tubes to amplify the scintillation light, direct detection with semiconductors has the advantage of fewer components introducing a response on the incoming signal and limiting the best spectral (energy) resolution attainable. Direct detection and higher densities also mean that faster timing characteristics can be achieved. For these reasons, semiconductor radiation detectors are a popular choice for X-ray detection and have seen much research and development since first used.

1.3 Compound semiconductors for hard X-ray spectroscopy

Compound semiconductors refer to crystals that are composed of two or more elements, generally from groups II to IV of the periodic table, and are neither great conductors nor insulators. The application of compounds in radiation detectors is of substantial interest given the shear range of compounds possible, compared to the limited number of elemental semiconductors. This creates the opportunity to engineer a material for use in a specific application and improve on the physical limitations of Si and Ge. Wide band gap compounds offer the ability to operate at room temperature and in extreme radiation environments, and high-Z (atomic number) compounds are capable of efficiently stopping hard X-ray (\sim 10-100 keV) and gamma-ray (>100 keV) photons. Detailed introductions on compound semiconductors and reviews of their use in detectors can be found in Owens and Peacock [4] and McGregor and Hermon [5].

Table 1.1 shows the physical properties of the elemental semiconductors compared with the high-Z wide band gap compounds that have in recent decades evolved sufficiently to produce working detection systems. The material properties largely define the performance of a detector. The smaller band gap of Si and Ge mean that the average pair creation energy is also small such that large numbers of electron-hole pairs are created during the ionisation process of X-ray detection. This has the effect of reducing the statistical variation of charge carrier generation, which improves both the signal-to-noise ratio and the energy resolution. Smaller band gaps however also make the material prone to significant thermal leakage currents (i.e. noise), requiring the detector system to be operated at cold (\sim -30°C) or even cryogenic temperatures (\sim -120°C) to take advantage of the excellent energy resolution. In addition, Si becomes practically transparent to photons with energies above 20 keV because of its low density and atomic number, restricting its application to the soft X-ray regime (\sim 0.1-10 keV). Ge can be used to detect hard X-rays and gammarays, although thick high-purity crystals (HPGe) are required, which are both expensive to produce and require operation at liquid-nitrogen temperatures.

The wide band gaps of the compounds listed in table 1.1 increases their resistivity, which reduces leakage currents and allows the detectors to be spectroscopic at higher temperatures, eliminating the need for bulky cooling systems. Higher Z and densities improves their stopping power such that the compounds are sensitive to hard X-rays without having to be made very thick (see the average absorption depth at 100 keV in table 1.1). Smaller thicknesses mean a lower bias voltage (electric field) can be used to sweep out the charge carriers to the collecting electrodes, which further helps reduce leakage currents. Compounds can also be alloyed with a substitute element of the same group to form ternary or quaternary compounds. Depending on the alloy atom and concentration, the properties of the material are modified - as for example CdTe alloyed with 10% ZnTe to produce $Cd_{0.9}Zn_{0.1}Te$ (see table 1.1).

Unfortunately, the transport of the charge carriers in the compounds is significantly worse than in the elemental semiconductors, with either much shorter carrier lifetimes or lower mobilities, or both. Together the two transport properties define the mobility-lifetime ($\mu\tau$)

| Parameter | Ge | Si | GaAs | CdTe | $\mathrm{Cd}_{0.9}\mathrm{Zn}_{0.1}\mathrm{Te}$ | HgI_{2} | PbI_2 | TlBr |
|----------------------------------------------------------------|--------------------|-------------|--------------------|--------------------|-------------------------------------------------|--------------------|--------------------|----------------------|
| Band gap (eV) | 0.67 | 1.12 | 1.43 | 1.44 | 1.57 | 2.15 | 2.32 | 2.68 |
| Pair creation energy (eV) | 3.62 | 2.96 | 4.2 | 4.43 | 4.64 | 4.2 | 4.9 | 6.5 |
| Average Atomic number Z | 32 | 14 | 31.5 | 50 | 49.1 | 62 | 63 | 58 |
| Density (g $\rm cm^{-3}$) | 5.33 | 2.33 | 5.32 | 5.85 | 5.78 | 6.4 | 6.2 | 7.56 |
| Electron mobility $(cm^2V^{-1}s)$ | 3900 | 1400 | 8000 | 1100 | 1000 | 100 | 8 | 30 |
| Hole mobility $(cm^2V^{-1}s)$ | 1900 | 1900 | 400 | 100 | 120 | 4 | 2 | 4 |
| Electron lifetime (s) | $> 10^{-3}$ | $> 10^{-3}$ | 10^{-8} | 3×10^{-6} | 3×10^{-6} | 3×10^{-6} | 10^{-6} | $2.5{\times}10^{-6}$ |
| Hole lifetime (s) | $2{\times}10^{-3}$ | 10^{-3} | 10^{-7} | 2×10^{-6} | 10^{-6} | 10^{-5} | 3×10^{-7} | 4×10^{-5} |
| Electron $\mu \tau$ product (cm ² V ⁻¹) | >1 | >1 | 8×10^{-5} | $3{	imes}10^{-3}$ | 4×10^{-3} | $3{	imes}10^{-4}$ | 10^{-5} | $5{	imes}10^{-4}$ |
| Hole $\mu \tau$ product (cm ² V ⁻¹) | >1 | ~ 1 | 4×10^{-6} | $2{\times}10^{-4}$ | 1.2×10^{-4} | 4×10^{-5} | 3×10^{-7} | 2×10^{-6} |
| Resistivity (Ω/cm) | 50 | $< 10^{4}$ | 10^{7} | 10^{9} | 3×10^{10} | 10^{13} | 10^{13} | 10^{12} |
| Av. abs. depth (mm) at 100 $\rm keV$ | 3.51 | 23.30 | 3.46 | 1.01 | 1.01 | 0.46 | 0.453 | 0.32 |
| Typ. $\Delta E_{\rm FWHM}~(\rm keV)$ at 60 keV | 0.3 | 0.4 | 0.7 | 1.1 | 1.5 | 3.5 | 1.8 | 7.9 |
| Fano-limited $\Delta E_{\rm FWHM}$ (keV) at 60 keV | 0.25 | 0.4 | 0.44 | 0.30 | 0.39 | 0.41 | 0.44 | 0.55 |

Table 1.1: Physical properties of the elemental semiconductors compared with the high-Z wide band gap compounds that are currently the most researched for use in radiation detectors, sorted from smallest to largest band gap. Values reproduced with permission from [4].

product of the material, which is one of the most crucial indicators of performance in these devices. The poor $\mu\tau$ -products is due to imperfections such as point and extended defects in the crystal which trap the moving charges and reduce lifetimes, and generally lower mobilities at larger band gaps due to lattice scattering effects [6]. The defect concentrations are higher in compounds because of greater growth challenges to produce high-purity crystals than with the simpler mono-crystals Si and Ge. Trapped charges do not contribute to signal induction (section 2.4.4), resulting in incomplete charge collection (charge loss) which can significantly degrade spectroscopic and counting performance. The decreased carrier drift lengths from poor $\mu\tau$ products also limit the maximum thickness and therefore energy range at which the detectors can effectively operate.

By inspection of the physical properties of the compounds shown in table 1.1, we can draw a few conclusions on their use in radiation detectors. Due to the smaller band gap, GaAs exhibits good spectral resolution but its poor carrier lifetimes and modest resistivity severely limit the maximum thickness at which it can be used practically. The large Z and resistivity of HgI₂, PbI₂ and TlBr offer attractive stopping powers and low leakage currents respectively, but the large band gaps come at the cost of reduced energy resolution and very low carrier mobilities. CdTe-based crystals, with their modest carrier transport and a band gap and Z positioned between the former and latter mentioned compounds, are therefore well placed for hard X-ray detection at room temperature.

1.4 The current state of CdTe-based detectors

Large crystals of Cadmium Telluride (CdTe) practical for radiation detection, were first synthesised by de Nobel in 1959 [7]. The potential of the material was quickly realised and although research was initially incremental, significant advancements in material growth in the mid-nineties has since lead to commercially available, high-quality CdTe-based crystals and a resurgence in their research [8, 9]. Notably, the addition of Zinc (Zn) to create $Cd_{1-x}Zn_xTe$ has increased the material's popularity due to a number of advantages, with CdZnTe now gradually superseding CdTe as the compound of choice for detectors [4]. Alloying with Zn increases the band gap [10] which improves the resistivity such that thicker crystals, larger bias voltages or high operating temperatures can be used due to lower leakage currents. Typically, the Zn concentration is of the order of 10-20% [11], at which the favourable photoelectric interaction probability of CdTe (over ZnTe) is mostly retained. The addition of Zn has also been shown to increase the energy of defect formation [12] and to reduce the formation of crystal dislocations during growth [13]. Both of these effects serve to decrease defect densities and improve crystal homogeneity, which is an important factor to ensure uniform performance across the volume of the detector.

High purity Cd(Zn)Te crystals can be grown using a number of different techniques. CdTe is typically grown using the travelling heater method (THM) and doped with Cl to compensate native defects and to improve resistivity [14]. CdZnTe is commonly grown using Bridgman methods [14, 15], although more recently the THM has also been used [16, 17]. Cd(Zn)Te detectors are generally fabricated using metal-semiconductormetal structures [8] as opposed to using semiconductor-junctions [18] which must be operated at cooler temperatures. Blocking metal contacts are used with CdTe to form Schottky diode detectors, which are required in order to suppress leakage currents to necessary levels. However, it is has been shown that CdTe used with blocking contacts under bias leads to temporal instabilities due to the so-called polarisation effect [19, 20]. In this effect, trapped charge carriers lead to the buildup of space charge which progressively degrade the electric field, and the blocking contacts prevent the space charge from leaving the detector. A weakened electric field damages both the counting and spectroscopic performance. Due to the greater intrinsic resistivity of CdZnTe, blocking contacts are not required and ohmic contacts can be used instead. As a result, CdZnTe detectors exhibit much better temporal stability as bias-induced polarisation is largely mitigated [21].

Despite advances in growth techniques, high-purity Cd(Zn)Te crystals still contain many imperfections such as Te inclusions, dislocations, grain boundaries, twins and even cracks [11]. Numerous studies have shown that these defects and compositional inhomogeneities directly limit the performance of Cd(Zn)Te detectors [22–25]. Inhomogeneities prevent the detectors from producing a uniform response and the defects act as trapping centres for the charge carriers. Greater trapping probabilities lead to a reduction in carrier transport properties and trapped charges can produce local electric fields which distort the field produced by the applied bias. The performance of Cd(Zn)Te crystals is particularly affected by its hole mobility which is approximately an order of magnitude smaller than the electron mobility. Hole trapping reduces the charge collection efficiency and produces low-energy tails (known as hole tailing) in spectra [26].

To minimise the impact of the poor hole transport, single carrier sensing techniques are often employed in Cd(Zn)Te detectors [8]. Amongst other methods, this can be implemented by using a pixelated detector design and taking advantage of the so-called small pixel effect [27], achieved when the pixel pitch is small compared to the detector thickness. This effect changes the weighting potential in the detector such that a significant charge is only induced by charge carriers drifting close to the collecting pixel. In such a design, it is possible to operate the detector such that it predominately measures the signal induced by the electrons. This improves the spectral performance due to the better transport of the electrons over the holes. The position sensitive characteristics of a pixelated detector also enable imaging and greatly improve photon counting capabilities due to the array of multiple collecting electrodes. Several application-specific integrated circuits (ASICs) have been developed such as Medipix [28], Timepix [28], IBEX [29] and HEXITEC [30] and used to readout Cd(Zn)Te detectors with pixelated electrode designs, the latter of which is used in this work (section 3.2).

One of the main drawbacks of using a pixelated detector is the onset of charge sharing, which has been shown to severely affect performance in Cd(Zn)Te detectors [31–36]. Charge sharing refers to when a single absorbed incident photon induces a signal that is distributed across multiple pixels (shared events), mainly due to the charge cloud spreading as a consequence of diffusion and Coulomb repulsion during drift [37]. This is an issue because of charge losses to the inter-pixel gaps which degrades spectral resolution. The reasons for these charge losses have been linked to the presence of distorted electric fields in the gaps which worsen charge collection efficiencies [33,38,39], and induced-charge pulses (or transient pulses) in pixels adjacent to the collecting pixel due to weighting potential cross-talk [32,40]. Charge sharing can also lead to the loss of counts if the energy is split amongst too many pixels and drops below a noise threshold. For small pixel array detectors, it has been shown that charge sharing affects the majority of detected events at hard X-ray energies [35, 36]. Due to the high Z of CdTe, the fluorescence from the material is of considerable energy (Cd K_{α}: 23 keV,Te K_{α}: 27 keV) that it can interfere with the incoming X-ray signal. This is further complicated due to the fluorescence having mean attenuation ranges in CdTe (60 - 100 µm) that can be comparable to the pixel size. As a result, the fluorescence can cause additional charge sharing events if it escapes into adjacent pixels, as has been observed [35, 36].

A first consideration to reduce the charge loss from charge sharing is to minimise the pixel gap to pixel pitch ratio as much as possible [33, 38]. Biased steering grids have also been used to redirect the electric field lines to the contacts and thereby reduce charge loss, but these introduce additional surface leakage currents which increase noise [32,41]. Wellestablished methods such as charge-sharing discrimination (CSD), where shared events are simply removed, or charge-sharing addition (CSA), where all energies in a shared event are summed, are often used to correct for charge sharing in post-processing. However, it has been shown that these methods are limited in Cd(Zn) Te detectors because CSD leads to the loss of many counts and CSA, while including all counts, does so at poor energy resolution due to the charge losses [42]. Recently, a novel energy-loss correction technique for charge sharing events has been developed [36] and applied to Cd(Zn)Te detectors [36,42–46]. Although this technique significantly improves the energy resolution of charge sharing events by recovering some of the lost charge, to optimise performance it needs to be calibrated for each type of charge sharing event specifically e.g. fluorescence shared events [42,46] or higher multiplicity (more pixels) shared events [46] due to differences in their energy response.

The ongoing interest in CdZnTe has led to the recent development and growth of a novel CdZnTe material by Redlen technologies optimised for high-flux applications (HF-CdZnTe) [47] (section 1.5). At high fluxes, the electric field in standard CdZnTe crystals can collapse due to a large number of local electric fields produced by the buildup of trapped charge carriers, in particular the holes [48]. In tests with HF-CdZnTe under irradiation by very high photon fluxes (>10⁶ ph s⁻¹ mm⁻²) [49–51], no flux-induced polarisation effects were observed. The better performance at high-flux is believed to be a consequence of the improved hole transport in the HF-CdZnTe material, which was measured by Thomas et al. [52]. The improved hole transport, at the cost of reduced electron transport, will likely also have implications on the spectroscopic performance.

A number of different ternary and quaternary alloys based on CdTe have been proposed as possible future replacements for CdZnTe detectors used for hard X-ray room temperature applications [4]. Of these compounds, the most promising candidates with which spectroscopic results have been obtained are $Cd_{1-x}Mn_xTe$ [53], $Cd_{1-x}Mg_xTe$ [54] and $Cd_{1-x}Zn_xTe_{1-y}Se_y$ [55]. Alloying with Mn or Mg instead of Zn has several theoretical advantages which could translate to higher-purity crystals and lower production costs, making these materials attractive potential alternatives to CdZnTe. A detailed review of the development and progress of CdMnTe and CdMgTe detectors is provided in section 7.1.

1.5 Hard X-ray CdTe-based detector applications

Owing to the higher operating temperatures and increased sensitivity to hard X-rays while retaining the benefits of semiconductor detectors in general, CdTe-based detectors are useful in several applications. Notably, CdTe-based detectors are of interest in fields such as nuclear medicine [56,57] and high-energy astrophysics [58,59] where portable or low mass designs are favourable while imaging and spectroscopy of hard X-rays and gamma rays is required. Since using CdTe allows for direct photon detection, and without bulky cooling equipment such as cryostats, volume and mass requirements are considerably reduced. Pixelated CdTe detector designs can be used to achieve the imaging (spatial resolution), photon-counting and energy-resolving requirements of its applications.

In nuclear medicine (NM) a radioisotope is administered into the body for diagnostic or treatment purposes. Detectors (gamma cameras) are then used to measure the gammarays emitted from the radioisotope to image the body's uptake and for dosimetry purposes. Commonly used radioisotopes are ^{99m}Tc, ¹³¹I and ¹³⁷Cs which emit characteristic highenergy photons at 140 keV, 364 keV and 662 keV respectively. Most current NM detectors are based on the Anger-type design [60] in which a NaI(Tl) scintillator is used to convert the high-energy photons into scintillation light which is then measured using an array of photomultiplier tubes. Gamma cameras based on CdTe enable better energy resolution and by using sub-millimeter pixel pitch, much higher spatial resolutions can also be achieved. This has motivated the development of Cd(Zn)Te detectors for NM [61]. To obtain the same absorption efficiency as NaI with a typical 9.5 mm thickness, very thick CdZnTe crystals of at least 8 mm are needed - shown by figure 1.1. In such thick, pixelated CdZnTe detectors, the poor $\mu\tau$ -products and charge sharing will severely place limits on performance.

The more violent an astrophysical phenomenon, the higher energy photons it tends to emit. Although high-energy gamma-rays can be detected from the ground, hard X-rays and low-energy gamma-rays struggle to penetrate the atmosphere and must therefore be



Figure 1.1: Theoretical photoelectric absorption efficiency as a function of photon energy for typical thicknesses of various semiconductors and NaI. Absorption coefficients obtained from NIST XCOM [62].

observed from space. Semiconductor detectors have become the workhorse X-ray detector technology in space due to their superior spectral performance and the strict mass and power constraints on space telescopes, which solid-state detectors lend themselves well to. Early large X-ray observatories in space (e.g. ROSAT, XMM-Newton, Chandra) all observed in the soft X-ray regime due to limits of the X-ray focusing optics' (i.e. Woltertype) sensitivity above 10 keV. At these energies Si detectors still show good efficiency (figure 1.1) and were therefore used. Pixelated Cd(Zn)Te detectors have successfully been used in space to detect hard X-rays (10 - 150 keV) on missions such as INTEGRAL, SWIFT and Astrosat, using coded apertures to focus the X-rays. The use of coded apertures however limits the use of CdTe-based detectors to large field-of-view (FOV) and coarse angular resolution applications, such as gamma-ray burst detection.

The NuSTAR observatory launched in 2012 was the first to focus hard X-rays using Wolter-type optics by increasing the focal length and applying multi-layer coatings to the mirrors [63]. This enabled the use of CdZnTe to detect X-rays from 3-79 keV and achieves much higher angular resolution (albeit smaller FOV) in the order of arcseconds, as opposed to arcminutes when using coded apertures. The ability to focus hard X-rays using Wolter-type mirrors and the ongoing development of several novel X-ray optics capable of achieving arcsecond angular resolutions even at hard energies [64–66], mean pixelated CdTe-based detectors may become the focal-plane detectors of choice for the next-generation of hard X-ray telescopes. To take advantage of the higher angular resolutions attainable, small pixels will be needed and consequently a CdZnTe detector based on the successful NuSTAR design is being developed in which the pixel pitch is being reduced from $605 \,\mu\text{m}$ to $\sim 150 \,\mu\text{m}$ [67].

With the development of the HF-CdZnTe material, CdZnTe detectors have the potential to be used in high-flux applications. Next-generation upgrades at synchrotron facilities [68] and the recent increase in new or planned commissions of X-ray free electron lasers (XFELs) [69], will deliver X-ray beams with greater brilliance and higher energies to probe and study materials. This demands detectors with fast timing characteristics and good absorption up to 100 keV, such that Cd(Zn)Te sensors are being investigated to replace Si sensors in these applications [70]. Small pixels ($\leq 100 \,\mu$ m) are preferred in order to provide the best possible spatial resolution for imaging and to reduce saturation of individual pixels under high-flux. Since the detectors will operate as charge integrators as opposed to photon counting in this application, precise calibration will be crucial for converting the recorded charge into the number of photons detected [70]. To achieve this, an understanding of charge sharing at these small pixel sizes is essential.

1.6 Synopsis

Whether pixel sizes are reduced or sensors are made thicker to meet the demands of the specific applications, design changes will impact the performance of CdTe-based detectors. The detection of higher energy photons and longer charge carrier drift times associated with thicker crystals will result in increased charge sharing, as will smaller pixels. Poor carrier transport properties limit charge collection efficiency and become more noticeable in thicker sensors. These effects however are not straightforward as they are influenced by numerous factors such as the detector geometry (e.g. small-pixel effect), electric field profile, sensor fluorescence and crystal uniformity. Given the large number of influencing factors, the utilisation of computational methods is a convenient approach to predict the performance and trade-offs of a detector as design parameters are changed.

In this thesis, we use Monte Carlo simulations combined with experimental measurements to describe the observed performance in pixelated Cd(Zn)Te detectors and predict the performance of future designs at hard X-ray energies (up to 140 keV). We focus on the spectral performance of a 2 mm thick HF-CdZnTe detector and how it is impacted by charge sharing and sensor fluorescence, as these effects are expected to become more severe as detectors become thicker and pixels smaller. We also use density functional theory (DFT) simulations to calculate from first-principles (*ab initio*), the properties of CdTebased crystals that influence performance. This is a particularly powerful tool for investigating new potential materials which have not yet received the same level of experimental investigation as Cd(Zn)Te, and we therefore apply it to study defects in Cd_{1-x}Mn_xTe and Cd_{1-x}Mg_xTe crystals.

In chapter 2 we review the theory of X-ray detection with semiconductor detectors and describe the DFT method. Chapter 3 describes the calibration and characterisation of the 2 mm HF-CdZnTe detector used with a HEXITEC ASIC to perform the spectroscopic readout, compared with a standard 1 mm CdTe detector. In chapter 4 we describe the development of a Monte Carlo model which simulates the response of Cd(Zn) Te detectors to hard X-rays. We validate the model against experiment and use it to estimate the Zn concentration in the HF-CdZnTe material, which has not previously been determined. In chapter 5 we calculate the spectral resolution of different types of charge sharing events, including those influenced by sensor fluorescence. We also calculate the charge sharing rates in the detectors from experimental and simulated data, and predict charge sharing rates in possible detector designs for high-flux imaging. In chapter 6 we introduce the frameworks used to simulate CdTe-based crystals in DFT and perform calculations for simple bulk CdTe crystals. In chapter 7 we calculate the physical properties and formation energies of the cadmium vacancy defect as a function of alloy concentration x in $Cd_{1-x}Mn_xTe$ and $Cd_{1-x}Mg_xTe$ crystals and compare with $Cd_{1-x}Zn_xTe$. Finally, chapter 8 summarises the conclusions of this work and suggests future directions for subsequent research.

1.7 Contribution to the work

The HEXITEC system and detectors were designed and manufactured independently of myself and the University of Leicester, and were loaned from STFC RAL for the purpose of this research.

I fully performed the characterisation of the HF-CdZnTe detector presented in chapter 3, including data collection, calibration and analysis. I also performed the calibration and analysis of the CdTe detector, but the data was collected by colleagues within the research group. I developed the tool chains used for the calibrations and analysis. The Monte Carlo detector model described in chapter 4 was fully developed and coded from the ground up by me. I also performed the charge sharing analysis and simulations presented in chapter 5. The density functional theory (DFT) calculations described in chapters 6 and 7 were

fully carried out by me, using existing third-party DFT codes.

Chapter 2

Theory and background

2.1 Introduction

In this chapter we present the theory behind the physics, technologies and methods used throughout this work. The principles of X-ray detection with semiconductors is described, which includes the interaction of X-rays with matter, the basics of charge generation and transport and how this results in the detection of a signal. Common designs and approaches to operation for detectors based on CdTe are reviewed and factors affecting detector performance, such as charge collection efficiency and energy resolution, are discussed. We also introduce the density functional theory (DFT) method. We provide the necessary background to understand the theoretical approach of the method and describe how it is used in practice to calculate the properties of materials from first-principles.

2.2 Interaction of X-rays with matter

2.2.1 Beer-Lambert law

When an X-ray is incident on matter, it either passes through the material or is attenuated by scattering or absorption. The Beer-Lambert law describes the transmission of light through a material by [71]

$$I = I_0 e^{-\mu x} \tag{2.1}$$

where I is the intensity of the beam after passing through the material, I_0 is the original intensity, x is the thickness of the material and μ is the linear attenuation coefficient which is a measure of the number of photons that interact (i.e. cross-section) with the specific material. The attenuation coefficient in equation 2.1 is a sum of the individual coefficients of all the possible forms of attenuation which, for X-rays, are the photoelectric effect (μ_{pe}), coherent scattering (μ_{cs}), incoherent scattering (μ_{incs}), and pair production (μ_{pp})

$$\mu = \mu_{pe} + \mu_{comp} + \mu_{coh} + \mu_{pp}. \tag{2.2}$$

The linear attenuation is a function of the energy of the X-ray and also depends on the material (i.e. atomic number, Z) and the density of that material. The mass attenuation coefficient, M, is independent of the density and therefore related to the linear attenuation coefficient by

$$M = \frac{\mu}{\rho} \tag{2.3}$$

where ρ is the density of the material. Figure 2.1 shows the mass attenuation coefficients for each form of attenuation in CdTe as a function of the incident photon energy. From 1 to ~200 keV, absorption via the photoelectric effect is the dominant form of attenuation and defines the energy region over which direct radiation detection with semiconductors is most effective. In energy regions where incoherent scattering is dominant, the response of a detector is complicated by the effects of Compton scattering (section 2.2.3), although complete detection of a photon signal is still possible.



Figure 2.1: Mass attenuation coefficients of CdTe for each attenuation form as a function of photon energy from 1 to 10,000 keV. Absorption edges due to the photoelectric effect are annotated. Adapted from [62].

From figure 2.1 we see that that attenuation by pair production, where a photon interacts with the strong electric field around the nucleus, does not begin to occur until 1.022 MeV. This is above the photon energy where the use of CdTe based detectors is practical. Pair production is therefore not further discussed in this work. The forms of attenuation which are important for radiation detection with CdTe in the hard X-ray range are described in sections 2.2.2 to 2.2.4.

2.2.2 Photoelectric Effect

The photoelectric effect occurs when a photon interacts with a bound electron in an atom and has an energy equal to or greater than the binding energy of that electron. The magnitude of the binding energy depends on the Z number of the element and the shell (or orbital) in which the electron is bound. The closer the shell is to the core of the atom, the greater the binding energy of its electrons. In the photoelectric effect the incident photon is completely absorbed, transferring all its energy to the absorber electron. The electron is thus freed from the shell with an energy equal to

$$E_e = E - E_b \tag{2.4}$$

where E is the incident energy of the photon, E_b the binding energy of the electron and E_e the total energy of the excited electron. Electrons freed from an atom due to the photoelectric effect are referred to as photoelectrons and the atom is in an excited state. Figure 2.2 is a simple schematic outlining the photoelectric effect, with path a showing the process described so far and path b illustrating the resulting cascading of electrons. The photoelectron leaves a vacancy site behind in the shell from which it was liberated. The atom will try to return from its less stable excited state to its lowest energy relaxed state (i.e. ground-state), by releasing the held energy. This occurs when an electron from a shell with a lower binding energy (i.e. a more outer shell) fills the vacancy left by the photoelectron. A new vacancy on the more outer shell is then created which will be filled by an electron from an even lower binding energy shell. The process continues until the most outer shell is reached and/or the vacancy is filled through capture of a free electron.

The transition of electrons towards the inner shells releases energy in the form of emitted photons, referred to as fluorescent X-rays. These may escape the atom or result in a non-radiative transition due to the Auger effect. Only certain transitions are allowed, each with a characteristic energy defined by the energy difference between the two shells involved. Possible transitions between the K, L, M and N-shells are shown in figure 2.3.



Figure 2.2: Schematic showing the photoelectric effect and the consequential emission of fluorescent photons as vacancies are filled. Path a shows the excitation of an electron due to incoming radiation. Path b shows the cascading of electrons and photon emissions as the atom relaxes. The representation of electrons as points along a shell is crude and only done to demonstrate the general behaviour.

The number of shells around an atom depend on the electron configuration of the element. The binding energies of the shells correspond to absorption edges, indicated in figure 2.1, where the attenuation coefficient sharply rises from the additional absorption cross-section of the shell.



Figure 2.3: Possible electron transitions and their typical notation (Siegbahn), when filling vacancies in the K or L shell. Adapted from [72].

The photoelectric attenuation coefficient is proportional to Z^5 . Since it is the only form

of attenuation which leads to the total absorption of the incident energy, maximising this value for radiation detection is crucial as it increases the energy range in which photoelectric absorption is dominant. For compounds, the absorption is generally most influenced by the element with the highest Z number rather than the average effective Z. This is convenient particularly for the ternary compounds like CdZnTe where one element has significantly lower Z, such that the benefits of alloying come at a minimal cost to absorption cross-sections.

2.2.3 Incoherent scattering

The primary form of incoherent scattering for X-rays is Compton scattering where a photon collides with a charged particle, usually a free electron. The direction of travel of the incident photon changes and a portion of its energy is transferred to the electron that the photon interacts with, referred to as the recoil electron. Compton scattering is therefore a partial absorption process (i.e. inelastic scattering) where the energy of the resulting scattered photon is related to the angle, θ , by which it is deflected and derived by Compton to be [73]

$$E' = \frac{E}{1 + \frac{E}{m_e c^2} (1 - \cos \theta)}$$
(2.5)

where E is the incident energy of the photon, E' the energy of the photon after it has been scattered, m_e the electron mass and c the speed of light. The angle by which the photon is scattered depends on the energy of the photon and is given by the Klein-Nishina formula, which is described as part of the detector model in section 4.4.1.2. The Compton scattering cross-sections are proportional to Z.

2.2.4 Coherent scattering

Coherent or Rayleigh scattering is a form of elastic scattering which occurs when the photon wavelength λ is much larger than the particle ($\lambda > 10$ times the particle size). This process is therefore only significant at relatively low photon energies and decreases as the photon energy increases with a dependence of λ^{-4} . In a Rayleigh scattering event, the photon does not have an energy greater than the binding energy of the bound electrons and so no energy is absorbed. Thus, when the photon scatters, its direction changes but its energy does not. The possible scattering angles have been determined empirically from numerical fitting and is described in section 4.4.1.1.

2.3 Charge carrier transport

2.3.1 Charge generation

The photoelectron produced in the semiconductor from the absorption of an X-ray excites valence electrons across the band gap into the conduction band due to impact ionisation. The average number of electron-hole pairs generated, N, is proportional to the energy of the photoelectron, E_e ,

$$N = \frac{E_e}{\omega} \tag{2.6}$$

where ω is the average electron-hole pair creation energy which is related to the band gap and is therefore material dependent. The number of electron-hole pairs (charge carriers) created is subject to random variations assumed to follow a Poisson distribution, with the standard deviation given by $\sigma = \sqrt{N}$. However, it is now well known that the variation of N is not fully described by Poissonian statistics. The actual variation in the number of electron-hole pairs created, against the predicted behaviour from Poisson statistics, is quantified by the Fano factor [74], F, as

$$F = \frac{\text{Observed variance in } N}{\text{Poisson predicted variance in } N}.$$
 (2.7)

The value of F is material specific with an average value of 0.14 for semiconductors [4]. The standard deviation in the number of electron-hole pairs created is then given by,

$$\sigma = \sqrt{FN} \tag{2.8}$$

The displacement over which the electron-hole pairs are created is given by the electron range. The photoelectron, as a charged particle, loses its energy continuously along its path due to the ionisation of the electron-hole pairs. The rate at which the charged particle loses energy was described by the Bethe formula [75] and is dependent on Z and density of the material. These two parameters, along with the mean excitation energy which must be determined empirically, define the electron range in the material. In practise, the electron range for a specific material is calculated using methods such as the continuous-slowing-down-approximation (CSDA) [76] or through the use of Monte Carlo simulations. Results from the latter method for CdZnTe are used in section 4.5.1. This process occurs within a few picoseconds and is therefore assumed instantaneous in this work as the time is negligible compared to the drift time of the carriers.

2.3.2 Charge drift

Under the influence of an electric field, the negatively charged electrons and positively charged holes will drift in opposite directions. In a uniform electric field of strength E_f , the drift velocity of the electrons, v_e , and holes, v_h , are equal to

$$v_e = \mu_e E_f, \qquad \qquad v_h = \mu_h E_f \tag{2.9}$$

where μ_e and μ_h are the electron and hole mobilities respectively. During motion of the charge carriers it is possible for the carriers to undergo trapping or recombination due to defects and impurities in the semiconductor crystal structure - see overview of common defects in CdTe in section 7.2. The defects act as trapping centres which prevent the carriers from drifting, and if both an electron and hole are trapped they may recombine by annihilation. The frequency at which this occurs determines the lifetimes of the electrons, τ_e , and holes, τ_h . The mean path length, λ , of the charge carriers before trapping occurs can then be defined as

$$\lambda_e = \mu_e \tau_e E_f, \qquad \lambda_h = \mu_h \tau_h E_f. \qquad (2.10)$$

This quantity, specifically the so-called $\mu\tau$ -product, is one of the most important properties influencing the performance of semiconductor radiation detectors. Maximising this value reduces the amount of charge that is trapped while a detector is read out, and this has multiple benefits which improve the charge collection efficiency in these detectors.

2.3.3 Charge diffusion

During drift, the charge carriers will undergo thermal diffusion away from their point of origin. This is governed by Fick's laws [77], which define a diffusion equation that is dependent on a diffusion coefficient D of units m²/s. From the theory of Brownian motion, the Einstein relation [78] gives the diffusion coefficient for electrical mobility as

$$D = \mu \frac{k_b T}{e} \tag{2.11}$$

where μ is the mobility of the charge carrier, k_b the Boltzmann constant, e the elementary charge and T the absolute temperature of the solid. The effect of diffusion is that it will cause the charge carriers to spread while they drift. This spread can be quantified by assuming each charge carrier as a Brownian particle moving in 1D. The solution to the 1D diffusion equation then gives the mean squared displacement, \bar{x}^2 , of each carrier as a function of time, t,

$$\bar{x}^2 = 2Dt \tag{2.12}$$

The diffusion of the charge carriers sets a limit on the precision of position measurements that can be made with semiconductor detectors and is the mechanism behind charge sharing in pixelated detector designs.

2.4 Semiconductor detector design and operation

Semiconductor radiation detectors work on the basis of the physical processes described in the previous sections 2.2 and 2.3. Incident X-rays interact with the semiconductor through the ionisation of electrons and holes whose number is proportional to the energy of the absorbed X-ray. By externally applying a potential difference to electrodes attached to the semiconductor material, an electric field is produced which causes both the electrons and holes to drift - in opposite directions. The motion of the charges results in an observed conductivity that, using readout electronics, can be recorded as an electrical signal which corresponds to the detection of an X-ray.



Figure 2.4: Schematic showing the basic principle of X-ray detection using semiconductor radiation detectors. The semiconductor material is in white, the electrodes in orange and the readout electronics in grey. The electrons (e^-) and holes (h^+) are swept to the respective electrode under the influence of the electric field. Although the purpose of this schematic is only to show the detection principle, the simple design depicted is that of a planar detector configuration that is back-illuminated.

Figure 2.4 is a schematic showing the basic principle of ionising radiation detection using

semiconductors. In the following sections, the individual structures making up the detector and possible design variations are described, with a focus on those employed in the CdTebased detectors used in this work. A more detailed overview of CdTe and CdZnTe detectors can be found in the review paper by Del Sordo et al. [8] or, for a general description of semiconductor radiation detectors and how they operate, see Knoll [79].

2.4.1 Semiconductor layer

The semiconductor layer of the detector is the medium where the photon interaction should occur so that it can be detected. Electrons excited across the band gap energy (E_g) into the conduction band and the vacancies (i.e holes) they leave in the valence band contribute to the electrical conductivity required for the detector to measure a signal. Semiconductors are the ideal detection medium as they typically have band gaps in the range 1 eV $\leq E_g \leq 5$ eV. As a result, in the absence of excitations such as from an X-ray, the semiconductor behaves as an insulator and no signal is detected. When excitations of charge carriers occur in response to an incident X-ray, the semiconductor behaves as a conductor and a signal is measured. However, valence electrons will also be excited across the band gap due to thermal energy at a probability per unit time of

$$p(T) = CT^{3/2} \exp\left(-\frac{E_g}{2k_b T}\right)$$
(2.13)

where C is a proportionality constant specific to the material. The exponential terms reveals the critical dependence of the thermal excitations on the band gap of the material and the detector operation temperature. Even in the absence of ionising radiation, charge carriers from thermal excitations in the bulk of the material will drift under the applied electric field contributing to some conductivity. This is referred to as the bulk leakage current in a detector and is a significant source of noise as it interferes with the signal (i.e. conductivity) from an X-ray detection event. Reducing the leakage current is one of the main considerations in the design of semiconductor detectors. The wider band gap semiconductors, like CdTe, can operate at higher temperatures (e.g. room-temperature) because of less leakage current compared to narrower band gap semiconductors like Si. This is apparent from equation 2.13 which indicates that for the same temperature, the larger band gap material will have a lower concentration of thermally excited electron-hole pairs.

In practise, the semiconductor material used will never be purely intrinsic (equal concentrations of electrons and holes) as it will contain at least some small level of impurities and native defects. These impurities and defects affect the concentrations of the charge carriers unequally and influence the electrical properties of the material. If the electrons are the dominant charge carrier, the semiconductor is considered n-type and if the holes are the dominant charge carrier, the semiconductor is considered p-type. This is caused, respectively, by donor impurities which introduce a filled state just below the conduction bands or by acceptor impurities which introduce an unfilled state just above the valence bands, as illustrated in figure 2.5. Because the energy gap between the impurity states and the conduction or valence bands is typically much smaller than the band gap, the total number of thermally excited charge carriers in n-type or p-type semiconductors will be much greater than in the intrinsic case. The impurities therefore significantly increase the conductivity of semiconductors, which in the application of detectors, increases the leakage current.



Figure 2.5: (a) Band structure of n-type material due to donor impurities. Donor impurities are atoms with more valence electrons than the host lattice atoms they replace. (b) Band structure of p-type material due to acceptor impurities. The acceptor impurity has fewer electrons than the host lattice atom it replaces. The conduction bands regions represent all the unfilled conduction states and the valence bands regions all the filled valence states.

Impurities can also be added intentionally via doping processes. This is typically done to semiconductors grown for radiation detection to compensate for n-type or p-type conductivity of as-grown crystals. Such a semiconductor is then considered compensated and designated i as it is returned closer to its intrinsic electrical properties. The compensated semiconductor will have a higher resistivity and therefore reduced leakage current in the detector. CdTe crystals for radiation detection are typically doped with Cl atoms (donor impurities) to compensate for p-type conductivity due to native defects, creating a i-CdTe layer. Some detectors employ multiple semiconductor layers. The most common examples of this are the p-n junction where purposely heavily doped p-type and n-type layers are in direct contact or the p-i-n structure where the p and n regions are separated by an intrinsic layer. Using these structures in diodes helps reduce leakage current as the heavily doped layers act as blocking contacts (see section 2.4.2). The CdTe based detectors used in this work only consist of an i-semiconductor layer positioned between two metallic contacts.

2.4.2 Electrode contacts

In order to provide the detector a means to collect the charge carriers and record the signal they produce, metal contacts (i.e. electrodes) are used at either end of the semiconductor material (anode and cathode). These contacts may be either ohmic due to a low Schottky barrier or blocking due to a high Schottky barrier, where the barrier is the excess energy the carriers require to conduct through the metal-semiconductor junction. Blocking contacts are therefore typically used in semiconductor detectors to reduce the leakage current through the bulk material. The blocking metal-semiconductor junction is known as a Schottky diode. For CdTe detectors, transition metals like Pt and Au are used as ohmic contacts or for blocking contacts poor metals like In and Al are used.

The electrodes are also used to apply the external voltage which generates the electric field in the semiconductor. For a planar detector as depicted in figure 2.4, with blocking electrodes on either side, the electric field across the semiconductor can be approximated as uniform with a field strength given by $E_f = V/L$, where V is the applied bias voltage and L is the thickness of the semiconductor layer. For diodes used in radiation detection, the external voltage is applied in the direction such that the semiconductor is reverse biased, as opposed to forward biased. This ensures that, under the applied voltage, only very little current will conduct such that the signals from X-ray events can be distinguished from leakage current. A reverse bias also increases the depletion region, which is the semiconductor region of high resistivity where the electric field sweeps out the charge carriers before they recombine. If a sufficiently large reverse bias is used, then the entire semiconductor layer can be fully depleted of charge.

Depending on the desired operation of the detector, the electrodes have to be designed accordingly. The detectors used in this work are position sensitive and also predominantly single carrier sensing to circumvent the issues associated with the poor hole transport in CdTe. This is achieved by using a pixelated electrode on the anode side where the electrons drift to. The pixels are electrically isolated such that each pixel effectively acts as an individual electrode, recording the signal induced by carriers over the respective pixel's position. Many other electrode designs exist depending on the detector type, such as microstrip detectors, drift detectors or Frisch-grid detectors.

2.4.3 Pixelated readout electronics

The current that is induced at the electrodes from the motion of charge carriers are measured by using readout electronics which, due to the often bespoke design and operation of detectors, are commonly application-specific integrated circuits (ASICs). The two most common technologies to read out pixelated detectors are charge-coupled devices (CCDs) and complementary metal–oxide–semiconductor (CMOS) pixels. In CCDs, the charges are transferred to one end of the pixelated array where they are converted to an analogue voltage signal via a serial readout. In CMOS detectors, each pixel incorporates its own circuit to record the voltage signal from the induced current. Lower power consumption and cheaper production costs mean CMOS detectors are slowly replacing CCD detectors. The readout ASIC design for the HEXITEC detector system is based on CMOS technology and is described in detail in section 3.2.



Figure 2.6: Schematic of a hybrid pixel detector where detector and CMOS ASIC have been bonded. The design shown is that of the HEXITEC detectors used in this work.

Figure 2.6 shows a schematic of a pixelated semiconductor detector coupled to a CMOS readout ASIC chip. We generally refer to the detector as the sensor (i.e semiconductor layer) and its electrodes. The combined detector and readout ASIC is commonly referred to as a hybrid pixel detector. Bump bonds are deposited on both the pixelated anode and pixelated ASIC using good conducting metals and then attached via flip-chip bonding. The ASIC is wire-bonded to an electronic board where further off-chip readout processes

are performed. To reverse bias the detector, a wire delivers a voltage to the cathode. To improve the response to soft X-rays, the detectors are typically back-illuminated (i.e. through the cathode) which avoids attenuation by the front-end electronics.

2.4.4 Signal induction

The movement of the charge carriers as they drift under the applied electric field induces a current on the electrodes. The Shockley-Ramo theorem [80, 81] describes this process and states that the instantaneous charge, Q, induced on an electrode by a moving charge, q, is

$$Q = -q\varphi(x) \tag{2.14}$$

where φ is the weighting potential at the charges instantaneous position x when the given electrode is at unit potential, all other electrodes at zero potential and all charges are removed. The weighting potential depends on the detector geometry and electrode arrangement, and describes the electromagnetic coupling between moving charges and the conducting electrodes. Thus, using the Shockley-Ramo theorem, signal induction is described from only the weighting potential of the detector and the moving charge. The motion of that charge, however, is still dependent on the electric field lines.

If we have N electron-hole pairs from an X-ray absorption event, we can take q = Ne. The charge induced, ΔQ_k , on a single electrode k by the carriers moving from position x_i to x_f is then

$$\Delta Q_k = -Ne[\varphi_k(x_f) - \varphi_k(x_i)]. \tag{2.15}$$

The charge collected at electrode k during drift therefore depends on the number of carriers in motion. If no carrier trapping were to occur, then the the total possible induced charge, Q_0 , would be obtained. In practise, some charges will always be trapped such that the number of carriers, N, remaining after time t is

$$N(t) = N_0 e^{\frac{-t}{\tau}}$$
(2.16)

where N_0 is the original number of carriers created and τ is the lifetime of the carrier. As carriers are trapped during drift, N decreases and this reduces the amount of induced charge and results in incomplete charge collection. Both the motion of the electrons and holes induce a charge on each electrode, such that the total induced charge on electrode k is

$$\Delta Q_{tot(k)} = \Delta Q_{e(k)} + \Delta Q_{h(k)}.$$
(2.17)

For a planar collecting electrode, the weighting potential is a linear function given by $\varphi(x) = x/L$, where L is the detector thickness and x the original position of the charge carriers. For such a detector, with a uniform electric field, the amount of charge loss can be determined from the Hecht equation [82] which determines the charge collection efficiency (CCE) by

$$CCE = \frac{Q_{tot}}{Q_0} = \frac{\lambda_h}{L} \left(1 - e^{-\frac{x}{\lambda_h}} \right) + \frac{\lambda_e}{L} \left(1 - e^{-\frac{L-x}{\lambda_e}} \right)$$
(2.18)

where $Q_0 = N_0 e$ and all other terms have been previously defined. The CCE is therefore dependent on both carrier path lengths, λ , and on the photon interaction position. To maximise CCE, the λ/L ratio should be kept as large as possible. In materials with relatively poor $\mu\tau$ products, like CdTe, this places a strong constraint on the thicknesses and therefore photon energies at which the semiconductor detector maintains practical performance.

Proof of the Shockley-Ramo theorem and a more detailed description of signal induction can be found in [83]. The charges induced at the collecting electrode produce a current that flows through the readout ASIC, where signals are then formed and processed by the electronics. The principles of signal processing are not described in this work, but can be found in [79].

2.4.5 Detector response and energy resolution

A detector's response refers to how the detector, as a result of the physical processes necessary for detection, converts the incoming signal (incident X-rays). Performance parameters such as the intrinsic efficiency and the spectral (energy) resolution of a detector are a consequence of this response. The energy resolution is of basic importance for spectroscopic detectors as it describes how close two X-ray lines can be in terms of energy and still be distinguishable. The smaller this quantity is, the better the spectral performance of the detector becomes as it can resolve smaller differences between incident X-ray energies.

The broadening of a photon signal (photopeak) due to a detector's response is typically expected to follow a Gaussian distribution with a standard deviation, σ , given by the sum

of the individual broadening components

$$\sigma = \sqrt{F\omega E + \sigma_a^2 + \sigma_c^2},\tag{2.19}$$

where the first term is the Fano noise which accounts for the statistical fluctuation of the charge carriers generated at incident X-ray energy E. The second and third terms are the variance in peak width due to the detector's leakage current noise and electronic readout noise, σ_a^2 , and the variance in peak width due to incomplete charge collection, σ_c^2 , from charge losses (e.g. charge trapping). The FWHM energy resolution, ΔE , is then given by the FWHM of a Gaussian distribution (2.355 σ) with standard deviation from equation 2.19,

$$\Delta E = 2.355 \sqrt{F\omega E + \sigma_a^2 + \sigma_c^2}.$$
(2.20)

The energy resolution can also be given relative to the X-ray energy as $\Delta E/E$. To improve the energy resolution of a detector, σ_a and σ_c should be minimised, since the Fano noise term is material limited. The best possible energy resolution that can be achieved with the particular semiconductor material, is found when σ_a and σ_c are equal to zero and is referred to as the Fano-limited energy resolution.

The two primary sources of electronic noise in the σ_a term are series noise and parallel noise. These are not further discussed, as in this work we only calculate a single noise value which equates to the combined total noise (i.e. σ_a). A comprehensive review of the individual electronic noise sources can be found in Bertuccio et al. [84].

2.5 Density functional theory method

Density functional theory (DFT) is a quantum mechanical method used to calculate the properties of many-body systems of atoms, molecules and solids. The name for the theory arises from the basis that functionals of the ground-state electron density are used in the calculations of the electronic structure of the many-body systems. This was first proved by Hohenberg and Kohn [85], who demonstrated in 1964 that the ground-state electron density could be used as the basic function to uniquely characterise a system. An extension to this work by Kohn and Sham [86] in 1965 lead to the modern version of DFT used today. In principle, the functionals in DFT are exact for an electronic system of particles, however in practice, to make the calculations feasible, approximate functionals are needed. In the 1990's, the use of DFT in quantum chemistry and materials science took off [87] as improvements in these approximations, coupled with increased computing

power, provided a useful balance between accuracy and computational cost.

2.5.1 Hohenberg-Kohn theorems

Hohenberg and Kohn (HK) outlined two theorems. The first HK theorem states that the external potential $V_{ext}(\mathbf{r})$ from the nuclei acting on any system of interacting particles is, except for a constant, determined uniquely by the ground-state electron density $n_0(\mathbf{r})$. From quantum mechanics we know that a system of N interacting particles is described by Schrödinger's equation,

$$\hat{H}\Psi(\mathbf{r}_1,...,\mathbf{r}_N) = \hat{E}\Psi(\mathbf{r}_1,...,\mathbf{r}_N)$$
(2.21)

where Ψ is the physical wavefunction of the particles with 3-D position **r** for each electron in the system, \hat{E} is the total energy of the system and \hat{H} the Hamiltonian operator which contains all the interactions (i.e. kinetic and potential energies) which effect the state of the system and is given by

$$\hat{H} = -\frac{1}{2} \sum_{i}^{N} \nabla_{i}^{2} + \frac{1}{2} \sum_{i \neq j}^{N} \frac{1}{|\mathbf{r}_{i} - \mathbf{r}_{j}|} + \sum_{i}^{N} V_{ext}(\mathbf{r}_{i})$$
(2.22)

in atomic units. If the first theorem is true, then the Hamiltonian, except for a constant shift of the energy, can be fully determined from only the ground-state electron density. Using this Hamiltonian to solve the Schrödinger equation, the many-body wavefunction for any state can be determined and consequently this implies that all properties of the system are a functional of the ground-state electron density.

The second HK theorem states that for any external potential $V_{ext}(\mathbf{r})$, a functional for the full, many particle energy in terms of the electron density $n(\mathbf{r})$ can be defined. The exact ground-state energy is the global minimum of this functional and the corresponding density is the exact ground-state electron density $n_0(\mathbf{r})$. Since all properties are uniquely determined by $n(\mathbf{r})$, the total energy functional can be expressed as

$$E_{HK}[n(\mathbf{r})] = T[n(\mathbf{r})] + U[n(\mathbf{r})] + \int V_{ext}(\mathbf{r})n(\mathbf{r})d^3r + E_{II}$$
(2.23)

where T and U are the kinetic energy and the internal energy from electron-electron interactions respectively and appear in the same order as the terms in equation 2.22 and are both functionals of the electron density $n(\mathbf{r})$. E_{II} is the interaction energy of the nuclei. The implication of the second HK theorem is that the exact ground-state energy,
wavefunction and electron density can be determined from the functional $E_{HK}[n(\mathbf{r})]$ alone. The proofs for the two HK theorems can be found in Hohenberg and Kohn's seminal paper [85].

2.5.2 Kohn-Sham DFT approach

Although the HK theorems provide the foundation for DFT by showing that the total energy and V_{ext} are functionals of $n(\mathbf{r})$, they give no information on how this simplifies solving the many-body interacting problem. A solution to this is the approach that Kohn and Sham (KS) presented in their 1965 paper [86]. Kohn and Sham suggested replacing the many-body interacting system with a fictitious system of non-interacting quasi-particles that, by construction, has the same electron density and total energy as the real system. This greatly simplifies the many-body problem because given that the electrons (i.e. quasiparticles) are non-interacting, only the single-electron equation needs to be solved,

$$\hat{H}_s \psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r}) \tag{2.24}$$

where ψ_i and ϵ_i are the single electron KS wavefunction and energy (i.e. eigenvalue) respectively, and \hat{H}_s is the Hamiltonian for a single particle (the subscript *s* denotes single-electron equation). This reduces the complexity of a system with *N* electrons from a problem of solving the Schrödinger equation with 3*N* degrees of freedom to one where only the single, 3-D electron equation needs to be solved *N* times.

The single-particle Hamiltonian H_s applied to all N electrons in a system is

$$\hat{H}_s = \sum_{i}^{N} \left(-\frac{1}{2} \nabla_i^2 + V_s(\mathbf{r}_i) \right)$$
(2.25)

were $V_s(\mathbf{r})$ is the total potential energy experienced by each electron

$$V_s(\mathbf{r}) = \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3 r' + V_{ext}(\mathbf{r}) + V_{xc}[n](\mathbf{r}).$$
(2.26)

The first term in equation 2.26 is called the Hartree potential which approximates the electron-electron interactions. Kohn and Sham also introduced the exchange-correlation potential, $V_{xc}[n](r)$, which incorporates all the difficult many-body interaction effects. The exchange-correlation potential is related to the exchange-correlation energy by

$$V_{xc}[n](\mathbf{r}) = \frac{\partial E_{xc}}{\partial n(\mathbf{r})}.$$
(2.27)

The KS total energy functional can therefore be written as

$$E_{KS}[n(\mathbf{r})] = T_s[n(\mathbf{r})] + E_H[n(\mathbf{r})] + \int V_{ext}(\mathbf{r})n(\mathbf{r})d^3r + E_{II} + E_{xc}[n(\mathbf{r})]$$
(2.28)

where T_s is the kinetic energy of the KS system and E_H is the Hartree energy. If we compare this against the HK energy functional for an interacting system (equation 2.23) we obtain

$$E_{xc}[n(\mathbf{r})] = (T_s[n(\mathbf{r})] - T[n(\mathbf{r})]) + (U[n(\mathbf{r})] - E_H[n(\mathbf{r})]).$$
(2.29)

This shows that the exchange-correlation term accounts for the difference in energy between the real interacting system and the fictitious KS non-interacting system and that it is also a functional of the electron density since all terms on the right of the equation are functionals.

By solving the KS equations, the ground-state density and energy of the original interacting system can be found and deviate only from the exact solutions by the approximations in the exchange-correlation functional which are, ideally, small. Figure 2.7 summarises schematically the application of the HK theorem and KS approach in the calculation of the many-body problem.



Figure 2.7: Schematic representation of the calculation of the many-body problem with the HK theorem and KS approach applied to the problem. The single arrows represent the steps which require solving the Schrödinger equation. The large, single-headed arrow represents the application of the HK theorem relating the ground-state electron density to the external potential. The large, double headed arrow represents the link between the real interacting system and the fictitious non-interacting system. Adapted from figure 7.1 in [88].

2.5.3 Self-consistent field (SCF) calculation

The electron density is calculated from the solution to equation 2.24. In order to solve this equation, the potential from equation 2.26, which is itself dependent on the electron density, must be known. The ground-state electron density must therefore be determined self-consistently with a set of self-consistent field (SCF) equations.

This process is illustrated in figure 2.8. First, an initial guess is made for the density $n_{in}(\mathbf{r})$. From this, the effective potential in the non-interacting system is calculated using equation 2.26. Using this potential, the wavefunction and eigenvalues for each electron in the system are determined by solving the KS single-particle equation obtained by combining equations 2.24 and 2.25,

$$\left(-\frac{1}{2}\nabla^2 + V_s(\mathbf{r})\right)\psi_i(\mathbf{r}) = \epsilon_i\psi_i(\mathbf{r}).$$
(2.30)

The output electron density is then calculated from

$$n_{out}(\mathbf{r}) = \sum_{i}^{N} |\psi_i(\mathbf{r})|^2.$$
 (2.31)

The total energy for the system obtained with n_{in} and n_{out} are compared. If the difference in energy is below an acceptable set tolerance, self-consistency has been reached and the ground-state electron density found, $n_{out} = n_0$. If the tolerance is not met, the process is repeated with a new input density obtained from mixing the two densities. This is repeated until the tolerance is achieved.



Figure 2.8: Flowchart illustrating the self-consistent field loop to solve for the ground-state electron density self-consistently from the Kohn-Sham equations. Adapted from figure 9.1 in [88].

2.5.4 LDA and GGA

DFT is the successful method that it is today because of approximate functionals that allow much larger systems to be calculated while retaining much of their accuracy. The exchange-correlation potential is the crucial quantity that is approximated such that the KS independent particle systems can be solved to practical accuracies.

The most widely used approximations are the local density approximation (LDA) or the generalised gradient approximation (GGA). The LDA was also proposed by Kohn and Sham in their paper [86] who argued that since the electron density varies slowly in space, a solid can be considered close to the special case of a homogeneous electron gas. The exchange-correlation energy, at a fixed position, can be therefore assumed equal to that of the homogeneous electron gas, with density $n(\mathbf{r})$ over all space,

$$E_{xc}^{LDA} = \int n(\mathbf{r}) \epsilon_{xc}^{hom}[n(\mathbf{r})] d^3r$$

= $\int n(\mathbf{r}) (\epsilon_x^{hom}[n(\mathbf{r})] + \epsilon_c^{hom}[n(\mathbf{r})]) d^3r$ (2.32)

where ϵ_{xc}^{hom} is the exchange-correlation energy in a homogeneous electron gas and can be separated into the exchange ϵ_x^{hom} and correlation ϵ_c^{hom} component. The exchange energy is known exactly in the homogeneous electron gas, whereas the correlation energy must be calculated accurately using Monte Carlo methods. Examples of this are the correlation energy by Perdew-Zunger (PZ81) [89] and Perdew-Wang (PW92) [90] which were both tested for a bulk CdTe system shown in chapter 6.

The shortcoming of LDA is that it approximates the exchange-correlation energy of the true electron density with the energy of the local constant density of the homogeneous electron gas, and this begins to fail in systems with rapidly changing density. GGA functionals attempt to correct for this by considering the gradient of the electron density in the calculation of the exchange-correlation energy

$$E_{xc}^{GGA} = \int n(\mathbf{r}) \epsilon_{xc}[n(\mathbf{r}), \nabla n(\mathbf{r})] d^3r$$

= $\int n(\mathbf{r}) \epsilon_x^{hom}[n(\mathbf{r})] F_{xc}[n(\mathbf{r}), \nabla n(\mathbf{r})] d^3r$ (2.33)

where $\nabla n(\mathbf{r})$ is the gradient of the electron density, ϵ_x^{hom} is the same as in LDA and F_{xc} is a dimensionless enhancement factor describing how much the exchange-correlation is enhanced over LDA. Numerous forms of F_{xc} have been proposed leading to various different GGA functionals. The most widely used one in materials science today is that

developed by Perdew-Burke-Ernzerhof (PBE96) [91], which we also tested for a bulk CdTe system in chapter 6. Derivations of the PBE exchange-correlation enhancement can be found in their work.

2.5.5 Accuracy

Despite the use of approximations and the Kohn-Sham equations, the properties of materials determined from DFT have proven to be so accurate that they can be compared to those from physical systems [88]. As such, DFT has been established as one of the most popular methods for *ab initio* calculations of condensed matter. Nevertheless, there are a few exceptions to this accuracy of which one must be aware.

Firstly, standard DFT (i.e. KS DFT) focuses on ground-state energy and density calculations. The KS eigenvalues of the excited states therefore do not have any physical meaning and there is no guarantee that the physical band structure is correct. However, as a result of advancements over the years, the shape of the band structure from groundstate calculations tends to be very accurate. Extensions that allow for the computation of excited states have since been developed such as time-dependent density functional theory (TDDFT) and density functional perturbation theory (DFPT), the latter of which can be used to simulate temperature effects and is discussed further in section 6.4. Perhaps the most well known shortcoming of DFT is the band gap problem [92], where the KS band gap of insulators and semiconductors is underestimated by typically a factor of ~ 2 due to a self-interaction error (SIE) of the electrons [93]. Many methods exist which build on standard DFT and the approximations to correct for this problem, these are discussed in more detail in section 6.1 where work including correcting the band gap for CdTe is also discussed.

Another inaccuracy is that neither LDA nor GGA reproduce the exact bond lengths, with LDA underestimating and GGA overestimating (both by usually a few percent). Therefore, it is advised to check both approximations to determine which is more suitable for the system being simulated.

2.5.6 Pseudopotentials

The underlying idea of a pseudopotential is to replace the original problem with another that is simplified and easier to solve. We know that the effects of the outer shell valence electrons play a larger a role in defining the properties of a material than the tightly bound core electrons. In the application of electronic structure calculations, the pseudopotential is used to describe an effective potential that approximates the effect of the nucleus and core electrons on the valence electrons. This reduces the number of electrons in the calculation by removing the core electron states, which are largely unaffected by the crystal environment.

The single-particle KS equations can then be rewritten

$$\left(-\frac{1}{2}\nabla^2 + V_{eff}(\mathbf{r})\right)\psi_i(\mathbf{r}) = \epsilon_i\psi_i(\mathbf{r}).$$
(2.34)

where V_{eff} is the effective potential described by the pseudopotential and contains all the terms in equation 2.26. For condensed matter calculations, it is convenient to employ periodic boundary conditions where a large volume, Ω , is repeated and allowed to go to infinity. Within this periodic system, and using Bloch's theorem, the wavefunction of the independent pseudo-electron can be described using a plane wave basis set as

$$\psi_i(\mathbf{r}) = \psi_{n\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{\Omega}} \sum_{\mathbf{G}} c_{n\mathbf{k}} e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}$$
(2.35)

where $\psi_{n\mathbf{k}}$ is the wavefunction for an electron in band n and wavevector \mathbf{k} in reciprocal space, \mathbf{G} is the reciprocal lattice vector and $c_{n\mathbf{k}}$ are the plane wave expansion coefficients. For feasible calculations, both the number of plane waves included in the basis and the number of wavevector \mathbf{k} -points (i.e. points in reciprocal or momentum space) must be limited.

The solution to this reveals the main advantage behind pseudopotentials as electrons nearer the core are highly localised and have wavefunctions with sharp oscillatory features. To describes these features, a large number of plane waves (i.e. Fourier components) are required, and the cost of the calculations scale as a power of the number of Fourier components. Therefore, by using pseudopotentials, a smaller number of plane waves suffice to describe the smoother wavefunction of the outer valence electrons while still accurately describing the system. The number of plane waves included can be described by a kinetic energy cut-off value, E_{cut} , given by

$$E_{cut} = \frac{|\mathbf{k} + \mathbf{G}|^2}{2}.$$
(2.36)

In principle, \mathbf{k} is a continuous variable and in order to solve for the density, the wavefunction needs to be integrated over all \mathbf{k} -space. However, since the wavefunctions vary slowly over \mathbf{k} -space, in practise each small region can be sampled by a single \mathbf{k} -point. By sampling with a certain number and arranged grid of **k**-points, the integral of **k**-space can be approximated. Both the number of **k**-points and plane wave cutoff, E_{cut} , must be converged on for the particular system being calculated, with the goal of finding the minimum values (to minimise computational cost) which still accurately describe the system.

Figure 2.9 is a schematic representation of the real all-electron potential and wavefunction versus the approximated pseudopotential ones, where r_c is a cut-off radius above which the all-electron and pseudo terms converge. The choice of r_c determines the hardness of a pseudopotential, where a small or large r_c results in hard or soft pseudopotentials respectively. Amongst the many pseudopotentials available, we use two different types in this work - these are described below.



Figure 2.9: Schematic illustration of all-electron (solid lines) and pseudoelectron (dashed lines) potentials and their corresponding wavefunctions. The radius at which the all-electron and pseudoelectron values converge is designated r_c . Reproduced with permission from [94].

2.5.6.1. Norm-conserving pseudopotentials

Early pseudopotentials were obtained empirically from fits to experiment. These would work well but were limited to the system they were generated for. Modern pseudopotentials are determined from *ab initio* atomic calculations and in 1979 Hamann, Schluter and Chiang [95] defined a set of requirements to achieve accurate and transferable *ab initio* pseudopotentials. This gave rise to the so called norm-conserving pseudopotentials (NCPPs) which, although constructed for use in one system, will perform equally well in a different system.

NCPPs tend to be hard pseudopotentials (low r_c) which are more transferable because of a smaller portion of the exact wavefunction being approximated by the pseudo wavefunction. Soft pseudopotentials (large r_c) tend to be less transferable. The benefit of NCPPs is therefore that it greatly simplifies the application of pseudopotentials to electronic structure problems, as the pseudopotentials can be created in a simple environment and then used in more complex ones.

2.5.6.2. Projector augmented-wave method

Ideally, pseudopotentials that are as "smooth" (i.e. soft) as possible and yet still accurate are desirable as fewer Fourier components (e.g. plane waves) are required to approximate a smooth wavefunction. NCPPs, although highly transferable, sacrifice some "smoothness" to achieve this. The projector augmented wave (PAW) method was introduced by Blöchl in 1994 [96] as an extension to the psedupotential approach to achieve greater computational efficiency and a more unified electronic structure method.

The PAW method employs spherical augmentation regions (atomic spheres) of radius r_c , similar to the core cut-off radius used for NCPPs, placed around the atom cores that contain the rapidly varying part of the wavefunction. Outside of the atomic spheres the pseudo wavefunctions also converge with the exact wavefunction. Within the atomic spheres, the PAW method introduces a linear transformation, \mathcal{T} , from which the exact allelectron wavefunction, ψ , can always be obtained from a smoothed pseudo wavefunction $\tilde{\psi}$,

$$|\psi\rangle = \mathcal{T} |\bar{\psi}\rangle. \tag{2.37}$$

In the PAW method, the wavefunctions within each sphere are described by an expansion of partial waves (as opposed to plane waves as in the norm-conserving pseudopotential approach) such that

$$|\tilde{\psi}\rangle = \sum_{i} c_{i} |\tilde{\phi}_{i}\rangle \tag{2.38}$$

and

$$|\psi\rangle = \sum_{i} c_{i} |\phi_{i}\rangle \tag{2.39}$$

where c_i are the expansion coefficients, ϕ_i the pseudized partial-waves and ϕ_i the allelectron partial-waves. The all-electron wavefunction can then be written as

$$|\psi\rangle = |\tilde{\psi}\rangle + \sum_{i} c_{i} (|\phi_{i}\rangle - |\tilde{\phi}_{i}\rangle).$$
(2.40)

Since the transformation \mathcal{T} is required to be linear, the coefficients can be given by a

projection of the pseudo wavefunction

$$c_i = \langle \tilde{\rho_i} | \tilde{\psi} \rangle \tag{2.41}$$

where $\tilde{\rho}_i$ are the projector operators and are bi-orthogonal to $\tilde{\psi}$. Evaluating equations 2.37, 2.40 and 2.41, the linear transformation is

$$\mathcal{T} = 1 + \sum_{i} (|\phi_i\rangle - |\tilde{\phi}_i\rangle) \langle \tilde{\rho}_i|, \qquad (2.42)$$

which is given only by the partial wave and projector functions which are stored in the PAW psuedopotential. Since the all-electron wavefunctions can be determined from the smooth wavefunctions by using only the transformation, it is possible to choose much larger r_c to reduce the amount of Fourier terms and save computation time, while maintaining the desired accuracy.

Due to their greater computational efficiency, we primarily use PAW pseudpotentials. The projectors are an additional variable to r_c with many possible options, which separates the many PAW pseudopotentials available. The construction of a PAW pseudopotential that is tested in chapter 6 on a bulk CdTe system is described in Appendix B.

2.5.7 ABINIT

The primary software used for the *ab initio* calculations in this work was ABINIT [97] which allows one to calculate the total energy, charge density and electronic structure of periodic solids using the DFT method [98]. ABINIT uses pseudopotentials with a plane wave basis and supports both NCPPs and the PAW method, although certain advanced features are often only possible or supported by one or the other - this is explored further in chapter 6.

ABINIT calculates the ground-state electron density self-consistently using the process outlined in figure 2.8. The tolerance used to determine if self-consistency is achieved is selected by the user and we give this value in the relevant chapters. ABINIT also supports the structural relaxation of the system based on the forces and stresses. This too is performed until a user defined threshold on the forces is met. From the calculated relaxed ground-state density, non-SCF calculations solving the KS equations at many different \mathbf{k} -points can be performed to determine the KS band structure of the system.

For validation purposes and to access more pseudopotentials, some calculations were per-

formed with the Quantum Espresso (QE) [99] or Vienna Ab initio Simulation Package (VASP) [100] DFT codes, which use the same approaches as ABINIT. When QE or VASP was used, it is clearly indicated in the text and figures.

Chapter 3

Calibration and characterisation of a high-flux capable pixelated CdZnTe detector with the HEXITEC ASIC

3.1 Introduction

The first results from the HF-CdZnTe material were reported in 2017 [52] and reported an improved hole lifetime compared with standard CdZnTe material - highlighting its potential for high-flux applications. Since then, a number of studies have been undertaken to further test this material in detector systems [21, 36, 49–51]. Intense light sources like the LCLS XFEL [49] and the ESRF synchrotron [50, 51] were used to irradiate the HF-CdZnTe with very high photon fluxes (>10⁶ photons s⁻¹ mm⁻²) up to X-ray energies of 30 keV, and no polarisation effects were observed. While these results first and foremost show the potential of this new material for high-flux applications, a further implication is that these crystals are of high-purity and good uniformity.

Veale et al. [21] investigated the uniformity across 10 HF-CdZnTe detectors using flood images of a 241 Am source. Tests of the performance and uniformity of the HF-CdZnTe detector at energies greater than 60 keV are therefore still missing. In this chapter, we characterise one of the HF-CdZnTe detectors from the work in [21] across a range of energies from the soft to hard X-ray regime (6 - 122 keV). In order to do this, a per-pixel

energy calibration of the detector and the development of a reconstruction algorithm to produce images and spectra from the raw detector output were required. The calibration products and reconstruction algorithm are also used in chapters 4 and 5.

The performance of the HF-CdZnTe detector is compared with that of an Acrorad CdTe detector. Acrorad CdTe detectors have been available for over a decade and have been used in a number of studies [29, 101–103], showing excellent energy resolution of < 1 keV FWHM at 59.5 keV and good uniformity. Comparisons with this detector therefore provide an ideal reference point to some of the best performance that can be achieved with current CdTe-based detectors.

We begin the chapter by describing the High Energy X-ray Imaging Technology (HEX-ITEC) system used to read out the signals and describe the pixelated CdTe and HF-CdZnTe detectors. Following this, the results from the calibration and characterisation are presented and discussed.

3.2 The HEXITEC detector system

The HEXITEC detector system consists of an ASIC and data acquisition system (DAQ) [30]. The HEXITEC ASIC is a spectroscopic imaging readout chip developed by the Science and Technology Facilities Council (STFC), designed to be hybridised to a high-Z compound semiconductor (as shown in figure 2.6).

The HEXITEC ASIC is manufactured on a standard $0.35 \,\mu\text{m}$ CMOS process with an 80×80 pixel array on a 250 μm pixel pitch [104]. Each ASIC pixel circuit contains a preamplifier, $2 \,\mu\text{s}$ CR-RC shaper and peak track-and-hold circuit such that the induced charge is recorded as an analogue voltage at each pixel. The CR-RC circuit shapes the photon induced voltage pulse output from the preamplifier. The peak track-and-hold circuit records the maximum detected voltage during a frame and this is held until the end of the frame when it is read out and then reset.

The ASIC is mounted in an electronic readout board which forms the DAQ [105]. The input/output pads of the ASIC are aluminium wire bonded to the readout board. A rolling shutter technique is used to read out the ASIC pixel array, as opposed to a global shutter. This helps increase the maximum possible frame rate and reduces readout noise as each pixel row is read out sequentially. Once a row is read out it is reset to integrate new data and the next row is read out, minimising detector dead time.

The rolling shutter readout is conducted by four parallel outputs of 4 blocks of 80 rows and 20 columns. For each block, the analogue voltage in the 20 pixels of each of the 80 rows is multiplexed through an off-chip analogue-to-digital converter (ADC) which digitises the analogue voltage held by the ASIC chip into a 14-bit value [106]. The four blocks of 80×20 pixels are read out in parallel as each is connected to a separate 20 element ADC. The four ADC outputs allow the entire pixel array to be read in a quarter of the time (i.e. $80 \times 20 \times 50$ ns) [104]. This results in a maximum possible frame read out rate for the entire ASIC of about 10 kHz.

The DAQ electronics are connected to a PC via ethernet and control the frame readout rate, the applied detector bias voltage and maintains the detector and ASIC at room temperature (28°C). The temperature is stabilised to ± 1 degree Celsius using a thermoelectric Peltier cooler, heat sinks a and fan. The ASIC preamplifier circuit has two feedback capacitance loops of 15 fF or 50fF [30] which correspond to low and high gain modes respectively. In low gain mode, the detection of higher energy photons before saturation (greater dynamic range) of the electronics is possible, but at the cost of increased electronic noise. For the energy ranges investigated (6 - 122 keV), the dynamic range provided by the high gain mode sufficed and was therefore used due to better noise performance.

The detectors were bonded to the HEXITEC ASIC by STFC using their interconnect facilities [107]. Silver loaded epoxy bumps with a diameter of \sim 120 µm and \sim 30 µm height are deposited on each anode pixel of the detector. In a separate process, a gold stud is produced onto the bond pad of each ASIC pixel with a diameter of \sim 50 µm and height of \sim 30 µm, and the detector and ASIC are then flip-chip-bonded together. The hybrid detector is attached to an aluminium carrier which is mounted into the DAQ. The DAQ board is inserted into an aluminium housing. Figure 3.1 shows close up images of the hybrid detector module, the hybrid mounted on the DAQ readout board and the complete HEXITEC detector system in its aluminium housing.

The HEXITEC system is designed for back-illumination of the detector (i.e. through the cathode). This is done due to the superior transport properties of the electrons over the holes. Since the HEXITEC ASIC only records a signal at the detector anode, backillumination ensures that on average the electrons (which drift towards the anode) have the longer drift distances and consequently induce the majority of the charge. When combined with a detector benefiting from the small pixel effect [27], the hole signal is reduced even further. Both detectors described in section 3.3 have a small pixel geometry and therefore benefit from the small pixel effect.



Figure 3.1: (a) The 2 mm thick HF-CdZnTe hybrid detector bonded to the ASIC, wire-bonded to the PCB and setup in the aluminium mount which is attached the the HEXITEC DAQ system. (b) view of the detector attached to the complete HEXITEC DAQ electronics board. Heat sink, fan and a 12 V power supply are not visible but are underneath the electronics board. (c) Aluminium housing for the HEXITEC detector system which contains all of the detector and DAQ readout components. The opening in the housing is where the detector is positioned.

3.3 The detectors

3.3.1 1 mm Acrorad CdTe detector

The CdTe detector used consists of a 1 mm thick CdTe sensor with a planar platinum cathode and a pixelated aluminium anode (Pt/CdTe/Al), manufactured by Acrorad Ltd. The electrodes form blocking (Schottky) contacts, required in CdTe to minimise leakage current and achieve a resistivity of $\sim 10^9 \ \Omega \ \mathrm{cm}^{-1}$ [4].

The pixelation of the anode consists of an 80×80 array with 250 µm pitch with an electrode pad size of $200 \,\mu\text{m} \times 200 \,\mu\text{m}$ and an inter-pixel spacing of 50 µm. The detector therefore has a total collecting area of 20 mm $\times 20$ mm. This is surrounded by a 100 µm wide guard ring along each edge. Guard rings are used because detector surfaces are known to exhibit greater leakage current than the material in the bulk due to surface damage sustained during detector fabrication. This results in edge effects which have been shown to degrade spectral performance in the edge pixels of high-Z semiconductor detectors without guard rings [108]. The presence of guard rings, which are also biased, minimises spectral degradation from edge effects by collecting some of the leakage current

from the edge pixels.

3.3.2 2 mm Redlen high-flux CdZnTe detector

The HF-CdZnTe detector, fabricated by Redlen technologies [47], consists of the semiconductor material as the sensor and platinum electrodes (Pt/CdZnTe/Pt). Despite the use of Pt-Pt electrodes which form ohmic contacts, the larger band gap of CdZnTe means a resistivity of $>10^{10} \Omega \text{ cm}^{-1}$ is still achieved [47]. The cathode is planar and the anode is pixelated by an 80 × 80 array with a pixel pitch of 250 µm consisting of a 225 µm × 225 µm electrode pad size and an inter-pixel spacing of 25 µm. The semiconductor sensor has a thickness of 2 mm and a collecting area of 20 mm × 20 mm.

Table 3.1 lists the carrier transport properties found by Thomas et al. [52] for the HF-CdZnTe material. The values are compared with typical transport properties expected in standard CdZnTe and CdTe crystals. The hole transport ($\mu\tau$ product) for the HF-CdZnTe material is a significant improvement in comparison to the quantities for standard CdZnTe material. This, however, comes at the cost of a reduction in the electron transport in HF-CdZnTe. It is assumed that a different approach is taken during HF-CdZnTe material growth which favours the lifetime of holes over electrons.

| Parameter | HF-CdZnTe [52] | Standard CdZnTe $\left[4,109\right]$ | CdTe [4, 110] |
|-----------------------------------------------------------------------------|----------------|--------------------------------------|---------------|
| Electron mobility, $\mu_e \ (\mathrm{cm}^2 \mathrm{V}^{-1} \mathrm{s})$ | 940 ± 190 | 1000-1100 | 1100 |
| Hole mobility, $\mu_h \ (\mathrm{cm}^2 \mathrm{V}^{-1} \mathrm{s})$ | 114 ± 22 | 88-120 | 100 |
| Electron lifetime, $\tau_e ~(\times 10^{-4} \text{ s})$ | 1.2 ± 0.8 | 3-11 | 3 |
| Hole lifetime, $\mu_e ~(\times 10^{-6} {\rm s})$ | 2.5 ± 1.4 | 0.2-1 | 2 |
| $\mu_e \tau_e$ product (×10 ⁻⁴ cm ² V ⁻¹) | 11 ± 6 | 40-100 | 30 |
| $\mu_h \tau_h \text{ product } (\times 10^{-4} \text{ cm}^2 \text{V}^{-1})$ | 2.9 ± 1.4 | 0.2 - 1.2 | 2 |

Table 3.1: Carrier mobilities, lifetimes and combined $\mu\tau$ transport product for the HF-CdZnTe material compared with typical values measured in standard CdZnTe and CdTe crystals. The errors for the HF-CdZnTe quantities are from [52]. A range is given for standard CdZnTe because the quantities were found to vary more depending on the study. The CdTe quantities are more consistent between different literature studies and therefore only a single value is given.

3.4 Spectral and image reconstruction

The HEXITEC DAQ saves the digitised voltage from each pixel in every frame of an observation into a binary file. In order to obtain the recorded spectrum and image of the observed source, the data in this file must first be reconstructed. The software provided with the HEXITEC system includes a reconstruction process but this does not distinguish between different charge sharing event types (see figure 3.4). This section describes the development of an algorithm for spectral and image reconstruction of the detector data used in this thesis, the different photon event types that can occur in pixelated detectors and which event types the algorithm considers.

3.4.1 Photon event types

Photon counts recorded by a pixelated readout ASIC can appear in many different pixel patterns ('event types'). Figure 3.2 is an image of a single frame (i.e. 80×80 pixel array) recorded by the HEXITEC ASIC and highlights examples of different event types. The recorded values in the frame are before an energy calibration has been applied, and are therefore in analogue-to-digital units (ADU).

If all of the charge is contained within a single pixel, it is an isolated event. If the charge is collected over multiple neighbouring pixels, it is a charge sharing (shared) event (e.g. bipixel, tripixel, quadpixel). Event types are also referred to by their multiplicity which is defined by the number of pixels the absorbed photon induces a charge in (e.g. m = 2 is a bipixel event and all m > 1 events are charge sharing events).



Figure 3.2: A single frame recorded by the HEXITEC from a ²⁴¹Am observation carried out with the HF-CdZnTe detector. ADU (analogue-to-digital unit) is the digitised voltage value. Examples of different event types have been highlighted, 1: isolated, 2: bipixel, 3: tripixel, 4: quadpixel. A noise threshold of 90 ADU was applied to each pixel.

3.4.2 Energy calibration and noise threshold

If an energy calibration is available, the ADU value recorded in each pixel of a frame is translated into an energy (in keV). The energy calibration must be produced for each pixel and detector specifically - this process is described for the HF-CdZnTe in section 3.5.

It is common practise to apply a threshold to the energy in each pixel of a frame in order to remove counts that are due to noise, instead of an absorbed photon. The exact value used for the noise threshold must be determined for the conditions under which the detector is operated, such as the temperature and applied bias voltage. The noise threshold is applied to each frame of an observation. The event type of all remaining recorded counts is then determined by using the reconstruction algorithm.

3.4.3 Event reconstruction algorithm

The reconstruction algorithm distinguishes between the different event types in each frame of an observation. The event types considered by the algorithm are shown schematically in figure 3.3. In addition to the multiplicity, the algorithm distinguishes between events depending on:

- the relative arrangement of the pixels (e.g. if neighbouring pixels are diagonally or linearly adjacent)
- the relative position of the pixel containing the maximum induced charge

Different orientations for identically shaped multi-pixel events (e.g. vertical or horizontal bipixels) showed no difference in their energy response and are therefore considered as the same event type by the algorithm. Events with multiplicity m > 4 have a very low incidence rate at hard X-ray energies in these detectors [42]. In the CdTe detector, for example, only 0.7% of all events have a multiplicity m > 4 for photons of energy 140.5 keV. Therefore, events with m > 4 are collected by the algorithm but are not distinguished any further. All other possible pixel arrangements not shown in figure 3.3 occurred at negligible incidence rates (<0.5%) and are therefore ignored by the algorithm.

Since pixels that form any one of the event types shown in figure 3.3 are considered as part of the same incoming photon event, their energies are summed. The addition of the energy in each pixel for multi-pixel events is a simple reconstruction technique, referred to as Charge Sharing Addition (CSA) [35]. It is used to correct for charge sharing events by



Figure 3.3: The event types considered by the reconstruction algorithm. The grids represent a 3×3 section of pixels in a frame. The empty pixels are pixels in which the energy is below the noise threshold. Yellow pixels indicate pixels above the noise threshold and red pixels are those which contain the maximum energy of the event. The event is assigned to the pixel which counts the maximum energy when constructing the image.

recovering the total energy deposited by an absorbed photon across the multiple pixels. If CSA reconstruction is not used, a spectrum will not be properly reconstructed and is referred to as a raw spectrum.

An example of a non-reconstructed raw spectrum is shown in figure 3.4a. This spectrum has an increased amount of background counts, larger fluorescence and escape peaks and more counts at lower energy. By applying CSA reconstruction, the large background is removed as the energy across multi-pixel events is combined and a total spectrum containing all event types is obtained. An alternative reconstruction technique referred to as Charge Sharing Discrimination (CSD) [35] can be used which ignores all charge sharing events. This approach also removes the large background and improves energy resolution by simply discarding shared events. The HEXITEC software includes CSD and CSA reconstruction such that the spectra in figure 3.4a can be obtained, but information on the different event types contributing to the CSA spectrum is not obtained. The event reconstruction algorithm we developed provides additional information by distinguishing between the event types such that the spectra as shown in figure 3.4b can be reconstructed. The isolated event spectrum is equivalent to the CSD reconstruction and by summing all event multiplicities, CSA reconstruction is obtained. The separation of individual event types provides additional information to analyse charge sharing in pixelated detectors





Figure 3.4: Comparison between the different event reconstruction techniques used on calibrated ²⁴¹Am data from the HF-CdZnTe detector. (a) reconstruction techniques provided by the HEX-ITEC GUI software: raw uncorrected spectrum, CSD reconstruction spectrum and CSA reconstruction spectrum. (b) individual event type spectra obtained from the developed event reconstruction. The bipixels and tripixels include all types shown in figure 3.3 - individual spectra for each type can also be extracted. The individual event types can be used to obtain the CSD and CSA reconstructions in (a), and isolated events are equivalent to CSD.

Both images and spectra are reconstructed by the algorithm. This is achieved by producing a spectrum for each pixel. An image is then obtained by summing the number of counts in each pixel spectrum, which produces a 2-dimensional image of the pixelated detector array. For multi-pixel event types, the count is assigned to the pixel which contains the maximum energy (i.e. red pixels in figure 3.3.)

The spectrum recorded in each pixel can be divided into a separate spectrum for each event type. For every pixel and each event type, the spectrum is obtained by binning all of the energies belonging to that event type and pixel. The energy spectrum bin size is set to a value similar to the noise from the HEXITEC ASIC and DAQ readout chain, determined to be 0.3 keV (section 3.8.2). Using a value equal to the readout noise is a good compromise ensuring that the spectral resolution is not limited by the bin size, and maximising the number of counts in each energy bin for improved statistics.

3.5 Calibration of the HF-CdZnTe detector

This section describes the data collection and calibration procedure for the HF-CdZnTe detector. The experimental arrangement used to acquire data, details of DAQ operation of the detector, the determination of an appropriate noise threshold and the energy

calibration are presented and described.

3.5.1 Experimental arrangement

The experimental arrangements used to collect data with the HEXITEC system are shown in figure 3.5. The arrangement in figure 3.5a is with a fixed source-to-detector distance of 380 ± 0.015 mm, with sources placed on a 4.92 ± 0.01 mm thick platform made of perspex (polymethyl methacrylate). The purpose of the perspex was only to hold and align the source with the detector. In the arrangement in figure 3.5b, sources are placed within a clamp arm with adjustable height in order to vary the source-to-detector distance. The source is placed within the opening of the clamp and is therefore not blocked by any material. This setup was used for soft X-ray sources (e.g. ⁵⁵Fe with emission at ~5.95 keV) where the perspex would otherwise absorb the majority of source photons, and in experiments where the source-to-detector distance was varied.



Figure 3.5: Experimental arrangements used to collect data with the HEXITEC system. The two arrangements are identical except that in (a) the source is placed on a perspex platform at 380 \pm 0.015 mm distance to the detector surface and in (b) the source is placed in a clamp arm with adjustable height. The thin plastic in the clamp in (b) was not used but shows where the source was placed.

For both experimental arrangements, the HEXITEC system was placed on an aluminium

platform which contained etched grid lines to align the centre of the detector with the source. The detector opening in the HEXITEC housing was covered with aluminium foil of 0.016 ± 0.01 mm thickness to block out all incident visible light. To further ensure a fixed detector temperature during acquisitions, a 12 V powered fan was placed behind the vents of the HEXITEC housing to circulate air away from the detector.

3.5.2 DAQ operation

For all measurements with the HF-CdZnTe detector, the HEXITEC DAQ was operated with a bias voltage of -750 V (375 V mm⁻¹) applied to the detector cathode. This is the maximum voltage that can be applied by the HEXITEC DAQ. The detector temperature was maintained at $28\pm1^{\circ}$ C. For Schottky contact CdTe detectors, it is necessary to periodically refresh the bias to minimise bias induced polarisation (see section 3.6). Due to the reduced charge build up in the HF-CdZnTe detector as a result of using the more ohmic Pt electrodes, it was not necessary to periodically refresh the bias. The ASIC frame rate was set to 1.6 kHz.

3.5.3 Noise performance and threshold determination

An acquisition with no incident ionising radiation ('dark' image) was taken to measure the magnitude of the noise signal in the detector. Using the dark image, a noise threshold for energy calibration was determined and the detector was checked for hot pixels.

The acquisition time of the dark image was set to 1200 seconds. Since recorded counts are a result of noise and not incident photons, no event reconstruction was performed. Figure 3.6a shows the spectrum including counts from all detector pixels (whole-detector) when no noise threshold is applied. A noise peak at the lowest ADU values is clearly visible, which decreases exponentially as ADU increases. At ADU values with significant noise counts, photon energies of equivalent ADU are difficult to measure due to poor signal-tonoise (SNR) ratio. Energies at which noise is expected to dominate are therefore removed using a noise threshold.

Statistically, a noise threshold can be determined by taking 5σ of the width of the noise peak, which should suppress 99.99994% of all noise counts. Using this method, a noise threshold of 34 ADU was found. When sources were used, this noise threshold was not large enough to achieve an adequate SNR (SNR < 100). A noise threshold of 90 ADU was therefore selected instead (figure 3.6a). Figure 3.6b shows the spectrum after removing all



Figure 3.6: (a) Un-calibrated whole detector spectrum recorded with the HF-CdZnTe detector with no source (i.e. dark image) and no noise threshold applied. (b) same spectrum as in (a) but with 90 ADU noise threshold applied. (c) detector image showing the number of counts recorded in each pixel (no event type reconstruction applied). The grey-shaded regions in (a) and (b) highlight energy bins which are removed by the 90 ADU noise threshold.

counts below the noise threshold, and figure 3.6c is a detector image showing the number of counts above the noise threshold recorded in each pixel.

During the dark acquisition, an average count rate of 0.0006 counts s^{-1} pixel⁻¹ was recorded above the noise threshold. Given the frame rate of 1.6 kHz, this equates to an average noise count rate of 0.0024 counts frame⁻¹. In terms of the frame occupancy, where frame occupancy is defined as the percentage of pixels in a frame recording a count above the noise threshold, this is equal to ~0.00004%. Even at the lowest frame occupancy of 0.1% when sources were used (section 5.2), this gives a very high SNR of ~2500. Applying a 90 ADU threshold therefore ensures that most isolated and multi-pixel events are not piled-up with noise events.

Hot pixels were defined as those recording a signal above the noise threshold in more than 1% of all frames of the dark image. None of the detector pixels were above this threshold and therefore no pixels were removed from analysis at this stage of the calibration.

3.5.4 Energy calibration

An energy calibration is required to convert the digitised voltage measured by the ASIC into the corresponding energy of the photon which produced the signal. A calibration is often produced using radioactive isotopes since they emit characteristic photons of known energy. The spectral peaks measured by a detector under illumination of radioisotopes can therefore be matched to the corresponding energy in order to produce the energy calibration.

The detector was calibrated using sealed radioisotopes of ⁵⁵Fe, ¹⁰⁹Cd, ²⁴¹Am and ⁵⁷Co. For each source, a flood (uncollimated) image was taken with the detector. The acquisitions

were taken with the sources in the arrangement illustrated in figure 3.5a (380 mm distance), with the exception of the ⁵⁵Fe source which was placed at a distance of 70 mm using the setup shown in figure 3.5b due to the low energy of the 5.95 keV X-ray emission line. Details of each observation and the most prominent emission lines from each source are listed in table 3.2. The energy calibration was performed using the photopeaks at 5.95, 22.00, 59.54 and 122.10 keV, other peaks were not used. The chosen peaks were used because they cover energies ranging from the soft- into the hard X-ray regime, such that the obtained energy calibration could be applied for analysis at all energies. Additionally, these peaks are the brightest from each respective source - making it easier to clearly identify the peak during calibration.

| Radioisotope source | Source activity (MBq) | Acquisition duration (s) | Photopeak energies (keV) |
|---------------------|--------------------------|-----------------------------|-------------------------------------------------------------------------------------|
| $^{55}\mathrm{Fe}$ | 201.1 | 300 | 5.95 ± 0.01 |
| ¹⁰⁹ Cd | 19.2 | 1800 | $\begin{array}{c} 22.00 \pm 0.10 \\ 24.90 \pm 0.01 \\ 88.00 \pm 0.01 \end{array}$ |
| ^{241}Am | 350.1 | 1200 | 59.54 ± 0.01 |
| ⁵⁷ Co | 39.7 | 3300 | $\begin{array}{c} 14.40 \pm 0.10 \\ 122.10 \pm 0.05 \\ 136.50 \pm 0.10 \end{array}$ |

Table 3.2: Radioisotope sources used to acquire flood images with the HF-CdZnTe detector. A nominal uncertainty of ± 10 eV is used for the photopeaks unless the photopeak energy is made up of multiple unresolved peaks (i.e. $K_{\alpha 1}$ and $K_{\alpha 2}$ emissions). In this case the error is estimated taking into account the relative intensity of each peak making up the photopeak.

3.5.4.1. Calibration algorithm

An energy calibration was produced for each pixel. This was done because the position (i.e ADU value) of the same photopeak varies from pixel to pixel due to non-homogeneity of the crystal and variation in the ASIC response. Figure 3.7a is a map of the recorded ADU of the ²⁴¹Am 59.5 keV photopeak in each detector pixel - revealing a variation from 1880 to 2050 ADU. Figure 3.7b shows the ²⁴¹Am spectrum recorded in three different pixels as an example, selected specifically to show the variation in peak position. Only isolated events (after applying the noise threshold) are included in the spectrum of each pixel during calibration. Multipixel events are not used to ensure that the process is not compromised by the effects of charge sharing, which can shift peaks to lower energies due to charge loss. The acquisition times (table 3.2) were long enough to ensure that the calibration

photopeaks in each pixel contained at least 500 isolated counts (statistical error in counts <5%) within a ±5 keV energy window around the photopeak. In order to identify the position of each photopeak in every pixel and perform the energy calibration, a calibration algorithm based on the method described by Scuffham et al. [111] was developed.



Figure 3.7: (a) Pixel map showing the 241 Am 59.5 keV photopeak position in ADU for each pixel. (b) the non-calibrated spectra for three individual pixels, showing the variation in peak positions. The colours of the peaks correspond to the colour bar from (a). The grey-shaded region highlights the range of ± 150 ADU search to identify peak positions. The black circles correspond to the peak positions at the peaks maximum counts.

The calibration algorithm first finds the average ADU position for each photopeak from the whole detector spectrum. A range of ± 150 ADU around the average photopeak position is then searched for the peak position in each pixel by turn. The search range and identified peak positions are shown schematically in figure 3.7b. The search range is large enough to account for the ADU variation across pixels, but limited so that the position of another peak associated with a different energy, or a noise peak, is not measured by mistake. Once the position of each calibration photopeak is found, a linear fit is performed between the identified ADU positions and known equivalent energies. Such a fit is produced for every detector pixel - an example fit for a single pixel is shown in figure 3.8a. The fit parameters (slope and intercept) as well as the coefficient of determination fit statistic (\mathbb{R}^2) found for each pixel are saved to an energy calibration file. This calibration file is used to convert the detector recorded ADU values into equivalent photon energies.

3.5.4.2. Calibration results

The slope, intercept and the R^2 value obtained from the linear calibration fit for each pixel of the HF-CdZnTe detector, are shown on pixel maps in figures 3.8b-d. Figure 3.8d shows



Figure 3.8: Energy calibration summary for HF-CdZnTe detector. (a) Energy calibration for a single pixel used to convert ADU signal to an energy in keV. A linear fit is obtain from fitting the measured peak positions and corresponding photopeak energies - the slope, intercept and \mathbb{R}^2 value are shown from the fit. (b) the slope from the linear fit for each pixel. (c) the y-axis intercept from the linear fit for each pixel. (d) the \mathbb{R}^2 fit statistic value from the linear fit for each pixel.

that the energy linearity of the individual pixels is very good, with a mean \mathbb{R}^2 value of 0.99998, and a minimum of 0.99924. Nonetheless, there is some variation in the slope and intercept of the calibration between pixels - which is expected due to the non-homogeneity of a crystal. The parallel readout structure of the four blocks of 80×20 pixels is visible in the pixel map of the slopes (figure 3.8b). The variation is therefore not solely due to the sensor material but is also a consequence of small differences in the response of the four ADCs in the HEXITEC DAQ system. The four block readout structure can also be seen from the ADU photopeak positions in figure 3.7a.

Pixels with calibration quantities (slope, intercept or \mathbb{R}^2) greater than 5σ from the median of all pixels were removed due to the performance being outside the range of expected statistical variation (i.e $5\sigma \times 6400 \approx 6399.999$). A distribution for each calibration quantity obtained from all pixels is shown in figures 3.9a-c, where grey-shaded regions represent values outside the 5σ range. In total, this led to the removal of the 83 pixels shown in figure 3.9d. The complete column of 80 pixels removed at the edge of the detector is expected to be due to an issue with one of the elements from the first readout ADC. After removing the faulty pixels, the mean linear fit with standard deviations obtained was

$$y = 0.0294 \pm 0.0002 \text{ keV ADU}^{-1}x + 0.79 \pm 0.27 \text{ keV}$$
 (3.1)

where x is the ADU value and y the energy in keV. From this equation, we can determine that the noise threshold of 90 ADU is approximately 3 keV. Energies recorded in any of the faulty (removed) pixels are ignored during spectral reconstruction and further analysis.



Figure 3.9: Distribution of the slope (a), y-axis intercept (b), \mathbb{R}^2 value (c) of all pixels obtained from the linear fits during energy calibration. The grey-shaded region highlights values that are greater than 5σ from the median. (d) pixels removed from analysis and labelled faulty due to performing significantly below expected variance.

The whole-detector spectrum for each of the sources listed in table 3.2 is shown in figure 3.10, before and after applying the calibration. For the spectra before calibration, the average ADU photopeak positions from the whole-detector spectrum were used to convert the energy axis from ADU to keV in order to enable comparison. By visual inspection, it is clear that the per pixel calibration improves the energy resolution at all photopeak energies and also increases the peak number of counts in the photopeaks. Some smaller peaks that could not be resolved before calibration are visible after calibration, such as the escape peaks at \sim 33 keV in the ²⁴¹Am spectrum, and at \sim 96 keV in the ⁵⁷Co spectrum. Escape peaks are due to the detector's response (section 3.7).



Figure 3.10: The whole detector spectrum containing isolated events only before and after applying the per-pixel energy calibration for the (a) ⁵⁵Fe, (b) ¹⁰⁹Cd, (c) ²⁴¹Am and (d) ⁵⁷Co spectrum.

3.6 Calibration of the CdTe detector

3.6.1 Energy calibration

The calibration for the CdTe detector was performed by Bugby et al. [42] using a procedure similar to the method described in section 3.5.4. Flood images were taken with the same sealed radioisotope sources as for the HF-CdZnTe detector (table 3.2) placed at a distance of 300 mm from the detector surface. The energy calibration was performed using all the photopeaks listed in table 3.2 from the ¹⁰⁹Cd, ²⁴¹Am and ⁵⁷Co sources. Pixel maps of the calibration quantities found for the CdTe detector are shown in figure 3.11. Using the calibration quantities and hot pixels identified from a dark image, 22 pixels were identified as faulty and are removed during analysis. A summary of the calibration details compared with those from the HF-CdZnTe detector are shown in table 3.3. The energy linearity of the CdTe detector pixels is also very good with a mean \mathbb{R}^2 value of 0.99991. Therefore, although different photopeaks were used for calibration between the two detectors, this should not influence the energy calibrations.

The slope from the linear energy calibration can be understood as the pixel's gain, as this

is the amplified energy equivalent to each digitised unit. As would be expected, this value is on average very similar between the two detectors as both detectors were operated in high-gain mode. Furthermore, some spatial correlation between pixel regions of steeper or shallower slopes between the HF-CdZnTe detector (figure 3.8b) and CdTe detector (figure 3.11b) can be observed. This is also true for the spatial distribution of the intercepts across the pixels - i.e. greater intercepts in the top pixels for both detectors. This spatial correlation of the calibration quantities between the two different detectors suggests some of the variability in pixel response is due to the DAQ readout (likely the off-chip ADC) and not solely the sensor material.



Figure 3.11: Energy calibration summary for CdTe detector. (a) Energy calibration for a single pixel used to convert ADU signal to an energy in keV. A linear fit is obtain by fitting the measured peak positions and corresponding photopeak energies - the slope, intercept and R^2 value are shown from the fit. (b) the slope from the linear fit for each pixel. (c) the y-axis intercept from the linear fit for each pixel. (d) the R^2 fit statistic value from the linear fit for each pixel.

3.6.2 DAQ operation

The CdTe detector was bonded to the same DAQ as with the HF-CdZnTe detector. The detector was operated at a bias voltage of -500 V (500 V mm⁻¹) and the detector temperature was maintained at $28\pm1^{\circ}$ C. The ASIC frame rate was set to 1.6 kHz. To minimise the

| Quantity | HF-CdZnTe | CdTe | | |
|---------------------------------------|-------------------------------------|--------------------------------------------|--|--|
| Photopeaks used (keV) | 5.95, 22.0, 59.5 122.1 | 14.4, 22.0, 24.9, 59.5, 88.0, 122.1, 136.5 | | |
| Slope (Gain) | 29.4 \pm 0.2 eV ADU ⁻¹ | 28.7 \pm 0.3 eV ADU ⁻¹ | | |
| 1000000000000000000000000000000000000 | $0.79 \pm 0.27 \text{ keV}$ | $0.70 \pm 0.5 \text{ keV}$ | | |
| N. pixels removed | 83 | 22 | | |
| Noise threshold | 3 keV | 3 keV | | |

Table 3.3: Summary of the calibration quantities obtained from the energy calibration of the HF-CdZnTe and CdTe detectors. Average values after removing faulty pixels are shown for the slope, intercept annd R^2 value.

bias-induced polarisation effect, the bias voltage was periodically reset every 60 seconds by switching the bias to 0 V for 2 seconds. This allows the space charge that has built up at the blocking electrodes to recombine.

The CdTe detector when biased to -500 V suffered from severe noise injections during some observations which would completely saturate some frames. This problem was investigated together with RAL STFC and is discussed in Appendix A.

3.7 Spectral detector response

The spectra obtained with the Cd(Zn)Te detectors do not only show the emissions from the source observed but also include additional features, due to the detector's response. Figure 3.12 is the whole-detector spectrum recorded from the ⁵⁷Co source flood image with the HF-CdZnTe detector. The figure is illustrated to help describe the detector response.

The spectrum shows the spectral response of the detector to the emissions incident on it from the ⁵⁷Co source. As expected, the response shows peaks at the most prominent gamma emission lines from ⁵⁷Co - 14.4, 122.1 and 136.5 keV. The peaks from 72 - 87 keV are due to fluorescence emitted from the lead (Pb) shielding surrounding the source and detector. The 122.1 and 136.5 keV photons are greater than the Pb K-shell electron binding energy (88 keV), causing the lead to emit K_{α} and K_{β} X-ray fluorescence (XRF) of which some is incident on the detector. The remaining peaks in the spectrum are not from photons incident on the detector but are instead due to self-fluorescence of the sensor material.

The K-shell fluorescence from the high-Z elements Cd and Te have energies (23 - 31 keV) large enough to have significant mean path lengths of $(60 - 120 \,\mu\text{m})$ in Cd(Zn)Te. For incoming photon energies greater than the K-shell electron binding energy in Cd (26.7)



Figure 3.12: The whole-detector ⁵⁷Co spectrum measured with the HF-CdZnTe detector containing only isolated events. The spectrum is annotated to help describe the detector response.

keV) and Te (31.8 keV), the XRF generated can escape the pixel of the original event, either by leaving the sensor completely or being reabsorbed beyond the nearest pixel neighbours. The remaining energy in a pixel after K-shell XRF has escaped produces the escape peaks. In figure 3.12, we only see the escape peaks from the XRF escaping pixels that absorbed 122 keV photons (although the same process occurs for the 136.5 keV photons, the escape peak incidence is too small to observe). The escaped XRF that is reabsorbed within the sensor causes the fluorescence peaks. The escape and fluorescence peaks are therefore a consequence of the detector response due to the high-Z material and pixelation.

3.7.1 Hole-tailing

A tailing effect can be seen on the low-energy side of some of the photopeaks. The tail arises from two distinct mechanisms. The first is due to the noise threshold, which removes any energy belonging to the main event that is in an adjacent pixel and lower than 3 keV. This is the dominant source of the tail in the lower energy photopeaks (e.g. 14.4 keV). The second mechanism is a consequence of hole trapping which results in tailing as charge from trapped holes is not fully collected. Hole tailing from charge trapping is more prominent at

the higher photopeak energies in small-pixel detectors, due to greater attenuation depths of the photons such that the charge carriers drift in the higher weighting field regions close to the anode.

3.7.2 Charge sharing

Figure 3.13 shows the 57 Co spectrum using only isolated events compared with the same spectrum using only charge sharing events (i.e. multiplicity > 1). It is clear that the spectral resolution of the charge sharing events suffers and is noticeably worse than for isolated events. Since charge sharing events contain more than one pixel, the energy resolution of spectra including these events will always be poorer than isolated events due to the noise contribution from each individual pixel. However, this alone does not account for the spectral degradation of the charge sharing events seen, which is particularly evident for the CdTe detector. The spectral response of charge sharing events is quite complex and is a combination of various components including electronics noise, sensor fluorescence, charge trapping, and charge loss within the inter-pixel regions. A significant contributor to the poorer energy resolution for charge sharing events in the CdTe detector is the larger inter-pixel spacing of 50 µm compared with 25 µm in the HF-CdZnTe detector.

Charge sharing is not discussed further here as charge sharing and the contributing factors are investigated in chapter 5.



Figure 3.13: ²⁴¹Am spectrum from isolated events only compared with the same spectrum including only the charge sharing event types (i.e. m>1), for the HF-CdZnTe detector (a) and the CdTe detector (b).

3.8 Performance characterisation

The calibrated and reconstructed data were used to extract key performance indicators, which include photon counting uniformity and the energy resolution recorded by each pixel, to characterise detector performance.

Each performance indicator was calculated at photons energies 5.95, 22, 59.5 and 122 keV. These energies were selected for this analysis as they contain sufficient counts that the performance of each individual pixel can be assessed. A per-pixel analysis is particularly useful as it also provides an insight into the quality and uniformity of the materials across the whole sensor volume.

3.8.1 Photon counting uniformity

The counting uniformity of the detectors is determined from the pixel to pixel variation in the number of counts detected. The sources (during calibration) were placed far enough from the detector to be approximated as a point source and therefore assumed to uniformly illuminate the detector surface. Energy windows of ± 5 keV were used around the HF-CdZnTe photopeaks, and +5/-10 keV windows around the CdTe photopeaks (due to the wider charge sharing peaks). Counts from all event types (i.e. the total recorded counts) were included in the photopeaks. It was ensured that the median number of counts per pixel (M_{counts}) was at least 3000 counts within the energy window. This minimised the Poisson counting error to a maximum of 1.8%. For the HF-CdZnTe detector, additional flood images using the same experimental arrangement as for the calibration images were taken to reach this counting statistic.



Figure 3.14: Photon counting uniformity distributions at 59.5 keV photons. The number of counts per pixel shown on a detector map and as a histogram respectively for the HF-CdZnTe detector in the top row panels (a)-(b), and for the CdTe detector in the bottom row panels (c)-(d). The number of counts has been normalised by the median counts per pixel. White pixels are the faulty pixels for which data has been removed and are not included in the analysis.

Figure 3.14 shows the variation in the number of counts across the detector pixels as an image and a histogram for the 59.5 keV photopeak. The distributions have been normalised

by the median counts M_{counts} . Pixels along the detector edges or adjacent to faulty pixels (e.g. bottom left corner in figure 3.14a) tend to record counts significantly above or below the average. These variations in pixel counts are thought to be due to edge effects or poor bonding issues. The distributions are therefore normalised using M_{counts} , as the median is less influenced by outliers. The photon counting uniformity was quantified by calculating the coefficient of variation (COV_{counts}) which is the standard deviation of counts divided by M_{counts} . To determine the standard deviation of counts, a Gaussian function was fit to the distribution of counts as shown in figures 3.14b,d. Table 3.4 lists the M_{counts} and the COV_{counts} at each energy investigated.

| Photon energy | HF-CdZnTe | | CdTe | |
|---------------|--------------|---------------------------|--------------|---------------------------|
| (keV) | M_{counts} | COV_{counts} (%) | M_{counts} | COV_{counts} (%) |
| 5.95 | 3763 | 4.9 | 3020 | 3.8 |
| 23.1 | 3861 | 4.4 | 3397 | 3.0 |
| 59.5 | 4058 | 4.3 | 3068 | 3.4 |
| 122.1 | 3092 | 3.4 | 4574 | 3.0 |

Table 3.4: The median counts per pixel and coefficient of variation (COV) for the HF-CdZnTe and CdTe detectors at multiple photon energies. The COV is a measure of the detectors photon counting uniformity and given by the standard deviation of all pixels counts divided by the median counts per pixel.

The HF-CdZnTe detector shows good photon counting uniformity with $\text{COV}_{counts} < 5\%$ at all energies. The uniformity across the CdTe sensor is slightly better with $\text{COV}_{counts} < 4\%$ at all energies. It is likely that this is in part related to the greater thickness of the HF-CdZnTe detector, however, from the detector images we also observe a greater number of defect features in the HF-CdZnTe detector (section 3.8.3).

3.8.2 Energy resolution

The energy resolution was calculated for each pixel by determining the FWHM of the photopeaks recorded by the individual pixels. Only isolated events were used in order to obtain the spectral performance of the detectors, independent of the effects from charge sharing. Furthermore, the spatial variation in energy resolution of individual pixels provides additional insight into detector uniformity and crystal quality.

3.8.2.1. FWHM calculation method

The energy resolution was found by fitting a Lorentzian function to the photopeak in question for each pixel, and extracting the FWHM from that fit. Energy windows of ± 5 keV were used around the photopeaks during fitting.

Although the broadening of the photopeaks is expected to follow a Gaussian distribution (section 2.4.5), the low energy tails on the LHS of the photopeaks from the noise threshold skew the photopeak shapes away from such a distribution - see figure 3.15. As a result, we found that a Gaussian function fit to the photopeak tended to overestimate the measured FWHM. Lorentzian functions were therefore fit to the photopeaks instead. The spectral photopeaks recorded with these detectors are not expected to physically follow a Lorentzian distribution, however, due to the tails in a Lorentzian distribution, the FWHM is skewed less by the low-energy tail of the photopeak. Figure 3.15 shows an example of the same 122 keV photopeak recorded by a single pixel fit with a Gaussian function (a) and Lorentzian function (b). The FWHM obtained from the Lorentzian fit is closer to the value measured empirically from the photopeak (i.e. 0.99 keV FWHM). Furthermore, using the Lorentzian function, an average pixel FWHM of 0.85 keV for the 59.5 keV photopeak recorded by the HF-CdZnTe detector was measured (table 3.5). This is consistent with the average FWHM of 0.84 keV found by Veale et al. [21] at the same photopeak energy using the same detector.



Figure 3.15: 122 keV photopeak from ⁵⁷Co spectra recorded by a single pixel from the HF-CdZnTe detector. Gaussian functions (a) and Lorentzian functions (b) were tested by performing fits to the photopeak and extracting the FWHM.

3.8.2.2. Energy resolution results

| Energy | HF-CdZnTe | | | CdTe | | |
|--------|--------------------|---------------------------|-------------------|--------------------|---------------------------|-------------------|
| (kev) | $\Delta E \ (keV)$ | $\sigma_{\Delta E}$ (keV) | $\Delta E/E~(\%)$ | $\Delta E \ (keV)$ | $\sigma_{\Delta E}$ (keV) | $\Delta E/E~(\%)$ |
| 5.95 | 0.93 | 0.12 | 15.6 | 0.98 | 0.15 | 16.4 |
| 22 | 0.79 | 0.12 | 3.6 | 0.71 | 0.15 | 3.2 |
| 59.5 | 0.85 | 0.16 | 1.4 | 0.81 | 0.20 | 1.4 |
| 122.1 | 1.33 | 0.24 | 1.1 | 1.08 | 0.36 | 0.9 |

The average FWHM (ΔE), energy resolution ($\Delta E/E$) and FWHM standard deviation ($\sigma_{\Delta}E$) calculated from all pixels at each photopeak energy is listed in Table 3.5.

Table 3.5: The pixel average photopeak FWHM (ΔE) and energy resolution for the HF-CdZnTe and CdTe detectors at multiple photon energies. The standard deviation of all pixel FWHM is also shown ($\sigma_{\Delta E}$).

The average pixel energy resolutions as a function of photon energy are plotted for both detectors in figure 3.16. The theoretical equation for energy resolution (equation 2.20)

$$\frac{\Delta E}{E} = 2.355\sqrt{F\omega E_0 + \sigma_a^2}.$$
(3.2)

was fit to the experimental values, where σ_a is the combined contribution to the photopeak width from electronic noise and carrier trapping and was left free to vary during fitting. The electron-hole pair creation energy ω used was 4.43 eV and 4.64 eV for CdTe and CdZnTe respectively [4]. The reported Fano factor values for CdTe and CdZnTe range from 0.06 to 0.14 [8] - we used a value of 0.1 for both materials [26].

The Fano-limited energy resolution for these detectors is shown for comparison in figure 3.16. The difference between the experimental curves and the fano-limited curve is due to the peak broadening from electronic and thermal noise and carrier trapping, accounted for by σ_a . The magnitude of σ_a was determined from the fits with equation 3.2 to be ~78 e⁻¹ in both detectors. This is equal to approximately 0.35 keV and was used to justify the spectral reconstruction energy bin size of 0.3 keV (section 3.4.3). An energy resolution of below or near 1 keV is excellent for Cd(Zn)Te detectors - and this is achieved by both detectors, at both soft and hard X-ray energies. The spectroscopic performance of the HF-CdZnTe detector is therefore excellent and performs nearly identically to the CdTe detector despite being twice as thick.

Figure 3.17 shows the FWHM measured for each pixel as a detector map and histogram for the 59.5 keV photopeak. The uniformity of the spectral performance is poorer in the


Figure 3.16: Energy resolution as a function of incoming photon energy. Solid lines are the fits using the theoretical equation for energy resolution in the colour of the respective detector data points. The dotted line shows the best achievable energy resolution, a limit set by the fano noise contribution.

CdTe detector, despite the average energy resolution at all energies (with the exception of the 5.95 keV photopeak) being better in this detector. In the CdTe detector, 6.8% of all pixels have a FWHM of <0.6 keV at 59.5 keV. Unfortunately, achieving this level of performance across the entire detector is limited by variations in the crystal quality across the sensor volume. In comparison, only 0.27% of all pixels have a FWHM of <0.6 keV in the HF-CdZnTe detector, but the performance is more uniform across the detector. This is true at all photon energies, shown by the smaller FWHM standard deviations (table 3.5). The greater spatial variation in spectral performance in the CdTe detector is believed to be linked to the presence of more charge trapping defects (section 3.8.3).

Figure 3.18 compares the spectral performance of the same two pixels of the HF-CdZnTe detector at each photopeak energy investigated. The two pixels selected are the worst spectral performing pixel and an average performing pixel observed at 59.5 keV. The spectral performance is observed to change with photon energy - improving at lower energies and worsening at larger energies. This suggests that the performance is linked to the sensor material quality and not the ASIC or bonding. This is discussed more in section 3.8.3.



Figure 3.17: FWHM energy resolution distributions as a histogram and pixel map at 59.5 keV for the HF-CdZnTe (a) and the CdTe detector (b). The red curve corresponds to the RHS y-axis and shows the proportion of pixels cumulatively with FWHM. The illustration of the figure has been adapted from a figure in [21].

3.8.3 Detector defects

From the pixel maps in figures 3.14 and 3.17 which show the spatial variation in photon counting and energy resolution, we can draw some conclusions on the crystal quality.

The photon counting pixel map for the HF-CdZnTe detectors (figure 3.14a) shows a number of features with higher intensity in counts. These appear as 'lines' of pixels moving



Figure 3.18: The spectrum of the same two pixels in the HF-CdZnTe detector compared at (a) 5.95 keV, (b) 22 keV, (c) 59.5 keV and (d) 122 keV.

across the detector image in any orientation recording counts above the median. These high intensity lines have also been observed in other studies using HF-CdZnTe detectors [21, 50, 51]. Veale et al. [21] using optical images of the pixelated anode before hybridisation, showed a correlation between some of the high intensity lines and superficial scratches on the electrode surface. In the FWHM pixel map for the HF-CdZnTe detector (figure 3.17a), no correlation with the features and the spatial variation of the energy resolution is observed. Therefore, it is expected that these features are not the result of bulk crystalline defects but instead due to damages incurred by the detector electrode during fabrication and handling. The scratches caused to the electrodes are thought to influence the local electric field, which alters the effective pixel size and causes the affected pixels to collect counts that would otherwise be registered in neighbouring pixels [50].

In the CdTe photon counting pixel map (figure 3.14c), the image shows better uniformity

with fewer defect features. The features which can be observed are narrow vertical bands with counts lower than the median instead of higher - most of these are located on the right side of the image. Some of these features can be correlated with pixel regions of increased FWHM (figure 3.17b). This suggests that the features are crystalline defects and impact the local carrier transport properties due to increased trapping by those defects. This results in greater charge loss which degrades the spectral performance of the affected pixels and also leads to a loss of counts. These findings are consistent with results in [50] which show similar defect regions recording fewer counts in Acrorad CdTe, and less significant changes in the effective pixel shape correlated with those regions. It is possible that these defects are grain boundaries within the bulk crystal which are known to be charge trapping defects [11].

Both detectors contain a few pixels with energy resolutions significantly worse (> 2 keV FWHM) than the average (e.g. figure 3.18c). This decrease in performance is possibly linked to Te inclusions, a different and more localised charge trapping defect [11]. Subpixel X-ray micro-beams have revealed the presence of Te inclusions and linked the pixels in which they are located with poorer energy resolution due to increased hole-tailing [102]. This could also explain the observed change in performance with photon energy (figure 3.18). At lower photon energies, when the depth of interaction in the sensor is smaller, photons are more likely to be absorbed before the Te inclusion. As a result, fewer holes would drift across the Te inclusion and become trapped.

3.9 Summary

The per-pixel energy calibration of a pixelated HF-CdZnTe detector bonded with the HEXITEC ASIC has been produced. An algorithm which processes the raw detector data into spectra and images has also been developed. The calibration of a CdTe detector bonded with the same ASIC was also discussed.

Using the calibrations, the performance of the detectors was investigated and compared. The photon counting uniformity and energy resolution of the HF-CdZnTe from the soft to hard X-ray regime was found to be excellent, for example achieving an average pixel FWHM of 0.85 ± 0.16 keV at 59.5 keV. The overall performance was shown to be only marginally below that of the 1 mm thick CdTe detector, despite a greater thickness of 2 mm.

Evidence of the presence of defects was found to be consistent with those observed in other

studies. It was observed how the crystal quality has a direct impact on performance. The results revealed fewer crystalline defects within the CdZnTe crystal and consequently better spectral resolution uniformity across the detector. Although the comparison between a single CdZnTe and CdTe detector alone cannot be used to draw a conclusion about which material has the greater crystal quality, particularly as variation between detector batches exists, the results do show the high quality and uniformity that can be achieved with CdZnTe.

Chapter 4

Monte Carlo Detector Model

4.1 Introduction

This chapter describes the development of a Monte Carlo detector model to simulate the spectroscopic response of pixelated Cd(Zn)Te detectors. The model was developed to better understand the response of the detectors described in section 3.3.

The Monte Carlo (MC) method relies on repeated random sampling to obtain numerical solutions to problems with probabilistic outcomes. This is particularly useful for simulating detectors due to the stochastic nature of photon detection. MC modelling is therefore a common method employed in detector research and development [112]. Consequently, over the last couple of decades many MC models have been developed for Cd(Zn)Te detectors and used to simulate performance and inform design decisions [110, 113–118]. Analytical models have also been used to investigate certain aspects of performance, such as charge sharing [29,58,119,120], using the geometrical and physical parameters of a detector with charge transport equations. However, analytical models are limited to monoenergetic photons, and do not take into account the effect of stochastic processes such as sensor fluorescence, Compton scattering and photon pileup on the detector response. MC models are therefore preferred for simulating Cd(Zn)Te detectors at hard X-ray energies where K-shell fluorescence and Compton scattering can significantly impact performance.

The model described in this chapter was developed from the ground up in the Python programming language [121]. A number of off-the-shelf software packages offer photon attenuation simulation using Monte Carlo methods (e.g. GEANT4 [122], PENELOPE [123]) while other packages offer finite element method (FEM) simulations of the electric and weighting field profiles in detectors and signal generation processes (e.g. COMSOL

[124], Synopsys [125]). Many of the Cd(Zn)Te models developed in the research community [110,114–116,118] employ a combination of these software packages to achieve a complete detector model. We opted not to use these packages and build our model from the ground up to allow greater control of the model inputs and outputs.

Our MC model incorporates photon attenuation by the photoelectric effect, Compton scattering and Rayleigh scattering. Charge transport equations are used to simulate the size of the electron cloud, approximated by a symmetrical 2D Gaussian distribution, as it drifts to the anode. Charge induction across pixels is modelled using the electron cloud size. Incomplete charge collection due to carrier trapping during drift is also taken into account.

Figure 4.1 provides an overview of the model. Each step is described in more detail in the following sections of the chapter. The chapter concludes with comparisons between the model and experiment, and an estimation of the Zn fraction in the HF-CdZnTe detector - which is required as a model input to simulate this detector.



Figure 4.1: Flowchart to summarise the steps occurring in the MC detector model. Black boxes represent deterministic processes and blue boxes stochastic processes.

4.2 Definition of simulation environment

The model assumes a detector consisting of a semiconductor sensor, a planar cathode and a pixelated anode, and that the detector is back-illuminated through the cathode. Figure 4.2 shows a schematic which represents how the detector is constructed in the model. As an example, the schematic shows the process of a single photon that is absorbed by the sensor, produces a fluorescence X-ray and the resulting excited charge clouds that induce a signal in various pixels at the anode. Table 4.1 lists all of the model parameters that can be defined by the user. Each parameter belongs to one of three components (Photon, Detector, Sensor) which together define the whole simulation environment.

Attenuation by pair production is not included in the model. The model is therefore most appropriate for X-ray energies of < 1 MeV.



Figure 4.2: Schematic of the detector as simulated by the model. The entire sensor is assumed to be depleted by the electric field. The cathode is planar and the anode is pixelated. The drift length of the electrons to the anode is given by d. The electron charge cloud will expand as it drifts towards the anode (represented by the triangle with its apex at the photon attenuation depth z_0). The width of the Gaussian charge cloud (i.e. standard deviation) at the anode is given by σ which induces a charge, Q, in pixels positioned at (x, y) in a certain frame, fn. The width of the pixel electrodes is given by w.

| Simulation environment component | Parameter name | Symbol |
|-------------------------------------|-------------------------------------|------------|
| Photon | Number of photons | |
| | Count rate | |
| | Source spectrum | |
| Detector | Cathode material | |
| | Cathode thickness | |
| | Pixel array dimensions | |
| | Pixel electrode size | W |
| | Bias voltage | V |
| | Temperature | T |
| | Readout noise | A |
| | Weighting potential | ψ |
| Sensor | Thickness | L |
| | Material (attenuation coefficients) | $\mu(E)$ |
| | Density | ho |
| | Electron mobility | μ_e |
| | Electron lifetime | $	au_e$ |
| | Hole mobility | μ_h |
| | Hole lifetime | $	au_h$ |
| | Fano Factor | F |
| | Pair creation energy | ϵ |
| | Atomic weight fractions | |

Table 4.1: Input parameters which define the simulation environment in the model and are selected by the user. The name of each parameter is listed and its symbol is also given where relevant.

4.3 Photon generation

The energy, E, of the generated photons incident on the detector is determined from the source spectrum supplied by the user. The source spectrum is also used to calculate the probability that a photon of certain energy is emitted. For example, the source spectrum can represent an emission line at a single energy, or a radioactive isotope such as ⁵⁷Co with multiple discrete emission lines of known rates.

Uniform illumination across the entire collecting area is modelled with each photon given a random incident position on the surface of the detector. The photons are assumed to be travelling perpendicular to the surface of the detector.

4.4 Photon attenuation

The distance the incident photons travel before attenuation is randomly sampled from the probability distribution P(x) obtained from the Beer-Lambert law (section 2.2.1)

$$P(x) = e^{-\mu(E)x} \tag{4.1}$$

where $\mu(E)$ is the total linear attenuation coefficient of the material in which the photons of energy E are travelling and x the distance the photons travel before being attenuated. Values for $\mu(E)$ are taken from the NIST XCOM database [62]. The database values are linearly interpolated on a log-log scale so that $\mu(E)$ can be sampled for continuous values of E.

Equation 4.1 is used to determine which photons are stopped in the cathode and which pass through unattenuated. Photons which are attenuated by the cathode (i.e $x \leq$ the cathode thickness) are removed from the simulation. Since typical electrode thicknesses are very thin (of the order of nanometres), the fraction of photons attenuated by the cathode is negligible at hard X-ray energies. When attenuation does occur (primarily at soft X-ray energies), it is predominantly by absorption where all the photon energy is deposited in the cathode. The model therefore only calculates the transmission through the cathode, and does not consider any further attenuation processes such as scattering or fluorescence by the cathode.

Photons which pass through the cathode reach the sensor. The distance, x, the incident photons travel in the sensor before attenuation is again calculated using equation 4.1, accounting for the $\mu(E)$ values for the sensor material. The z-axis is defined in the model from the bottom of the cathode to the top of the anode (see figure 4.2). The initial attenuation depth z_0 of the incident photons is therefore the position along the z-axis after distance x. If the calculated attenuation depth z_0 is greater than the thickness of the sensor L, the photon is not detected by the sensor and instead passes through unattenuated. In this case, the photon is removed from the simulation.

For photons attenuated within the sensor, the type of attenuation which occurred at position z_0 is determined by random sampling from the relative likelihoods of each attenuation type. For example, the probability of attenuation by the Photoelectric effect $P_{\mu_{pe}}$ at photon energy E is

$$P_{\mu_{pe}} = \frac{\mu_{pe}(E)}{\mu(E)} \tag{4.2}$$

where μ_{pe} is the attenuation coefficient for the Photoelectric effect only. Once the type of attenuation at position z_0 is known, the photon is passed on to the appropriate attenuation routine.

For compounds, it is necessary to determine which atom the interaction was with. The probability, P_{Cd} , of a photon interacting with a Cd atom in CdTe, for example, is [126]

$$P_{Cd} = W_{Cd} - \frac{\left(\frac{\mu(E)}{\rho}\right)_{Cd}}{\left(\frac{\mu(E)}{\rho}\right)_{CdTe}}$$
(4.3)

where W_{Cd} is the weight fraction of Cd in CdTe (0.468) and ρ is the density of the sensor material. The interaction probability of each atomic element in the sensor material is sampled to determine the atom each photon attenuated within the sensor interacted with.

4.4.1 Scattering

For scattered photons, the scattering angle, θ , is determined. From this, the new direction of a scattered photon can be calculated using spherical coordinates (θ, ϕ) . Scattering in the polar direction is given by the scattering angle θ and the azimuthal direction ϕ of the scattered photon is isotropic and therefore obtained by uniformly sampling in the interval $[0, 2\pi]$.

Once the new direction and energy of a scattered photon is known, equation 4.1 is used to calculate whether it interacts at a new position within the sensor or escapes the sensor, in which case it is removed from the simulation. For every further interaction position of a scattered photon that is within the sensor, the relative likelihoods of the attenuation types are used to determine if the photon is again scattered or finally absorbed.

Determination of the angle θ through which the photons are scattered and if the energy of the scattered photon changes, depends on whether the photon was Rayleigh or Compton scattered.

4.4.1.1. Rayleigh scattering

In the case of Rayleigh scattering, the possible scattering angles θ are defined by a probability distribution that depends on the energy E of the photon being scattered and the Z number of the atom involved in the interaction. The probability distribution function, $P(\cos\theta)$, for the angular deflection θ of the scattered photon is given by [127]

$$P(\cos\theta) = \frac{1 + \cos^2\theta}{2} [F(q, Z)]^2$$
(4.4)

where F(q, Z) is the atomic form factor and q the magnitude of the momentum transfer equal to

$$q = 2\frac{E}{c}\sin\frac{\theta}{2} \tag{4.5}$$

where c is the speed of light. The form factor is a measure of the scattering amplitude of a wave due to the electron cloud of an atom. Therefore, the greater the form factor, the more likely the photon is to be scattered by the atom. Analytical approximations [128], that have been found by numerically fitting the form factors calculated and tabulated in the work by Hubbel et al. [129], are used by the model to determine the appropriate form factor;

$$F(q, Z) = f(x, Z)$$

$$= Z \frac{1 + a_1 x^2 + a_2 x^3 + a_3 x^4}{(1 + a_4 x^2 + a_5 x^4)^2} \quad \text{or}$$

$$\max[f(x, Z), F_K(x, Z)] \quad \text{if } Z > 10 \text{ and } f(x, Z) < 2 \quad (4.6)$$

where

$$F_K(x, Z) = \frac{\sin(2b \arctan Q)}{bQ(1+Q^2)^b},$$
(4.7)

with

$$x = 20.6074 \frac{q}{m_e c}, \qquad Q = \frac{q}{2m_e c a}, \qquad b = \sqrt{1 - a^2}, \qquad a = \alpha \left(Z - \frac{5}{16}\right),$$
(4.8)

where α is the fine structure constant and $F_K(x, Z)$ the contribution of the two K-shell electrons to the atomic form factor [128]. The values for the *a* parameters are from the work by Baró et al. [128].

With the correct form factor for the energy E of the scattered photon and the Z number of the interacting atom, the probability distribution for all possible scattering angles is obtained from equation 4.4 and sampled randomly to determine the scattering angle θ .

Since Rayleigh scattering is a form of elastic scattering, no energy is deposited at the interaction position and only the direction of the photon is altered.

4.4.1.2. Compton scattering

Photons that are attenuated by Compton scattering are assumed in the model to only interact with free electrons. Under this assumption, the Klein-Nishina formula can be used to determine θ since it describes the differential cross section $\left(\frac{d\sigma}{d\Omega}\right)$ of a photon scattering from a single free electron as a function of the photon energy E and scattering angle θ . This can be used to give the probability distribution function, $P(\cos\theta)$, of all possible scattering angles for a photon with energy E [130]

$$P(\cos\theta) = \frac{d\sigma}{d\Omega}$$
$$= \alpha^2 r_c^2 \left(\frac{E'}{E}\right)^2 \frac{\left(\frac{E'}{E} + \left(\frac{E'}{E}\right)^{-1} - 1 + \cos^2\theta\right)}{2}$$
(4.9)

where α is still the fine structure constant, $r_c = \frac{\hbar}{m_e c}$ is the reduced Compton wavelength of the electron and E' is the energy of the scattered photon given by the Compton equation (section 2.2.3)

$$E' = \frac{E}{1 + \frac{E}{m_e c^2} (1 - \cos \theta)}.$$
 (4.10)

Once the scattering angle θ has been randomly sampled from the Klein-Nishina probability density function, equation 4.10 is used to calculate the energy of the scattered photon E'. The energy lost from the scattered photon is deposited at the interaction position, given by

$$E_e = E - E' \tag{4.11}$$

where E_e is the energy transferred to the Compton recoil electron.

4.4.2 Photoelectric absorption

If attenuation occurs via the photoelectric effect, the photon is completely absorbed and deposits all of its energy at the interaction position. The energy, however, that is transferred to the photoelectron in the model, depends on the atom and shell the photon is absorbed by and any resulting fluorescence.

The atom the photon interacted with is determined using equation 4.3. Which shell the photon interacts with will firstly depend on the binding energy of the shells relative to the energy of the photon. If the energy of the photon does not exceed the binding energy E_b

of a shell, absorption by that shell is not possible. Where $E > E_b$, the shell the photon is absorbed by is determined by comparison of the mass attenuation coefficients of the individual shells. Electrons bound to the K, L₁, L₂ and L₃ shells are considered in the model. The mass attenuation for an individual shell can be calculated from the total mass attenuation of the atom and its jump factor, J, [126]

$$\left(\frac{\mu}{\rho}\right)_{shell} = \frac{J-1}{J} \left(\frac{\mu}{\rho}\right)_{tot}$$
(4.12)

The jump factor is the fraction of the total photoelectric absorption coefficient due to absorption by electrons of the respective shell. The binding energy of the shells used in the model are taken from [72] and the jump factors from [131].

4.4.2.1. Fluorescence

A vacancy is created in the shell that the photon interacts with. The fluorescence yield for the respective shell is used to determine whether the filling of the vacancy by a cascading electron results in a fluorescence photon. The model uses the fluorescence yields from [131].

If fluorescence does not occur, the complete energy of the absorbed photon is assumed to be transferred to the photoelectron such that,

$$E_e = E. (4.13)$$

Equation 4.13 is a simplification that does not take into account non-radiative transitions (such as Auger transitions) which may create new vacancies in higher energy shells. As a result, the model will underestimate vacancies left in the L-shell by $\sim 25\%$ [132]. However, since L-shell fluorescence in CdTe has an average energy of 3.5 keV (see table 4.2), which has a mean path length of $\sim 4 \,\mu\text{m}$ in CdTe, the majority of L-shell fluorescence will be absorbed close to the interaction position and have a minimal effect on the detector response.

If a fluorescence photon is emitted from the excited atom, the relative radiative rates for each possible transition are used to determine the energy of the emitted fluorescence photon. Possible transitions, their line energies and their relative rates for Cd and Te as an example are shown in table 4.2 - the values used are from [72].

A vacancy left in an L-shell of the same atom due to a $K\alpha$ transition may also fluoresce, producing an additional fluorescence photon. The energy transferred to the photoelectron,

| Transition | Cd | | Te | |
|-------------------------------|-------------------|------|-------------------|------|
| 110110101011 | Line energy (keV) | Rate | Line energy (keV) | Rate |
| $K\alpha_1 (\mathrm{KL}_3)$ | 23.174 | 0.55 | 27.473 | 0.53 |
| $K\alpha_2 \ (\mathrm{KL}_2)$ | 22.984 | 0.29 | 27.202 | 0.29 |
| $K\beta_1 \ (\mathrm{KM}_3)$ | 26.095 | 0.09 | 30.996 | 0.10 |
| $K\beta_2 \ (\mathrm{KM}_2)$ | 26.654 | 0.02 | 31.700 | 0.03 |
| $K\beta_3 (\mathrm{KM}_2)$ | 26.061 | 0.05 | 30.945 | 0.05 |
| $L\alpha_1 (L_3M_5)$ | 3.134 | 0.77 | 3.769 | 0.75 |
| $L\alpha_2 (L_3M_4)$ | 3.127 | 0.08 | 3.758 | 0.08 |
| $L\beta_2 (L_3N_4)$ | 3.528 | 0.12 | 4.302 | 0.14 |
| $Ll (L_3M_1)$ | 2.767 | 0.03 | 3.336 | 0.03 |
| $L\beta_1 (L_2M_4)$ | 3.317 | 0.91 | 4.030 | 0.88 |
| $L\gamma_1 (L_2N_4)$ | 3.717 | 0.09 | 4.571 | 0.12 |
| $L\beta_3 (L_1M_3)$ | 3.401 | 1.00 | 4.120 | 1.00 |

Table 4.2: Possible transitions for Cd and Te atoms used in the model, along with line energies and relative radiative rates for each transition [72] rounded to three and two significant figures. The naming convention of the transition in the brackets gives the shell of the initial vacancy and then the shell of the final vacancy e.g. KL_3 indicates that an initial K-shell vacancy is filled by an electron from the L_3 .

 E_e , is therefore calculated by

$$E_e = E - \sum_{i=K_{shell}}^{L_{3shell}} E_{XRF_i}$$

$$\tag{4.14}$$

where E_{XRF_i} is the energy of the fluorescence photon, if any, from the *i*th shell. Vacancies that arise in an M or N shell due to the cascading of electrons or otherwise, are ignored. Given that the binding energy for these shells is very small (e.g. 0.618 keV for M₃ shell in Cd [72]), and that any resulting fluorescence will consequently be of very low energy (0.603 keV for M_{γ} line [133]), the fluorescence will be reabsorbed very close to the original vacancy (mean path length of 1 keV in CdTe is ~0.2 µm). The energy from the ignored vacancies is therefore included in the photoelectron energy E_e at the interaction position (i.e. the energy is never subtracted from the incident photon energy E in equation 4.14).

The possible direction the fluorescence photons may travel is described by a uniform distribution over all solid angles. As for the scattered photons, this is calculated using spherical coordinates. The polar direction θ is determined by randomly sampling $\cos\theta$ in the interval [-1, 1] and ϕ is randomly sampled in the interval $[0, 2\pi]$. The distance the fluorescence photons travel along this direction before interaction is calculated using equation 4.1. If the fluorescence photons escape the sensor, they are removed from the simulation. If they interact at a new position within the sensor, the entire process, beginning by determining

if the photon was scattered or absorbed, is repeated.

When a photon is attenuated by the photoelectric effect but absorption by K and L shells can no longer occur (i.e. when the photon energy is less than the binding energy of the L_3 shell in the lowest Z value atom, e.g. 1.022 keV for Zn [72]), the photon is assumed to be absorbed in either an M or N shell.

4.5 Charge transport

After the photon attenuation routines, the energy E from the incident photons has been transferred to photoelectrons¹ of energy E_e . The position of the photoelectrons are the interaction positions of the photons at depth z_0 . The number of electron-hole pairs created by the ionisation process, N, at depth z_0 is calculated as (section 2.3.1)

$$N = \frac{E_e}{\varepsilon} \tag{4.15}$$

where ε is the average pair creation energy. Fano-noise is applied to all calculations of N using Fano adjusted Poisson statistics ($\sigma_N^2 = FN$).

The model assumes a uniform electric field across the sensor material with field strength, E_f , given by

$$E_f = \frac{V}{L} \tag{4.16}$$

where L is the sensor thickness and V the applied bias voltage. The field lines go from the anode to the cathode (parallel to the z-axis). Due to this field, holes drift towards the cathode (z = 0) and electrons towards the pixelated anode (z = L).

4.5.1 Charge cloud size

The charge carriers will spread during drift due to thermal motion and electrostatic forces, forming a so-called cloud of charge. Using the carrier transport equations from section 2.3, we can calculate the size of the electron charge cloud that arrives at the anode. By evaluating its size against the pixelated anode, we can estimate the number of pixels that the charge carriers induce a signal in.

¹these are actually either photoelectrons or recoil electrons from the attenuation processes, but treated the same by the model and therefore collectively referred to as photoelectrons for simplicity.

The size of the electron charge cloud is calculated in the model, approximated by a symmetrical 2D Gaussian distribution [117,134] in the plane perpendicular to the electric field lines (i.e. the z-axis). The final size of the cloud will depend on the initial size, σ_i , due to the range of the photoelectron and the growth of the cloud, σ_d , from diffusion and electrostatic repulsion of the charges as the cloud drifts to the anode. The final size of the charge cloud at the anode, σ , is found by adding the two components in quadrature (under the assumption that their magnitudes are not correlated [135]),

$$\sigma = \sqrt{\sigma_d^2 + \sigma_i^2}.\tag{4.17}$$

The cloud growth during drift, σ_d , is calculated using the diffusion equation (section 2.3.3)

$$\frac{\partial \sigma_d(t)^2}{\partial t} = 2D \tag{4.18}$$

where D is the diffusion coefficient and $\sigma_d(t)^2$ is a function of time. The diffusion coefficient is given by the Einstein relation

$$D = \mu_e \frac{k_b T}{e} \tag{4.19}$$

where μ_e is the electron mobility, k_b Boltzmann's constant, e the elementary charge and Tthe temperature of the sensor. For a uniform field, the total drift time t_d for the electron cloud to reach the anode is equal to

$$t_d = \frac{d}{\mu_e E_f} \tag{4.20}$$

where d is the drift length of the electron cloud to the anode (given by $L - z_0$). The electrostatic repulsion between the electrons that occurs during drift is included by using an effective diffusion constant D' in place of D in equation 4.18 [134],

$$D' = D + \frac{\mu_e N_e(t)e}{24\pi^{3/2}\epsilon} \frac{1}{\sigma(t)}$$
(4.21)

where ϵ is the permittivity of the sensor material, $\sigma(t)$ is the size of the electron cloud after time t and $N_e(t)$ is the number of electron carriers after time t, given by equation 2.16. By combining equations 4.18, 4.19 and 4.21, the differential equation which gives the size of the electron cloud due to diffusion and electron repulsion after drifting some period of time t is

$$\frac{\partial \sigma_d(t)^2}{\partial t} = \frac{2\mu_e k_b T}{e} + \frac{\mu_e N_e(t)e}{12\pi^{3/2}\epsilon} \frac{1}{\sigma(t)}$$
(4.22)

Equation 4.22 must be solved numerically to get a well approximated solution for σ_d after the total drift time. In the model we use the 4th order Runge-Kutta method [136] with 10^3 iterative time steps between t = 0 and $t = t_d$ where $\sigma(t) = \sigma_i$ at t = 0. Once $\sigma_d(t_d)$ is known, equation 4.17 is used to compute the final size of the electron cloud when it has arrived at the anode.

GEANT simulations by Blevis and Levinson [137] give estimates for the initial charge cloud size σ_i generated by a photoelectron at different energies, which have previously been used in Monte Carlo simulations to model X-ray spectra from a CdTe detector [117]. The values determined in [137] are the average range (i.e. displacement) of the photoelectron and can therefore be used to approximate a diameter for the initial charge cloud. For a Gaussian cloud, we can estimate its diameter as the FWHM [119] such that diameter $\approx 2.355\sigma$. Using this approximation, the values of σ_i determined for our model are 0 µm, 1 µm, 4 µm for photons of energy 0 keV, 35 keV and 100 keV. These are fit with a second order polynomial in order to find σ_i for any continuous value of E_e .

4.5.2 Signal induction

From section 2.4.4, we know that the charge induced ΔQ_k on a single electrode k by a moving charge can be expressed by

$$\Delta Q_k = -q[\psi_k(\mathbf{r}_f) - \psi_k(\mathbf{r}_i)] \tag{4.23}$$

where \mathbf{r}_i and \mathbf{r}_f are the 3D start and end positions of the moving charge q, and ψ_k the weighting potential of the corresponding electrode k.

Ideally, to achieve the most accurate modelling of charge induction, equation 4.23 would be solved numerically for each electron and hole in motion over each pixel electrode, using a 3D weighting potential and electric field profile determined for the specific electrode configuration of the detector. In our model, we use the approximation of the electron charge cloud of width σ to estimate how the induced charge is distributed over the pixelated anode (section 4.5.3) and so we need only to calculate how much of the original charge in the cloud is induced at the anode in total, not per pixel. In this case, we can use the Hecht relation [82] as a simpler approximation which is less computationally demanding than numerically solving with equation 4.23.

4.5.2.1. Small pixel signal induction

The classical Hecht relation (equation 2.18) can be used to calculate the total induced charge Q for planar detectors or large pixel geometries where the pixel size is equal to or greater than the thickness of the sensor (w/ $L \ge 1$). When the pixel pitch is smaller than the sensor thickness, a more significant fraction of charge is induced by carriers drifting close to the anode than carriers further away - described by the small pixel effect. This changes the weighting potential of the detector, and the classical Hecht relation is no longer suitable.

To account for this, we use a modified Hecht relation that employs a 1D weighting potential along the z-axis,

$$CCE = \frac{\lambda_h}{L} \left(1 - e^{-\frac{\psi(z_0/L)L}{\lambda_h}} \right) + \frac{\lambda_e}{L} \left(1 - e^{-\frac{L - \psi(z_0/L)L}{\lambda_e}} \right)$$
(4.24)

where $\lambda_h = \mu_h \tau_h E_f$, $\lambda_e = \mu_e \tau_e E_f$ are the mean drift lengths of holes and electrons respectively, and $\psi(z_0/L)$ is the weighting potential at the normalised interaction depth z_0/L of the photon. Figure 4.3 shows the 1D weighting potential for two different small pixel detector geometries compared with the weighting potential for a planar detector. The weighting potentials for the small pixel geometries were calculated by Thomas et al. [52] using finite element simulations, and correspond to the geometries of the CdTe and HF-CdZnTe detectors characterised in chapter 3.

We see from the figure that for a planar electrode configuration $\psi(z_0/L) = z_0/L$. Inserting this into equation 4.24, we obtain the classical Hecht relation. The weighting potentials for the small pixel geometries (w/L < 1) exponentially approach 1 at the anode side. The weighting potentials therefore account for charge carriers inducing a greater fraction of the charge signal when moving in closer proximity to the anode. Since the model assumes a back-illuminated detector where most of the photon interactions take place closer to the cathode side, electrons will primarily traverse the more dominant regions of the weighting field and correspondingly induce a greater fraction of the charge signal as opposed to the holes. For this reason, only the electron cloud size is used to estimate charge distribution across the pixelated anode.

The CCE is calculated for each charge cloud by first sampling the weighting potential at the normalised interaction depth z_0/L and then using equation 4.24. The effective number of carrier pairs, N', equivalent to the induced charge on the anode after consideration of



Figure 4.3: Weighting potential for a planar detector $(w/L \ge 1)$ and for the small-pixel geometries of the HEXITEC CdTe (w/L = 0.25) and HF-CdZnTe (w/L = 0.125) detectors. A normalised interaction depth of 0 is at the cathode and 1 at the anode. The weighting potentials for the small pixel geometries were calculated by Thomas et al. [52].

the weighting field and trapping during carrier drift, is then

$$N' = CCE \times N. \tag{4.25}$$

4.5.3 Readout at the pixelated anode

For each charge cloud, a 2D Gaussian distribution with standard deviation σ , containing N' charges, is evaluated against the pixelated array, centred on the absorption position. The number of charges distributed to a pixel are multiplied by the pair creation energy ε to obtain the signal induced on that pixel in energy (eV).

We know that charges drifting in close proximity to the inter-pixel gap may result in additional charge loss due to the changes in the electric and weighting field in these regions [38]. Using the 1D approximation for a weighting potential only sensitive to the z position of the charge cloud, it is not possible to model this effect. As a result, the model assumes charges are always drifting perpendicular to the electrodes and charge loss in the pixel gaps is not considered. This is a limitation of the model, however, in practice only a small fraction of the signal is induced by carriers drifting in the gaps as the majority of the weighting field has already been traversed.

The signal induced on each pixel electrode is subject to electronic noise from the pixel readout and digitisation process. Individual sources of electronic noise are not considered in the model, instead we define a single parameter A which encapsulates all the noise to the signal from the readout electronics. The electronic noise is assumed to follow a Gaussian distribution with variance $\sigma^2 = A$ where A is equal to the equivalent noise charge (ENC) of the detector. Electronic noise is added to each pixel that contains an energy.

4.6 Model output

During a simulation run, the energy in each pixel, its position on the pixelated array and the frame in which it was recorded is written to an eventlist. The eventlist format is similar to that of the outputs produced by the HEXITEC ASIC. The simulated eventlists can therefore be processed using the reconstruction algorithm described in section 3.4.3, from which a spectrum and image for each individual event type can be extracted.

4.7 Model validation and tests against experiment

To assess that the Monte Carlo detector model, which consists of multiple separable stages (definition of simulation environment, photon generation, photon attenuation, charge transport) is working as intended, comparisons with experimental data collected in chapter 3 were performed.

The model was used to simulate data for both the 1 mm thick CdTe detector and the 2 mm thick HF-CdZnTe detector. Unless otherwise stated, the input parameters used in the simulations of the detectors are those listed in table 4.3. The pixel electrode pad size is used for the detectors instead of the pixel pitch. This was done because it has been shown that for the same pitch, more charge sharing events are recorded when larger pixel gaps are used due to the smaller pixel pads [33]. To account for this in the model and since processes in the pixel gaps are not simulated, the electrode pixel size is used.

To simulate the HF-CdZnTe detector, a Zn fraction of x = 0.1 (Cd_{1-x}Zn_xTe) is used. The choice of this Zn fraction was determined from the analysis discussed in section 4.7.3. The simulated data is processed using the reconstruction algorithm to obtain spectra from the eventlist. A noise threshold of 3 keV was applied in all cases and an energy bin size of 0.3 keV was used - this is consistent with the reconstruction performed on the experimental data in chapter 3.

| Parameter name (unit) | CdTe | HF-CdZnTe |
|--------------------------------------------------------------------|---------------------|----------------------|
| Number of photons | 10^{7} | 10^{7} |
| Count rate (cts/frame) | 1 | 1 |
| Source spectrum (keV) | 1 - 1000 | 1 - 1000 |
| Cathode material | Pt | Pt |
| Cathode thickness (µm) | 200 | 200 |
| Pixel array dimensions | [80, 80] | [80, 80] |
| Pixel electrode size (µm) | 200 | 225 |
| Bias voltage (V) | -500 | -750 |
| Temperature (K) | 301 | 301 |
| Readout noise (e^-) | 60 | 60 |
| Weighting potential (w/L) | 0.25 | 0.125 |
| Thickness (mm) | 1 | 2 |
| Material attenuation, $\mu(E)$ | CdTe | $Cd_{0.9}Zn_{0.1}Te$ |
| Density $(g \ cm^{-2})$ | 5.85 | 5.78 |
| Electron mobility (cm ² V ^{-1} s) | 1100 | 940 |
| Electron lifetime (s) | 3×10^{-6} | 1.2×10^{-6} |
| Hole mobility $(\text{cm}^2 \text{ V}^{-1} \text{ s})$ | 100 | 110 |
| Hole lifetime (s) | 2×10^{-6} | 2.5×10^{-6} |
| Fano Factor | 0.1 | 0.1 |
| Pair creation energy (eV) | 4.43 | 4.64 |
| Atomic weight fractions, Cd/Zn/Te | 0.468/0.532 | 0.430/0.028/0.542 |

Table 4.3: Values used as the input parameters to setup the simulation environment when modelling the CdTe and HF-CdZnTe detectors. Horizontal lines within the table body indicate which simulation environment component parameters belong to (Photon, Detector, Sensor - from top to bottom). The Fano factor, density and pair creation energy for both sensor materials, and the transport properties for CdTe are from [4]. The transport properties for the HF-CdZnTe are from [52].

4.7.1 Quantum efficiency

Simulations were performed at line energies ranging from 1 keV to 160 keV in 1 keV intervals to calculate the quantum efficiency (QE) across a range of energies. Spectra including all photon event types (i.e. total recorded counts) were reconstructed at each simulated energy. Then, for each line energy, the quantum efficiency was calculated by dividing the number of counts belonging to the photopeak and all escape peaks with the number of incident photons simulated (10⁷). Figure 4.4 shows the QE for a 1 mm CdTe and 2 mm thick CdZnTe detector calculated from the simulated data. For comparison, the expected theoretical QE determined simply by calculating the transmission through the Pt cathode and the absorption within the sensor is shown. The theoretical and simulated results are similar, where the differences are due to additional effects included in the model such as the noise threshold and edge effects. As expected, the simulations show a greater

QE for the thicker detector.



Figure 4.4: Quantum efficiency (QE) calculated from simulated data for a 1 mm CdTe and 2 mm thick CdZnTe sensor. The theoretical QE was calculated at 1 keV intervals from 1-160 keV using attenuation coefficients from the NIST XCOM database [62].

4.7.2 Detector energy response

The model can simulate the spectrum measured by the detector from a specific source. The measured spectrum tells us about the energy response of the detector. To validate the detector responses predicted by the model, we compared simulated spectra to the experimental spectra obtained from the flood images with radioisotope sources from chapter 3.

Simulations were run for the 1 mm CdTe detector illuminated by a ⁵⁵Fe, ¹⁰⁹Cd, ²⁴¹Am and ⁵⁷Co source. The spectrum of each radioisotope, which is passed to the model to simulate the source, was produced using the transition energies and relative rates from measurements by the Laboratoire National Henri Becquerel (LNHB) [138–141]. Figure 4.5 shows the model simulated detector response to each source for the CdTe detector compared with the equivalent experimentally measured response. Both the simulated and experimental responses only include isolated events and were normalised by the peak height of the primary photopeak.

By visual inspection, the simulated detector responses show good agreement with exper-



Figure 4.5: The simulated detector response compared with the experimentally measured response from the CdTe detector to a (a) ⁵⁵Fe source, (b) ¹⁰⁹Cd source, (c) ²⁴¹Am and (d) ⁵⁷Co. The spectra were normalised to the peak height of the primary photopeak and only include isolated events.

iment. The ⁵⁵Fe source emits soft X-rays at ~5.9 keV and ~6.5 by decay to ⁵⁵Mn. The detector cannot resolve these energies due to its energy resolution, and this is shown by the simulated response. Counts in the low energy tail are underestimated by the simulated response as many of these will be due to thermal noise, which is not simulated by the model. The simulated response to the ¹⁰⁹Cd source estimates the relative peak heights (22, 25, 88 keV) well. For the ²⁴¹Am and ⁵⁷Co sources, which emit photons with energies above the absorption energies in CdTe, the simulated responses show the peaks due to fluorescence emissions. The fluorescence peaks measured from experiment and calculated from simulation are compared in more detail in section 4.7.2.1. In the ⁵⁷Co detector response, the peaks visible in the experimental response between 70 - 90 keV from the Pb shielding fluorescence are not simulated by the model. The escape peaks between 95 - 99 keV are underestimated by the model, believed to be due to additional counts recorded experimentally in this energy range due to scattering from the Pb shielding.

The simulated responses show the low energy tails similar to the experimental photopeaks. Both mechanisms contributing to the low energy tails, the noise threshold and carrier trapping, are considered in the model, with the latter process taken into account by the modified Hecht relation (equation 4.24) used with the appropriate weighting potential for the small pixel geometry of the detector.

4.7.2.1. Fluorescence peak proportions

The ²⁴¹Am source used for the experimental measurements is contained within a steel housing of 0.5 mm thickness. The lower energy X-ray L-shell lines emitted from the radioisotope are therefore not observed. As a result, this allowed us to obtain an experimental detector response to the 59.5 keV line only. Any additional peaks observed in the spectra recorded from this source can be attributed to the detector's response alone. The ²⁴¹Am measured spectra were therefore selected to calculate the effect of sensor fluorescence on the detector response. This was done by calculating the size of the escape peaks and fluorescence peaks relative to the 59.5 keV photopeak. The same calculations were performed from simulated responses to evaluate the performance of the model.

Figure 4.6 shows the HF-CdZnTe and CdTe detector response to 59.5 keV photons from experiment and simulation. All the peaks visible in the response are listed in table 4.4. The total number of isolated absorbed 59.5 keV events is the sum of counts in the primary gamma photopeak and all escape peaks. The proportion of counts in each of the peaks relative to this total sum are shown in table 4.4. The model predicted peak proportions agree well and within error to experiment for most peaks. The Cd K_{β} fluorescence peak is noticeably underestimated by the model in both the CdTe and HF-CdZnTe response the source of this disagreement is not clear.

The number of counts measured experimentally in the Cd fluorescence and escape peaks is greater for the CdTe detector compared with the HF-CdZnTe detector. It is possible that this is a consequence of the lower Cd concentration in CdZnTe from alloying with Zn. However, given the difference in thickness and pixel electrode size between the two detectors, this cannot be established for certain. The greater thickness of the HF-CdZnTe detector will also reduce the size of the escape peaks, as fluorescence photons are less likely to escape the detector. In turn, this also means fluorescence is more likely to be reabsorbed within the detector - increasing the fluorescence peaks. However, both the Cd K_{α} fluorescence and escape peaks are smaller in the HF-CdZnTe response, changes expected with increasing Zn concentration.



Figure 4.6: Simulated detector response to 59.5 keV photons compared with the experimentally measured response to the same energy for the (a) HF-CdZnTe and (b) CdTe detector. The spectra were normalised to the peak height of the 59.5 keV photopeak and include only isolated events. The blue shaded regions highlight the energy windows used to calculate the total number of counts belonging to each peak.

4.7.3 Estimating the Zn fraction in the HF-CdZnTe material

The Zn fraction in the HF-CdZnTe material is not known exactly, as this is proprietary information. It is expected that the Zn fraction lies between x = 0.1 - 0.2 (Cd_{1-x}Zn_xTe) as this is a typical composition used in CdZnTe for radiation detectors [8]. However, other studies [4,142] have suggested Zn fractions as high as x = 0.7, 0.8 may provide the best spectroscopic performance for room-temperature operation of CdZnTe detectors. Given that the Zn concentration impacts the rate of fluorescence from the sensor, the presence of specific peaks and their relative magnitudes can be used to estimate the Zn fraction in the material.

| Peak | Energy Window (keV) | Proportion of counts (%), CdTe | | Proportion of counts (%), CZT | |
|-----------------------------------------|------------------------|--------------------------------|---------------|-------------------------------|---------------|
| | | Experiment | Model | Experiment | Model |
| γ | 50 - 62 | 85.0 ± 1.0 | 84.0 ± 0.8 | 85.7 ± 0.8 | 86.5 ± 0.7 |
| Cd K_{α} escape | 35 - 38 | 6.6 ± 0.3 | 7.9 ± 0.2 | 5.8 ± 0.3 | 6.1 ± 0.3 |
| C d ${\rm K}_\beta$ escape | 33 - 34.5 | 3.0 ± 0.3 | 3.0 ± 0.2 | 2.8 ± 0.3 | 2.5 ± 0.3 |
| Te K_{α} escape | 31 - 33 | 3.6 ± 0.3 | 3.6 ± 0.3 | 4.1 ± 0.2 | 3.8 ± 0.2 |
| Te \mathcal{K}_{β} escape | 27.5 - 29.5 | 1.8 ± 0.4 | 1.4 ± 0.3 | 1.8 ± 0.3 | 1.3 ± 0.3 |
| $\operatorname{Cd} \mathrm{K}_\beta$ | 25 - 27 | 3.1 ± 0.4 | 1.9 ± 0.2 | 3.0 ± 0.3 | 1.6 ± 0.2 |
| $\operatorname{Cd} \mathrm{K}_{\alpha}$ | 22 - 24 | 3.6 ± 0.2 | 4.2 ± 0.1 | 3.2 ± 0.3 | 2.9 ± 0.1 |

Table 4.4: All detected peaks and their proportional size in the detector response to 59.5 keV photons from simulated and experimental data for the CdTe and HF-CZT detector. The energy window corresponds to the shaded region underneath the respective peak in figure 4.6. The percentages are the proportion of counts in the respective peak from the total number of absorbed incident isolated events (i.e. γ photopeak and escape peak counts summed). The errors for the proportion of counts were determined by increasing the energy window by 0.5 keV at both the lower and upper bound and calculating the difference.

The fluorescence and escape peaks in the detector response can be simulated for any Zn fraction by varying the atomic weight fractions and attenuation coefficients provided to the model simulation environment. The detector response to a line energy of 59.5 keV was simulated for the HF-CdZnTe detector for a range of Zn fractions from x = 0.0 (CdTe) to x = 0.9. Figure 4.7 shows the simulated detector responses in the region of the fluorescence and escape peaks for a number of the simulated Cd_{1-x}Zn_xTe compositions. Each simulated response is compared to the experimental HF-CdZnTe detector response of the ²⁴¹Am source. Figure 4.8 shows the proportion of counts in each fluorescence and escape peak (those listed in table 4.4 and calculated using the same energy window and relative normalisation) as a function of the Zn fraction, calculated from the simulated detector responses. The proportion of each peak obtained from the experimental HF-CdZnTe response is highlighted along the respective simulated curve. This is shown by an area to represent all possible values considering the error.

The sum of the squared residuals (SSR), where the residuals are the difference between the experiment and simulated proportion at each Zn fraction, was calculated to combine all the information into a single curve which indicates the most likely Zn concentration of the HF-CdZnTe material. The inverse of the SSR is shown in figure 4.8 on a separate y-axis.

Figures 4.7 and 4.8 show that as the Zn fraction increases, the number of counts in Cd fluorescence and escape peaks decreases while peaks caused by Te fluorescence increase.



Figure 4.7: Detector response to 59.5 keV photons - simulated for $Cd_{1-x}Zn_xTe$ detectors of different Zn fractions x, panels (a)-(i), compared with the experimental HF-CdZnTe detector response. Only the energies at which the fluorescence and escape peaks are observed are shown. The counts have been normalised to the maximum counts in the 59.5 keV photopeak and only include isolated events.

This is expected since the atomic weight fraction of the Te in the crystal begins to dominate as Te (127.6u) has almost twice the atomic mass of Zn (65.4u). The Te K_{α} peak therefore dominates at high Zn fractions. This is not observed in the experimental response, such that it is clear the Zn fraction in the HF-CdZnTe must be at least less than x < 0.4. The experimental response is in fact very close to the simulated CdTe response, therefore the Zn fraction is likely quite low. The difference between the experimental fluorescence peaks and simulated ones, quantified by the SSR, is at a minimum at x = 0.15. Given the errors, we therefore estimate the Zn fraction in the HF-CdZnTe to be between x = 0.10 - 0.15.

For all further simulations of the HF-CdZnTe detector, a Zn fraction of x = 0.1 was used. This value is within the estimated range determined and in line with typical Zn



Figure 4.8: Simulated proportion of counts (relative to the total number of absorbed counts) in each fluorescence or escape peak in $Cd_{1-x}Zn_xTe$ detectors of different Zn fractions x. The grey rectangles show the experimentally measured value in the HF-CdZnTe detector with errors along the curve of the respective peak. The red curve and axis correspond to the inverse of the sum of squared residuals (1/SSR) between simulation and experiment.

concentrations expected in $Cd_{1-x}Zn_xTe$ for radiation detection [4,8].

4.8 Summary

In this chapter a Monte Carlo detector model which can simulate the spectral response of pixelated Cd(Zn)Te detectors was described in detail. The model incorporates photon attenuation by the photoelectric effect, Compton scattering and Rayleigh scattering to determine the interaction positions of incident and secondary photons in the detector sensor. Using charge transport analysis, the signals induced at the pixelated anode by the energies deposited by the photons are calculated. This analysis includes computing the electron cloud size, approximated as a 2D Gaussian, which can be used to estimate charge distribution across pixels. The model therefore has the capability to predict charge sharing in pixelated detectors - and is used for this purpose in chapter 5.

The model was compared with experimental detector results reported in chapter 3 to validate its performance. For isolated events, the simulated detector responses showed good agreement with experiment in terms of energy resolution, relative source peak heights, fluorescence peaks and hole-tailing due to charge trapping and noise thresholding. The Zn fraction in the HF-CdZnTe material was estimated at 10-15% by comparison of the fluorescence peak heights in the experimental response with simulated responses of different Zn alloy compositions. From this, an appropriate Zn fraction of x = 0.1 to simulate the HF-CdZnTe detector was determined. The effect the alloying composition has on the size of the various fluorescence and escape peaks in a detector response was also observed from the estimation of the Zn fraction.

Chapter 5

Measurement and simulation of charge sharing in pixelated Cd(Zn)Te detectors

5.1 Introduction

In this chapter we analyse the presence of charge sharing in the 1 mm CdTe and 2 mm thick HF-CdZnTe detectors calibrated in chapter 3. We quantify the different components that make up the response of charge sharing events, including sensor fluorescence and charge loss. Many recent works using pixelated Cd(Zn)Te detectors have focused on energy-loss correction algorithms for charge sharing events that are more advanced than simple charge sharing addition (CSA) [36,42,46,143], and will become increasingly important in detector designs with thicker sensors and smaller pixels used to image hard X-rays. Using the Monte Carlo detector model, we show that we can predict the rates of charge sharing for individual pixel event types, including those due to fluorescence. This will help in the development of the correction algorithms for higher order multiplicity events.

We begin the chapter by briefly summarising in sections 5.2 and 5.3 the experimental and simulated data used to investigate charge sharing. In section 5.4 we calculate the energy response of charge sharing events. In section 5.5 we measure the proportion of charge sharing, and show that the detector model is able to estimate well the rates of the various charge sharing event types. In section 5.6 we summarise and discuss the results and make comparisons to the literature. Finally, in section 5.7 we use the detector model to simulate the rate of charge sharing for pixel sizes of potential interest for high-flux imaging.

5.2 Experimental data

The radioisotope flood image data acquired for detector calibration and characterisation (chapter 3) is used for charge sharing analysis in this chapter. Additional flood image data was collected with a 99m Tc liquid radioisotope source using the same experimental arrangement as for calibration. All the characteristic line energies obtained from the radioisotope sources are summarised in table 5.1. The frame occupancy for every acquisition is shown and is below 1% in each case. A low frame occupancy is important to ensure that photon pileup does not affect the measured detector response. This was a particularly important requirement for accurately calculating the charge sharing rates (section 5.5).

| Radioisotope source | Photopeak energies (keV) | Frame occupancy (%) | |
|---------------------|-------------------------------------------------------------------------------------|---------------------|------|
| | 9 () | HF-CdZnTe | CdTe |
| 55 Fe | 5.95 ± 0.01 | 0.4 | 0.2 |
| $^{109}\mathrm{Cd}$ | $\begin{array}{l} 22.00 \pm 0.10 \\ 24.90 \pm 0.01 \\ 88.00 \pm 0.01 \end{array}$ | 0.2 | 0.4 |
| ^{241}Am | 59.54 ± 0.01 | 0.4 | 0.5 |
| $^{57}\mathrm{Co}$ | $\begin{array}{c} 14.40 \pm 0.10 \\ 122.10 \pm 0.05 \\ 136.50 \pm 0.10 \end{array}$ | 0.3 | 0.2 |
| $^{99m}\mathrm{Tc}$ | $\begin{array}{c} 18.30 \pm 0.10 \\ 140.50 \pm 0.10 \end{array}$ | 0.1 | 0.4 |

Table 5.1: A nominal uncertainty of ± 10 eV is used for the photopeaks unless the photopeak energy is made up of multiple unresolved peaks (i.e. $K_{\alpha 1}$ and $K_{\alpha 2}$ emissions). In this case the error is estimated taking into account the relative intensity of each peak making up the photopeak.

Additional data collection with the detectors is described in relevant sections of this chapter. Unless otherwise stated, the detector DAQ operation was the same as for the calibration acquisitions - i.e. a bias voltage of -750 V and -500 V for the HF-CdZnTe and CdTe detectors respectively, a frame rate of 1.6 kHz and fixed detector temperature at 28 ± 1 °C.

In all cases, the experimental data were calibrated using the per-pixel energy calibrations and faulty pixels were removed before any analysis. The event reconstruction algorithm (section 3.4.3) was used to build the energy spectra for each individual event type. Unless otherwise stated, a noise threshold of 3 keV (determined during calibration) was applied during event reconstruction.

5.3 Simulated data

The Monte Carlo model described in chapter 4 was used to simulate the detector response to different inputs (e.g. photon energy, count rate, pixel size). The simulation environment in all cases was defined using the input parameters listed in table 4.3 (for the respective detector) unless stated otherwise.

Simulated data was processed using the same event reconstruction algorithm with a noise threshold of 3 keV (as for the experimental data). A spectrum for each individual event type is therefore also obtained from simulation.

5.4 Energy response of charge sharing events

5.4.1 Multi-pixel event type spectra

Figure 5.1 shows the different event type spectra for the ²⁴¹Am observation with the CdTe and HF-CdZnTe detectors. By inspecting the individual event type spectra, the effect charge sharing can have on a pixelated detector's response is observed. The photopeaks for each of the multi-pixel events are broader than the same photopeak using only isolated events and the peak positions also shift to lower energies. For example, in figure 5.1a, the 59.5 keV emission line was measured at 59.85 keV with isolated events but 57.15 keV for the bipixel photopeak, and the FWHM energy resolution of the peaks were 0.92 keV and 4.65 keV respectively. The increase in energy resolution for the bipixel events cannot be attributed to the additional noise contribution from the multiple pixels alone. Indeed, it is also a consequence of charge loss due to incomplete charge collection across the inter-pixel regions and, for energies above the K-shell absorption edges, sensor fluorescence.

The energy response to charge sharing events recorded by the HF-CdZnTe detector (figure 5.1b) shows significantly better performance in terms of spectral resolution and peak position when compared with the CdTe detector. The smaller pixel gaps of 25 µm in the HF-CdZnTe detector anode compared with 50 µm gaps in the CdTe detector anode achieve a smaller pixel gap to pixel pitch ratio (0.1 versus 0.2) which is known to reduce the amount of charge loss to the inter-pixel regions [38]. The comparison between the two detectors in figure 5.1 therefore also confirms that charge loss to the pixel gap is one of the primary factors contributing to the degraded energy resolution of the charge sharing events in the CdTe detector. Nevertheless, even with the smaller gap to pitch ratio, some



Figure 5.1: Whole detector spectra for each event type from the ²⁴¹Am observation with the (a) CdTe detector and (b) HF-CdZnTe detector. Inset plots are a magnification of the fluorescence and escape peak energies (21-38 keV). Annotations in the figure apply to both (a) and (b). Figure is from [144].

charge loss still occurs.

It is possible that transient pulses with negative polarity in pixels adjacent to the collecting pixel are also responsible for some of the charge losses in both detectors, as has been observed by Abbene et al. [36] in HF-CdZnTe detectors. Unfortunately, the HEXITEC ASIC does not output the measured induced pulses during a collection event. Therefore, the presence (or absence) of transient pulses during charge sharing events has not been measured in the detectors studied in this work.

5.4.2 Energy split analysis and charge loss

Further analysis to better understand the response of the charge sharing events was carried out by looking at how the energy is split between the pixels. This was done by producing 2D distributions of the energy in each pixel from all recorded bipixels events. The distributions for the 22 keV and 59.5 keV bipixel events for both detectors are shown in figure 5.2. The energy split analysis reveals if the energy across bipixel events is fully recovered or if instead charge loss is occurring. The diagonal path through the middle of the distributions, shown by the solid white lines, indicates an energy split across the two pixels that always adds up to the photopeak energy. Counts on this line therefore do not show any charge loss, whereas counts deviating below the line do.



Figure 5.2: Energy split distributions of the energy recorded in each pixel of all bipixel events. (a) and (b) show the energy split for all 22 keV bipixels using an energy window from 15-24 keV for the CdTe and HF-CdZnTe detector respectively. (c) and (d) show the energy split for all 59.5 keV bipixels using an energy window from 50-65 keV for the CdTe and HF-CdZnTe detector respectively. The diagonal white line in each panel indicates an energy split with no charge loss.

The 22 keV bipixel energy splits confirm the severity of charge loss in the CdTe detector (figure 5.2a), and the improved charge collection for charge sharing events for the HF-CdZnTe pixelated design (figure 5.2b). Figure 5.2a also reveals that charge loss becomes most severe when the energy is split equally between the two pixels - shown by the point
at which the curve deviates most from the solid line. This is expected to correspond to the photons absorbed directly in between two pixels.

For energies above the K-shell absorption edges of Cd and Te, the energy response of charge sharing events is further complicated. This is shown by the 59.5 keV energy split distributions (figures 5.2c,d). In addition to the continuous curves, concentrations of counts forming bright spots are now visible. The two distinct features within the distributions are due to different types of charge sharing – those created by fluorescence and those created by the charges from one cloud centre spreading. In the case of fluorescence shared events, a K-shell fluorescence photon escapes into a nearest-neighbour pixel and deposits its energy there directly. Bipixels due to fluorescence therefore have characteristic energy splits where in one pixel the fluorescence photon energy is recorded, and in the other pixel the escape peak energy. This results in a large collection of counts at specific energies, forming the bright spots.

The bright spots are along the solid line, indicating that fluorescence shared events do not suffer from charge loss, since they are not created by charges drifting within the inter-pixel region. In contrast, when charge sharing occurs due to carriers drifting within the pixel gaps, any energy split combination between the pixels can occur as well as charge loss to the inter-pixel regions. This results in the continuous curve of counts which, in the case of the CdTe detector, shows clear charge loss for these events. For the HF-CdZnTe detector, negligible charge loss is observed at 22 keV, but some charge loss does occur at higher energies, seen for the 59.5 keV events (figure 5.2d). For higher photon energies, the greater interaction depth means hole trapping occurs in high weighting potential regions, which will reduce the CCE and result in more charge loss.

The observed charge losses can be attributed to a number of effects. Charge trapping in the bulk of the sensor leads to a reduction in CCE which will account for some charge loss. Due to the small-pixel geometry of the detectors which helps reduce the hole signal, this effect is minimised and only observed for photons absorbed close to the collecting pixels. Figure 5.3 shows the CCE as a function of absorption depth for the two detectors as simulated by the model. This effect is estimated to be small since the CCE only drops very close to the anode side of the sensor. Induced charge in pixels adjacent to the primary collecting pixel that is below the noise threshold and consequently removed also results in charge losses. These two effects generally cause the low-energy tailing of photopeaks. Electric field distortions at the inter-pixel regions [32,33,38,39] are believed to cause charge losses to the gap as the charge drift trajectories they create are not collected by the pixels. This causes the curvature of the energy split correlations (figure 5.2) which increases the more central an event is in the gap. In agreement with the findings by Bolotnikov et al. [38], we observe that the detector with the smaller inter-pixel gap (due to a larger pixel electrode) reduces this problem.



Figure 5.3: Charge collection efficiency (CCE) as a function of normalised interaction depth in sensor (where 0 is at the cathode and 1 at the pixelated anode). CCE is simulated from the Monte Carlo detector model.

5.4.3 Bipixel energy response

The bipixel events include two different types:

- Linear bipixels bipixels in a linear arrangement.
- Diagonal bipixels bipixels where pixels are diagonally adjacent.

The energy response of the diagonal bipixels was found to vary significantly from linear bipixels. Figure 5.4 shows the energy split distributions for the diagonal and linear bipixels separately for the ²⁴¹Am data collected with the CdTe detector. The majority of counts are concentrated within the characteristic fluorescence bright spots for the diagonal bipixels (figure 5.4a). Diagonal bipixels are therefore primarily a result of fluorescence charge sharing. This is consistent with the ellipsoidal shape charge clouds are believed to take through thermal diffusion and electron repulsion during drift [134], which is unlikely to produce a diagonal pattern. The linear bipixels (figure 5.4b), on the other hand, show



counts at all energy pairs as well as the bright spots and are therefore a combination of charge spreading and fluorescence shared events.

Figure 5.4: (a) Energy split distribution of 59.5 keV events from the CdTe detector for (a) diagonal bipixels only and (b) linear bipixels only. The diagonal white line in each panel indicates an energy split with no charge loss. Note the logarithmic colour bar.

Both linear and diagonal bipixels include events that are not the result of charge sharing, but due to photon pileup instead. These are labelled in figure 5.4 and occur either when two source photons form a bipixel pattern (γ pileup) or with a source photon in one pixel and a K-shell fluorescence photon or escape energy in the second pixel (fluorescence pileup), occurring in the same readout frame. Although both bipixel types show pileup, the proportion of pileup is greater for the diagonal bipixels.

The proportion of piled-up counts versus photopeak counts will influence whether in order to recover the correct photon energy, if diagonal bipixels should in fact be treated as one event or instead as two single events. To investigate this, data with different frame occupancy rates were collected. This was done because as the frame occupancy increases, so does the probability of photon pileup. The effect of photon pileup on the spectral response of charge sharing events, in particular the diagonal bipixels, could therefore be observed from the data. This in turn was then used to establish the best event reconstruction method for the diagonal bipixels.

5.4.3.1. Frame occupancy measurements

Using the HF-CdZnTe detector, additional flood images were taken with the ²⁴¹Am source to collect data with different frame occupancy rates. Both the distance of the source and

| Source distance (cm) | Frame rate (Hz) | Photon flux $(\cdot 10^3 \text{ ph s}^{-1} \text{ mm}^{-2})$ | Frame occupancy (%) |
|-------------------------|--------------------|-----------------------------------------------------------------|------------------------|
| 38^a | 1600 | 0.2 | 0.4 |
| 22 | 1600 | 0.6 | 1.3 |
| 18.5 | 1600 | 0.8 | 2.2 |
| 13.5 | 1600 | 1.5 | 4.0 |
| 11 | 1600 | 2.3 | 5.9 |
| 7 | 1600 | 5.5 | 13.2 |
| 6.5 | 1600 | 6.4 | 13.9 |
| 5 | 1600 | 10.7 | 20.1 |
| 3 | 1600 | 27.8 | 31.1 |
| 7 | 560 | 5.5 | 32.8 |
| 7 | 440 | 5.5 | 39.5 |
| 7 | 378 | 5.5 | 44.7 |
| 7 | 312 | 5.5 | 51.1 |

the ASIC readout rate were varied to alter the frame occupancy. The details of each observation and the average frame occupancy of the data obtained is shown in table 5.2.

Table 5.2: List of 241 Am flood images taken with the HF-CdZnTe detector. Different source distances and ASIC frame rates were used to obtain a range of frame occupancy rates in the data. ^{*a*}This is the flood observation also used for calibration, listed in table 5.1.

Figure 5.5 shows the energy spectrum as a probability density function (PDF) for the diagonal bipixels, linear bipixels and isolated events from 241 Am observations. For the HF-CdZnTe detector, the event type spectra are shown for two observations of different frame occupancy - 0.4% (figure 5.5b) and 4% (figure 5.5c). The lower frame occupancy gives a direct comparison to the CdTe observation of the same frame occupancy shown in figure 5.5a. The 4% frame occupancy data serves to show how the recorded energy response of the diagonal bipixels changes with frame occupancy.

Within a $\pm 10\%$ window of the 59.5 keV photopeak in figure 5.5a, ~3.8% of all bipixels (1.5% of all events) were found to be diagonal bipixels. Since the diagonal bipixels are formed by fluorescence, they are less effected by charge loss and therefore show better spectral performance in terms of recorded peak position and energy resolution - with an energy resolution of 1.56 keV FWHM compared with 4.85 keV FWHM for the linear bipixels. For the HF-CdZnTe detector (figure 5.5b), where charge loss to the gap is less severe, the performance between the two bipixel types is similar. For detectors which exhibit large amounts of charge loss due to large pixel gaps (such as the CdTe detector), including diagonal bipixels has, in addition to recovering more counts, the further benefit of recovering those counts at a better energy resolution.

The frame occupancy of an observation has an impact on the spectral response because the



Figure 5.5: The whole detector (all pixels) ²⁴¹Am spectra for isolated events, linear bipixels and diagonal bipixels. The spectra are all given as probability density functions (the amplitude of the different event type peaks therefore do no reflect the relative number of counts), obtained by normalisation of the total number of counts and bin size (0.3 keV). (a) calibration data from the CdTe detector with a frame occupancy of 0.4%. (b) the data collected with HF-CdZnTe detector with the source at 38 cm, giving a frame occupancy of 0.4%. (c) the data collected with HF-CdZnTe detector with the source at 13.5 cm, giving a frame occupancy of 4%. Figure is from [144].

probability of photon pileup increases. The spectra in figure 5.5c show that the diagonal bipixel response is more susceptible to pileup than the linear bipixel response. The γ pileup peak at 119 keV, which consists of two distinct 59.5 keV photons, contains ~25% of all diagonal bipixels at just 4% frame occupancy. For comparison, only about 1% of all linear bipixels are in the γ pileup peak. Some fluorescence pileup can also be observed in the diagonal bipixel response between 82 - 96 keV.

5.4.3.2. Event reconstruction method

As the response of diagonal bipixels changes with event occupancy, it is necessary to adjust the reconstruction parameters used in order to recover the maximum number of counts at the correct photopeak energy. We define a ratio, R, as the number of counts recovered at the correct peak energy when treating diagonal bipixels as two isolated events, over the number of counts recovered at the correct energy when treating diagonal bipixels as a shared event. The number of counts for either of these cases can be extracted from the peaks in the diagonal bipixel spectrum (seen clearly in figure 5.5c), such that R is defined as

$$R = \frac{(\text{Counts in } \gamma \text{ pileup peak}) \times 2 + \text{Counts in fluorescence pileup peaks}}{\text{Counts in primary } \gamma \text{ photopeak}}$$
(5.1)

with energy windows of $\pm 10\%$ used around each peak. If R < 1, the energy in the two diagonally adjoined pixels should be summed (i.e shared events are assumed) in order to recover more counts at the correct energy. If R > 1, diagonal bipixels should be treated as two isolated events. R was calculated for the data at each frame occupancy rate listed in table 5.2. For comparison, R was also calculated for linear bipixels and using simulated data from the detector model for the same event types. Figure 5.6 shows the value of Rcalculated as a function of frame occupancy for both bipixel types.

At a frame occupancy of 3.4%, R = 1 for the diagonal bipixels. This suggests that below a frame occupancy of 3.4%, more counts will be recovered at their correct energy by treating diagonal bipixels as shared events instead of isolated events. Above this frame occupancy, diagonal pixels should be regarded as photon pileup events and consequently be treated as two isolated events. The fraction of linear bipixels due to photon pileup is much lower. Even at the highest frame occupancy obtained experimentally (51%), R = 0.91 for the linear bipixels. The model slightly overestimates the number of piled-up linear bipixels at all frame occupancy rates - predicting R = 1 at a frame occupancy of 41%. For the diagonal bipixels, the simulated results from the model show excellent agreement to experiment up to a frame occupancy of 15%.

Simulations from the detector model can be used to inform on the frame occupancy threshold at which the treatment of diagonal bipixels should be altered in order to recover as many counts as possible. This could prove useful for non-flood images, such as collimated images with a point spread function, or detectors of different design, particularly pixel size, where simulations would be used to determine the threshold R. The frame occupancy is the ideal metric to use as it is determined directly from the data with no prior information



Figure 5.6: Equation 5.1 (*R*) as a function of frame occupancy for the experimental observations from table 5.2 and simulated data. The filled circles are the result from simulated data and the empty squares from experiment. The solid lines connect the simulated values. Different colours are used to distinguish the event types. Error are estimated at $R \pm 0.05$ determined by the change when using $\pm 15\%$ energy windows. The figure is from [144].

such as pixel size or frame rate needed. The choice of the diagonal event reconstruction method can therefore be adopted automatically during an acquisition if required, with the choice of the threshold R chosen based on the statistical requirements of the application.

5.4.4 Energy resolution and charge loss of multi-pixel events

The spectral performance of the charge sharing events was quantified by calculating the energy resolution for the multi-pixel event types. Since the dominant factors which influence the energy resolution in compound semiconductors are known (fano noise, electronic noise, incomplete charge collection), the contribution to photopeak broadening from the separate components can be extracted. By calculating the FWHM energy resolutions of the different event types, we separated and determined the magnitude of the pixel gap charge loss component only. Quantifying this charge loss further assesses the performance of pixelated Cd(Zn)Te detectors at hard X-ray energies, where the majority of detected counts undergo charge sharing. The calculations were performed for both the CdTe and

HF-CdZnTe detectors.

5.4.4.1. Energy resolution calculations

The FWHM energy resolution (ΔE) was calculated for the isolated, linear bipixel and quadpixel event photopeaks at energies 14.4, 22.0, 59.5, 88.0, 122.1 and 140.5 keV using whole-detector spectra. This was done by fitting a Lorentzian function to the counts in the photopeak in question. Energy windows of ±5 keV were used around the photopeaks during fitting in all cases except for the CdTe multi-pixel photopeaks for which +5/-10 keV windows were applied (due to the wider peaks). A Lorentzian function was used to minimise the influence of the tail on the measured photopeak width. This helped ensure that the measured photopeak width was not dependent on charge losses due to trapping in the bulk and the applied noise threshold. The energy resolution was calculated from whole-detector spectra because for the multi-pixel events the individual pixel spectra at some energies did not contain enough peak counts (<100 counts) to clearly define the peaks. The energy resolution for the isolated events, which were calculated in chapter 3, are therefore calculated again using the whole-detector spectra for consistency with the multi-pixel energy resolution measurements.

Fluorescence charge sharing events modify the spectral response such that it is difficult to extract the influence of charge loss on energy resolution. Diagonal bipixels were therefore removed from the bipixel photopeaks since they are due to fluorescence only and do not exhibit charge loss to the gap. As a result, only the linear bipixels were used in the following energy resolution calculations. Tripixels were not included in this analysis for the same reason, as they are primarily the result of fluorescence and the noise threshold (see section 5.5.2).

For the CdTe linear bipixel photopeaks, at energies above the Cd K-edge, the fluorescence events were also removed. The fluorescence events were identified and removed by applying 2D energy windows (i.e. an energy window to each pixel in the event) to the linear bipixels. Figure 5.7a is a magnification of the ²⁴¹Am bipixel energy split distribution from figure 5.2c and shows the energy positions of the 2D windows applied around the fluorescence counts. Figure 5.7b shows the 59.5 keV linear bipixel photopeak before and after removing the fluorescence counts, as well as a peak containing only the fluorescence linear bipixels within the 2D energy windows. The figure shows that removing the fluorescence events has a significant affect on the measured FWHM (13% reduction). The optimum energy window width, at which the maximum amount of fluorescence events were removed without



Figure 5.7: Plots contain data of only linear bipixels from ²⁴¹Am data collected with the CdTe detector, within an energy window of 40 - 70 keV. (a) Energy split distribution from figure 5.2c (magnified around the fluorescence spots) show the positions of the 2D energy windows applied in order to remove the fluorescence events. (b) The linear bipixel photopeak before and after removing the fluorescence events within the 2D energy windows in (a), and a peak containing only the fluorescence events within the energy windows. XRF refers to the X-ray fluorescence events. The figure is adapted from [144].

removing charge spreading events, was determined to be 1.8 keV. This is consistent with the fluorescence energy window used in [42] to separate fluorescence events for an energyloss correction technique. Fluorescence events were not removed from the HF-CdZnTe linear bipixels as this could not be done without also removing many charge spreading events (figure 5.2d). However, since the response of the fluorescence and charge spreading events is more similar in the HF-CdZnTe detector (figure 5.5b), it is expected that the fluorescence events will have less of an affect on the measured FWHM.

The resulting FWHM for each fitted photopeak for the different event types in both detectors are plotted in figure 5.8a. Errors for some photopeak FWHM values, particularly for the CdTe multi-pixel event peaks, are relatively large. This is due to charge loss distorting the peak shapes away from standard distributions such as Lorentzian or Gaussian.

5.4.4.2. Charge loss calculations

To calculate the charge loss of charge sharing events, we modified the FWHM energy resolution equation (section 2.4.5)

$$\Delta E = 2.355 \sqrt{F\omega E_0 + m\sigma_a^2 + \sigma_c^2},\tag{5.2}$$

to include an event multiplicity term m. The first term in equation 5.2 accounts for the photopeak broadening due to the Fano noise. The second and third terms are the variance in peak width due to electronic noise, $m\sigma_a^2$, and the variance in peak width due to incomplete charge collection, σ_c^2 . Since we are calculating the energy resolution for multi-pixel events, and each pixel in the HEXITEC ASIC contains its own readout circuit, m is used to consider the electronic noise contribution from each individual pixel.



Figure 5.8: (a) FWHM energy resolution at different photopeak energies. Lines represent the fit of equation 5.2 to the FWHM values. Errors on the FWHM values are the standard errors obtained from least-squares fitting of the Lorentzian function to the photopeaks. (b) The contribution of the charge loss component to photopeak broadening, expressed as a standard deviation of a Gaussian distribution. The solid horizontal lines indicate the electronic noise contribution from all pixels in the event for bipixels ($\sqrt{2\sigma_a^2}$) and quadpixels ($\sqrt{4\sigma_a^2}$). A sufficient amount of quadpixels were not recorded at 14.4 keV - this value is therefore missing from both plots. The figure is from [144], with a correction to the FWHM value for the CdTe 122 keV isolated events.

For isolated, linear bipixels, and quadpixel events, equation 5.2 was fit to the calculated FWHM values as a function of photopeak energy E_0 . The fitted FWHM relationships are shown in figure 5.8a by the solid (CdTe) and dotted (HF-CdZnTe) lines. For isolated events (m = 1), we assumed the energy resolution is not affected by charge loss to the gap and therefore set $\sigma_c = 0$. From the isolated events fit, the peak broadening due to the electronic noise from a single pixel (σ_a) was determined. The value for σ_a for the CdTe and HF-CdZnTe detector are shown in table 5.3. The bipixel and quadpixel FWHM values were fit by setting m to the multiplicity of the event and fixing σ_a to the value determined from the isolated events fit. A fit could not be found to the CdTe detector FWHM values for both the bipixel and quadpixel photopeaks due to the significant increase of the FWHM values with energy. For the HF-CdZnTe detector, fits were achieved with the σ_c values shown in table 5.3. The fits however are poor because the FWHM values, as for the CdTe

| | Isolated $(m = 1)$ | Bipixel $(m=2)$ | Quadpixel $(m = 4)$ |
|-----------|-------------------------|------------------------------|------------------------------|
| | $\sigma_a ~({\rm keV})$ | $\sigma_c \; (\mathrm{keV})$ | $\sigma_c \; (\mathrm{keV})$ |
| CdTe | 0.36 ± 0.03 | - | - |
| HF-CdZnTe | 0.37 ± 0.03 | 0.41 ± 0.12 | 0.64 ± 0.16 |

detector, increase at a faster rate with energy than is predicted by equation 5.2. The source of this discrepancy is believed to be related to depth of interaction effects with photon energy and the poor hole transport.

Table 5.3: Fitting results of equation 5.2 in figure 5.8a. The fit parameters correspond to the standard deviation due to electron noise σ_a and incomplete charge collection σ_c . For isolated events, it was assumed $\sigma_c = 0$. For multi-pixel events, it was assumed σ_a is equal to the value obtained for the isolated events of the respective detector. No fit was found for the CdTe bipixel and quadpixel FWHM values. The errors are standard errors obtained from the least-squares fit of equation 5.2.

Since good fits could not be obtained by fitting equation 5.2 to all FWHM values for the multi-pixel event types, σ_c was calculated separately at each energy. This was done using equation 5.2 with the σ_a value in table 5.3 for the respective detector, and m equal to the multiplicity of the event. The values for σ_c determined this way are shown in figure 5.8b. For comparison, figure 5.8b also shows the magnitude of the electronic noise broadening component from two and four pixels.

In the HF-CdZnTe detector, the broadening of the photopeaks due to charge loss is less significant than the electronic noise contribution from the pixels in the event. This applies up to energies of at least 60 keV, for both bipixels and quadpixels. At 59.5 keV, by considering only the electronic noise contribution per pixel (i.e. $\sigma_c = 0$) under the experimental conditions, the best achievable energy resolution for bipixels is 1.30 ± 0.11 keV FWHM. This target energy resolution for charge sharing events was achieved in the photopeak including only fluorescence bipixels (figure 5.7b). The FWHM of the bipixel peak by the HF-CdZnTe detector is not far from this value at 1.63 ± 0.08 keV. This is significantly better performance over the CdTe detector, for which bipixels have an energy resolution of 4.22 ± 0.08 keV FHWM.

5.4.4.3. Depth of interaction and charge loss correlation

The amount of charge loss was shown to vary with photon energy (figure 5.8b). For this reason, the FWHM values of the multi-pixel event photopeaks (figure 5.8a) could not be described with the analytical equation for detector energy resolution (equation 5.2). The variation of σ_c with energy is thought to be correlated with the photon depth of interaction

due to the poor hole transport in Cd(Zn)Te crystals.

Figure 5.9a shows the average photon interaction depth with photon energy - simulated using the Monte Carlo detector model for a 1 mm and 2 mm thick block of CdTe and CdZnTe material respectively. For a detector of finite thickness, the average depth at which photons are attenuated will level off and plateau at half the detector thickness. This levelling-off is observed in the measured FWHM and σ_c values for the multi-pixel events in both detectors (figure 5.8). A similar trend with energy has been observed by Bugby et al. [42] in calculations of a charge loss correction parameter.



Figure 5.9: (a) Average interaction depth for photons of different energy in a 1 mm and 2 mm block of CdTe and CdZnTe respectively. The values ranging from 1 to 141 keV, in steps of 0.1 keV, were calculated using simulated data from the detector model by determining the average attenuation depth from 10^7 incident photons. (b) Correlation plot of the charge loss contribution to photopeak broadening for linear bipixels, against the average interaction depth of the photon energy at which σ_c was measured. The interaction depth is normalised by the detector thickness. R is the Pearson correlation coefficient from the linear fits, while m and c are the slope and y-axis intercept respectively. The figure is adapted from [144].

For smaller photon energies, the average depth of interaction is much further from the anode than at larger photon energies. Due to the small-pixel effect in these detectors, only a very small fraction of the induced charge will come from holes drifting far from the anode. Therefore, at lower energies, σ_c is smaller because the poor hole transport has less of an impact on the energy resolution of shared events than at larger energies.

Using the relationship between photon energy and average interaction depth from figure 5.9a, the σ_c values for the linear bipixels from figure 5.8b were plotted against their equivalent average interaction depths (shown in figure 5.9b). The interaction depths were normalised by the detector thickness for better comparison between the CdTe and HF- CdZnTe. Linear fits were performed to determine the correlation between the two parameters. The results show a strong correlation between σ_c and the photon interaction depth for both detectors, with Pearson's correlation coefficient (*R*) equal to 0.994 and 0.968 for the CdTe and HF-CdZnTe values respectively. However, given the large errors on σ_c and a limited number of data points, it is possible the correlation is not linear and other effects influencing the trend of σ_c cannot be ruled out.

The reduced charge loss to the gaps in the HF-CdZnTe detector will predominately be due to the larger pixel electrode and therefore smaller 25 µm gaps. The correlation in figure 5.9b, however, suggests that the hole transport influences the amount of charge loss that occurs. For photons absorbed immediately below the cathode (i.e at an interaction depth of zero), the charge loss can be assumed to be due to the inter-pixel spacing and electron transport, rather than the hole transport. As expected, at this depth (z=0), σ_c is greater in the CdTe detector (50 µm pixel gaps) than in the HF-CdZnTe detector (shown by the intercept values from the fits in figure 5.9b). The slope for the HF-CdZnTe fit is smaller than for the CdTe fit. This could be due to the improved hole transport in the HF-CdZnTe material, but is likely also related to the effective electric field across the detector, which is thought to be more uniform in the HF-CdZnTe detector (section 5.5).

5.5 Charge sharing proportions

The energy response for charge sharing events has been investigated and discussed. Although the use of smaller pixel gaps was shown to significantly improve charge sharing performance by reducing charge loss, it did not eliminate charge loss entirely. Moreover, given the additional noise contribution from each pixel in charge sharing events, charge sharing will always degrade a detector's spectral performance. The onset of fluorescence further complicates the response of charge sharing events.

When choosing a pixelated detector design it is therefore essential to know the amount of events expected to undergo charge sharing. In this section, the proportion of charge sharing events is calculated from the experimental data and compared to predictions from simulation using the model. The dependence of charge sharing on photon energy and the noise threshold were investigated. From these dependency studies, performance insights such as the impact of fluorescence on charge sharing rates and the electric field stability in the detectors could be obtained.

5.5.1 Photon energy dependence of charge sharing

5.5.1.1. X-ray tube measurements

Since K-shell fluorescence has been shown to effect charge sharing, photopeaks close to the absorption edges of Cd and Te ($\sim 26-31 \text{ keV}$) were desired to study the charge sharing dependence on photon energy in Cd(Zn)Te detectors. From the radioisotope sources, no emission lines between 24.90 keV (¹⁰⁹Cd) and 59.5 keV (²⁴¹Am) were obtained. An experiment using an X-ray tube was therefore set up to collect data at energies above, but as close as possible, to the sensor absorption edges. The experiment was carried out with the CdTe detector. Using this data, the impact of fluorescence on charge sharing could be studied more closely.

Using a X-ray tube (Amptek Mini-X [145]), additional photopeaks at 32.5 keV, 38.0 keV and 45.8 keV were obtained. The tip of the Amptek X-ray tube was placed 3 cm from the surface of the detector and equipped with a 2 mm collimator. A silver (Ag) transmission target was used to obtain the three photopeaks, with electrons accelerated at the target across a tube voltage of 35 kV, 40 kV and 50 kV. Since only photons above the CdTe absorption edges were of interest, Niobium (Nb), Gold (Au) and Chromium (Cr) filters were used to remove lower energy photons. Therefore, peaks were effectively created from the bremsstrahlung continuum emitted from the X-ray tube. Table 5.4 shows the peaks at which data were acquired from the X-ray tube measurements and the filter(s) used, and table 5.5 gives details on the filters.

| Tube | Tube | Photopeak | Acquisition | Frame | Filte | er(s) ı | used |
|------|-----------|--------------|-------------|------------------|-------|---------------|------|
| (kV) | (μA) | (keV) | (s) | occupancy (%) | Au | \mathbf{Cr} | Nb |
| 35 | 110 | 32.5 ± 3.5 | 1800 | 0.2 | Х | | |
| 40 | 80 | 38.0 ± 3.5 | 1800 | 0.2 | Х | Х | |
| 50 | 5 | 45.8 ± 3.5 | 1200 | 0.2 | | | Х |

Table 5.4: Photopeak energies obtained from X-ray tube measurements by accelerating the electrons with different electric field strengths. The uncertainty of the photopeak energies is determined from the peak FWHM. The applied filter(s) is marked by an X.

Uniform illumination of the entire detector surface could not be achieved due to the small source distance. The collimated beam illuminated $\sim 20\%$ of the centre detector pixels. The filters therefore also helped ensure a very low frame occupancy of 0.2% (table 5.4) which is low enough to negate effects from photon pileup (even at 20% detector illumination).

Figure 5.10 shows the event type spectra for each acquisition of different tube voltage. It

| Filter Density (g/cm ³) | | thickness (mm) | XRF emission (keV) | | |
|-------------------------------------|-------|----------------|--------------------|--------------------|--|
| 1 11001 | |) | K_{α} | K_{eta} | |
| Au | 19.32 | 0.25 | 68.12 ± 0.10 | 77.98 ± 0.01 | |
| Cr | 7.19 | 1.00 | 5.41 ± 0.05 | 5.95 ± 0.01 | |
| Nb | 8.57 | 1.00 | 16.50 ± 0.10 | 18.62 ± 0.01 | |

Table 5.5: The different filters used for the X-ray tube measurements shown in table 5.4. The K-shell fluorescence photon emission energies from the filters is also shown. The $K_{\alpha 1}$ and $K_{\alpha 2}$ peaks were combined and errors were determined in the same way as for the radioisotope photopeaks.



Figure 5.10: The spectrum for isolated, bipixel, tripixel and quadpixel events detected with the CdTe detector using the X-ray tube with electrons accelerated across a tube voltage of (a) 35 kV (b) 40 kV and (c) 50 kV. The photopeaks for the multi-pixel events are positioned at a lower energy due to charge loss to the inter-pixel gap. The figure is adapted from [146].

can be seen that, using the filters, photopeaks from the bremsstrahlung continuum were obtained and that the photopeak of each event type is resolved from lower energy K-shell fluorescence lines coming from the Ag target and filters. This meant that charge sharing at the energy of the main photopeak could be analysed without interference, identically to the radioisotope source peaks. However, since the X-ray tube acquired photopeaks are not from a discrete energy as for the radioisotope peaks, and have a FWHM of \sim 7 keV, the uncertainty on the energy for counts from these peaks is ±3.5 keV.

5.5.1.2. Method to calculate charge sharing proportions

The proportion of each event type was calculated by using energy windows around the photopeak of interest and counting the number of events belonging to each specific event type. The number of counts of each event type was normalised by the total number of all counts for the given photopeak to obtain a rate.

The rate of each event type was calculated experimentally at all of the energies listed in table 5.6 for the CdTe detector, and at the radioisotope peaks for the HF-CdZnTe detector (since no X-ray tube peaks were collected with the latter detector). Due to the significant shifting and broadening of the multi-pixel photopeaks, the energy windows associated with each event type photopeak for the CdTe detector was varied - these are listed in table 5.6. For the HF-CdZnTe detector, the better energy resolution of shared events meant $\pm 10\%$ keV energy windows around all photopeaks could be used instead.

Simulated data were generated by running the model at multiple incoming photon energies covering the experimental photopeak energy range from 5.95 keV to 140.5 keV. Energy windows of $\pm 10\%$ keV were also used around the simulated photopeaks to calculate the charge sharing rates.

For the CdTe detector simulations, a bias voltage of -425 V was used instead of the experimentally applied bias of -500 V. This was done to account for the bias induced polarization of the electric field profile, which was shown to decrease in strength from the anode to cathode even seconds after biasing Schottky contact CdTe [147]. Cola et al. [147] calculated an effective bias of -425 V (assuming a uniform field) when applying a -500 V bias to account for this effect. Using the effective bias, better agreement between the simulated and experimental charge sharing rates was found (section 5.5.1.3). For the HF-CdZnTe detector, the experimentally applied bias of -750 V was used in simulations.

5.5.1.3. Results

Figure 5.11 shows the calculated total charge sharing and event type proportions from experiment and simulation. At 59.5 keV, 61.6% and 54.8% of all events are charge sharing events in the HF-CdZnTe and CdTe detectors respectively. This is consistent with the

| Source | Peak energy | Energy window (keV) | | | |
|------------------------------|-------------------|---------------------|-----------|-----------|-----------|
| | (ке v) | Isolated | Bipixel | Tripixel | Quadpixel |
| 55 Fe | 5.95 ± 0.01 | 4-11 | 4-11 | 4-11 | 4-11 |
| 109Cd | 23.10 ± 1.00 | 13-28 | 12-28 | 13-28 | 14-28 |
| Ou | 88.00 ± 0.01 | 77-92 | 75 - 91 | 73-91 | 73-91 |
| ²⁴¹ Am | 59.54 ± 0.01 | 50-63 | 50-63 | 50-63 | 50-64 |
| | 14.40 ± 0.10 | 9-16 | 6-16 | 6-15 | 11-16 |
| $^{57}\mathrm{Co}$ | 122.10 ± 0.05 | 105 - 126 | 105 - 126 | 105 - 125 | 105 - 124 |
| | 136.50 ± 0.10 | 126-140 | 125-140 | 124-140 | 123-140 |
| 99 <i>m</i> T - | 18.30 ± 0.10 | 14-19 | 14-19 | 14-19 | 14-19 |
| 10 | 140.50 ± 0.01 | 125 - 145 | 120 - 145 | 120 - 145 | 118-145 |
| X-ray tube (35 kV) | 32.5 ± 3.5 | 27-36 | 25-36 | 23-36 | 23-36 |
| X-ray tube (40 kV) | 38.0 ± 3.5 | 28-42 | 28-42 | 28-42 | 28-42 |
| X-ray tube (50 kV) | 45.8 ± 3.5 | 31 - 51 | 26 - 50 | 24-49 | 25 - 48 |

Table 5.6: Photopeak energies at which the charge sharing proportions are calculated. The peak energy uncertainties have been defined in the same manner as in table 5.1. The ¹⁰⁹Cd 22.00 keV and 24.90 keV peaks have been combined and are treated as a single photopeak with average energy of 23.10 keV when considering the relative intensities. The custom energy windows used for each event type for the CdTe detector data are also shown.

charge sharing rates measured in similar pixelated Cd(Zn)Te detectors in other works [35,36] and shows the significance of charge sharing in these detectors.

The change in charge sharing proportion with photon energy reveals many of the factors which influence charge sharing rates (figure 5.11a). The primary factors are the charge cloud size, the noise threshold and X-ray fluorescence from the sensor. At low photon energies, the number of shared events is heavily suppressed by the noise threshold. At these energies, it is more likely that the energy shared with an adjacent pixel is below the noise threshold, resulting in a failure to identify true shared events. As the energy increases and the noise threshold is less likely to suppress a shared event, the shared events proportion increases before it begins to level off. Due to the onset of fluorescence above the sensor absorption K-edges (>26 keV), the proportion of charge sharing events rises sharply. Charge sharing data at the energies obtained from the X-ray tube measurements (marked in figure 5.11a) confirm this trend experimentally. The jump in attenuation at the absorption edges also causes an increase in charge sharing as the electron charge cloud will, on average, need to drift further to reach the anode and therefore increase in size. Above the K-edge absorption energies of the Cd and Te atoms, the charge sharing proportion gradually rises as the dependence is only on the charge cloud size (and not the noise threshold or fluorescence) which increases with photon energy.



Figure 5.11: The total percentage of charge sharing events as a function of energy for (a) the CdTe detector and (b) the HF-CdZnTe detector. The proportion of each individual event type is shown for (c) the CdTe detector and (d) the HF-CdZnTe detector. (a) and (c) include three additional data points from the X-ray tube measurements taken with the CdTe detector. The dotted lines indicate the energy of the absorption edges of Cd and Te - these are only annotated once in (a). Errors on the experimental measurements are estimated at $\leq 2\%$ determined by the change in percentage when varying the energy window from $\pm 10\%$ to $\pm 15\%$ where possible.

The detector model, due to the inclusion of fluorescence, computation of the charge cloud size and noise threshold, is able to predict the total charge sharing rates in both detectors to within 2%. The weaker effective bias voltage of -425 V instead of -500 V was required in simulations of the CdTe detector to achieve this accuracy (figure 5.11a). In contrast, the HF-CdZnTe charge sharing rates were simulated accurately using the same bias voltage of -750 V in the model as was applied experimentally (figure 5.11b). The model estimated proportions for each individual event type shows excellent agreement with experiment for the HF-CdZnTe detector (figure 5.11d). This is not the case for the CdTe detector for which the proportion of quadpixels measured experimentally is significantly greater than model predictions (figure 5.11c). This suggests a stable and uniform electric field profile across the HF-CdZnTe detector which is not degraded by bias-induced polarization effects,

unlike the CdTe detector. This is likely a result of the Pt ohmic contacts used in the HF-CdZnTe detector compared with the CdTe Schottky contacts, which leads to less space charge build up at the electrodes [148] and therefore fewer distortions of the electric field profile.



Figure 5.12: Pixel maps showing the spatial distribution of charge sharing for the 122 keV photopeak, energy windowed between 105-125 keV. The total amount of charge sharing per pixel is shown in (a) for the CdTe detector and (b) for the HF-CdZnTe detector. The proportion of quadpixels per pixel is shown in (c) for the CdTe detector and (d) the HF-CdZnTe detector. The pixels at the edge of the detector have been removed as these do not accurately record charge sharing events due to having fewer neighbouring pixels.

The pixel maps in figure 5.12, which show the spatial distribution of charge sharing for 122 keV photons across the detectors, provide further evidence of the electric field uniformity in the detectors. As expected, we observe that the total amount of charge sharing is less in the CdTe detector due to its 1 mm thickness compared to the 2 mm thick HF-CdZnTe detector. Despite this, the proportion of quadpixels is greater at 11% in the CdTe detector compared with 8% in the HF-CdZnTe detector - which is the opposite of what is expected considering the geometry of the detectors. The CdTe detector also shows greater spatial variation of recorded quadpixels (figure 5.12c). These findings support the presence of

local variations in the electric field profile across the CdTe detector.

The trapping of carriers during drift leads to a build-up of charge which forms internal electric fields that act against the externally applied voltage [149]. This polarization phenomenon results in localised fields that are weaker than the desired field strength expected from the applied bias - and a consequence of this is an increase in charge sharing. The model underestimates the proportion of quadpixels in the CdTe detector (figure 5.11c) as it assumes a uniform field across the detector and therefore no spatial variation in charge sharing. In the case of the HF-CdZnTe detector, the model predicted event type rates are in excellent (i2%) agreement to experiment at all energies. It is conceivable that this is due to a more uniform and stable electric field profile across the sensor, such as that assumed in the simulations. It is also possible that the superior hole transport in the HF-CdZnTe material contributes to the uniform field due to less carrier trapping and therefore fewer localised distortions in the electric field.

The electron cloud sizes computed by the model are shown in figure 5.13 for both detectors. Given the good agreement between experiment and simulation, the simulated cloud sizes can be assumed to be good approximations of the true carrier cloud sizes. The figure shows the average contribution to the final cloud size at the anode in terms of the σ of the two distinct components (growth during drift and initial size) of the Gaussian cloud. This suggests that the final cloud size is dominated by the growth during drift towards the anode at the investigated X-ray energies. This is consistent with previous findings that cloud growth during drift is the dominant mechanism in charge sharing [37]. The average total charge cloud size is found to be relatively constant between 1 and 100 keV at $\sigma \approx 13 \,\mu\text{m}$ and $18 \,\mu\text{m}$ for the CdTe and HF-CdZnTe detectors respectively. A charge cloud containing ~99.7% (i.e. $\pm 3\sigma$) of all charges would extend ~78 μm and ~108 μm in diameter for the two detectors respectively. This is an appreciable size relative to the pixel pitch of 250 μm and is therefore consistent with the significant charge sharing rates observed.

Above the Cd and Te K-edges (> 26 keV in figure 5.13), photons are absorbed closer to the cathode, increasing the drift time of the excited charges and therewith the cloud size. The relatively constant cloud size supports the argument that at low energies it is the noise threshold that prevents much larger proportions of charge sharing, although it will depend somewhat on their being fewer charge carriers in the cloud (section 5.5.3).



Figure 5.13: The average electron cloud size at different energies due to the initial width from photoelectron ionisation and due to growth during drift as computed by the model. The combined average total cloud size is also shown. (a) for the 1 mm thick CdTe detector and (b) for the 2 mm thick HF-CdZnTe detector. The model was simulated between 1 and 141 keV with 1 keV intervals - only the curve is shown.

5.5.2 Fluorescence charge sharing proportions

In section 5.5.1 it was shown that fluorescence from the sensor material considerably impacts the proportion of charge sharing in a detector's response. The energy response of fluorescence shared events has also been shown to differ from charge spreading events (section 5.4.4.1). As a result, fluorescence events can often be recombined through simple addition to recover the original photon energy, without the need for more complex correction techniques to recover charge loss to the inter-pixel gap [36, 42]. It is therefore of interest to quantify the portion of shared events that are due to fluorescence. By showing that the detector model accurately estimates these rates, simulated data can confidently be used to estimate expected fluorescence charge sharing proportions in future detector designs of, for example, different thickness and pixel sizes.

The analysis in this section, for both experiment and simulation, is limited to the CdTe detector only. This was done because the experimental rates could be extracted more easily from the CdTe detector data by taking advantage of the significant charge loss in this detector to separate the fluorescence shared events.

5.5.2.1. Calculation method from simulation

Determining the proportion of shared events due to fluorescence is relatively straightforward with the model, as it is achieved simply by simulating data with X-ray fluorescence switched off and comparing to the charge sharing rates when X-ray fluorescence was switched on. This comparison as a function of photon energy is shown in figure 5.14a for all charge sharing events and figure 5.14b for individual event types. By taking the difference between the curves with and without X-ray fluorescence included in the model, the proportion of charge sharing events due to fluorescence was calculated. This was done at 59.5 and 122 keV for all multi-pixel event types, with the results shown in table 5.7.



Figure 5.14: The proportion of charge sharing events as a function of photon energy from simulated data for the CdTe detector. The solid lines are the same simulated curves for the CdTe from figure 5.11 which include fluorescence photons, the dotted lines are the same result but when fluorescence was switched-off in the model. (a) the total proportion of charge sharing events. (b) the proportion of the individual event types.

5.5.2.2. Calculation method from experiment

Bipixels

Given the severe charge loss of charge spreading events in the CdTe detector, it was possible to estimate the proportion of bipixels that are due to fluorescence only. This was done by applying two-dimensional energy windows around the fluorescence spots in the energy split distribution, as was done in section 5.4.4.1 to remove fluorescence events before calculating the magnitude of charge loss. The counts in the energy windows were summed and normalised by the total number of bipixels. All bipixels types (i.e. both linear and diagonal) are included in the analysis here. The calculation was performed at 59.5 keV and 122 keV photons.

Tripixels

The proportion of tripixels due to fluorescence could also be calculated from experiment. This was possible because of differences in the energy response between the four types of tripixels. The four tripixel types were defined in section 3.4.3 in the description of the event reconstruction algorithm. For the analysis presented here, each tripixel type is designated the following name:

- RA centre event where the pixels make a right-angle (RA) and the maximum energy is recorded in the centre pixel
- RA edge event where the pixels make a right-angle and the maximum energy is recorded in an edge pixel
- Line centre event where the pixels are in a linear arrangement and the maximum energy is in the centre pixel
- Line edge event where the pixels are in a linear arrangement and the maximum energy is in an edge pixel

The four tripixel event types are shown schematically in figure 5.15 where the filled pixel indicates the pixel with the maximum recorded energy. The majority of tripixel events were found to be in the RA arrangement for both the 59.5 keV and 122 keV photopeak experimental data, at 93.0% and 91.5% respectively, with the rest being line events. The number of RA centre and RA edge events was found to be approximately equal.

The location of the maximum energy in a tripixel event is an indication of whether charge sharing occurred due to fluorescence or charge spreading. This can be seen in figure 5.15 which shows the energy split distribution across the two non-maximum pixels for each of the four tripixel types. The equivalent energy split distributions from simulated data at 59.5 keV are shown for comparison and reveal similar energy split distributions as observed from experiment. By visual inspection, it is clear the distributions for the edge and centre events are distinctly different. Edge events are mostly made up of events where summing the energy in the two non-maximum pixels equals the energy of Cd (\sim 23 keV) or Te (\sim 26 keV) K-shell fluorescence. For example at the bright streaks in the distribution at 20 and 23 keV. Counts along the downwards sloping curve are cases where the energy from the fluorescence photon spreads between the two non-maximum pixels, with charge loss across the pixel gap causing the curvature in the experimental data. The correlation in the simulated edge event distributions are linear since the model does not account for charge



Figure 5.15: Energy split distributions of the two non-maximum pixels from all tripixel events at 59.5 keV from the ²⁴¹Am data collected with the CdTe detector. From top to bottom the two rows of images correspond to experiment and simulation respectively. Each column of images corresponds to one of the specific tripixel event types - RA centre, RA edge, line centre and line edge events. A schematic of the tripixel event type is shown in the first image of each column, with the filled pixel indicating the pixel containing the maximum energy. The energies in the unfilled pixels is therefore what is shown in the distributions. Figure is adapted from [146].

loss across the pixel gap. Edge tripixel events appear to be caused by fluorescence, where either an isolated or bipixel event becomes a tripixel due to the fluorescence photon.

The distributions for the tripixel centre events show a larger proportion of events with nonmaximum pixel energies much lower around 3-5 keV – well below fluorescence energies. This suggests that centre events are more likely the result of charges drifting within the pixel gaps. Some of these events are still due to fluorescence (i.e. the bright streaks), but at lesser rates than for edge events. It is expected that many of the RA centre events are in fact quadpixels where one of the pixels is below the noise threshold and thus removed, creating the tripixel event.

By determining all edge events as resulting from fluorescence, and centre events from charge spreading (with the exception of the bright spots/streaks at 23 and 26 keV), the fraction of tripixels due to fluorescence could be calculated experimentally. The same analysis was performed for tripixel events in the 122 keV photopeak.

Quadpixels

Since the complexity of the energy response increases with event multiplicity, it was not possible to accurately distinguish quadpixels which included fluorescence from the experimental data.

5.5.2.3. Results

Table 5.7 lists the fluorescence shared events proportions calculated both by the model and experiment. For quadpixels, only estimates from simulation are given.

| | Experiment (%) | | Mode | l (%) |
|------------|-----------------------|----------------|------------------|----------------------|
| | $59.5 \ \mathrm{keV}$ | 122 keV | $59.5~{\rm keV}$ | $122 \ \mathrm{keV}$ |
| Bipixels | 14.2 ± 2.1 | 11.3 ± 1.6 | 18.2 | 9.4 |
| Tripixels | 61.1 ± 1.1 | 57.0 ± 2.5 | 72.1 | 62.2 |
| Quadpixels | - | - | 34.0 | 22.8 |

Table 5.7: Percentage of multi-pixel event types that are due to fluorescence as calculated and simulated from the CdTe detector data. The uncertainties on the experimental rates were obtained from the difference when using 2 keV and 3 keV two-dimensional energy windows around the fluorescence spots/streaks.

The experimentally determined fluorescence shared events proportions (table 5.7) show that the majority of tripixels ($\sim 60\%$) are a result of fluorescence, whereas bipixels are predominately due to charges drifting within the pixel gaps. The simulated proportions support this conclusion and estimate similar rates of fluorescence charge sharing for each event type compared with experiment. The model also predicts that a significant fraction of quadpixels in these detectors are caused by fluorescence, although at a lesser rate than tripixels. Both experiment and simulation consistently show a decrease in the proportion of fluorescence shared events at 122 keV. This can be reasoned since at larger photon energies, more events will already exhibit charge sharing even in the absence of fluorescence.

The energy split distributions in figure 5.15 revealed the different charge sharing mechanisms involved depending on the tripixel event type. Depending on which charge sharing mechanisms are involved, impacts the energy response of the event. Figure 5.16a shows the total tripixel photopeak from the 59.5 keV peak recorded with the CdTe detector, and figure 5.16b is the same photopeak separated into its individual event type components. Differences in the energy response are observed by shifts in peak position and changes in energy resolution. The peak position for the RA centre events is lower at 54.5 keV compared to 56.5 keV for the RA edge events. This reinforces that centre events are mostly due to charge spreading and not fluorescence as they exhibit more charge loss. Centre line events show the poorest energy resolution as the peak contains a more equal number of both fluorescence and charge spreading events (which will result in two unresolved peaks, as was observed for the bipixel events in figure 5.7).



Figure 5.16: ²⁴¹Am 59.5 keV tripixel energy response from CdTe detector. (a) photopeak for all tripixel events combined. (b) Individual photopeak for each type of tripixel event type. In all cases, the peaks have been normalised as a probability density function. Figure is adapted from [146].

Understanding the different processes and factors influencing charge sharing will help inform methods of energy reconstruction and correction for multi-pixel events. The corrections required differ depending on the multiplicity and arrangement of the shared event [46], and whether charge sharing occurred via fluorescence or not [42]. The insights presented here regarding the different possible energy responses of tripixel events will assist in improving corrections for higher multiplicity events. As detector designs shift towards smaller pixels or thicker sensors, and the proportion of higher multiplicity events increases, such correction techniques will be essential - particularly if the detectors exhibit significant charge loss. Furthermore, simulations were shown to correctly predict the energy distribution across pixels depending on the tripixel event type (figure 5.15). The model is therefore a useful tool to study and predict the charge sharing processes behind different multi-pixel events.

5.5.3 True charge sharing proportions

In section 5.5.1.3, the suppression of shared events due to the noise threshold was discussed. In this section we estimate the true charge sharing proportions when no noise threshold is applied by using simulations from the detector model. Very low energies recorded by a detector will be dominated by noise events due to thermal leakage currents. At room temperature, it is therefore impossible to experimentally measure the number of shared events at a threshold of 0 keV as multi-pixel events due to charge sharing or noise cannot be distinguished. For the HF-CdZnTe detector at 28°C, a minimum noise threshold of 2 keV is required to suppress the majority of noise counts. This can be seen by figure 5.17 which shows the average number of events per frame (including all event types) as a function of the noise threshold for the ¹⁰⁹Cd and ²⁴¹Am HF-CdZnTe observations. Above a 2 keV threshold the average events per frame vary little, indicating that the majority of events are due to absorbed photons and not noise. The detector model does not simulate thermal or electronic noise events, meaning shared events can be estimated down to a 0 keV threshold.



Figure 5.17: Average number of all event types per frame as a function of the noise threshold for the ¹⁰⁹Cd and ²⁴¹Am observations with the HF-CdZnTe detector. Figure is from [144].

Figure 5.18 shows the proportion of shared events as a function of the noise threshold at four different photopeak energies, for both the HF-CdZnTe experimental data and simulated data. The proportions were again calculated using 10% energy windows around the photopeaks, for every applied threshold. For the experimental data, the analysis was done down to 2 keV. The charge sharing predictions from the model show good agreement with the experimental values. As larger noise thresholds are applied, the number of shared events decreases exponentially. For the 59.5 and 122 keV photopeaks (energies above the material absorption edges), the exponential decrease is interrupted by sudden drops at the fluorescence photon energies.



Figure 5.18: Proportion of charge sharing as a function of the applied noise threshold for the (a) 14.4 keV, (b) 22 keV, (c) 59.5 keV and (d) 122 keV photopeaks, comparing experiment and simulation. The noise thresholds used on the experimental data are shown by the markers. For the simulated data, noise thresholds were applied at 1 keV intervals. The errors on the experimental values are estimated at $\pm 2\%$ from varying the energy window around the photopeak between ± 10 -15%. K-shell fluorescence energies are only labelled once in panel (d), but indicated by the solid vertical lines in both (c,d). Figure is from [144].

Figure 5.19 shows the total amount of charge sharing and the proportion of each event type as a function of incoming photon energy when no noise threshold is applied. The 0 keV threshold curve in figure 5.19a shows the true percentage of events that are shared in the HF-CdZnTe detector, which is significantly larger than when a 3 keV threshold is applied. At a photon energy of 5.95 keV, the true amount of charge sharing is 63%, compared to 3.0% when a 3 keV threshold was used. The number of true shared events increases rapidly at very low photon energies as more charge carriers are excited by the absorbed photon. At 122 keV, 86% of all events exhibit some charge sharing in the HF-CdZnTe detector. Although this is a very large proportion, 21% of those shared events

are sharing 3 keV or less. Nevertheless, the model predicts that from a photon energy of 4 keV, the majority of events are bipixels (figure 5.19b). Interestingly, the onset of sensor fluorescence reduces the proportion of bipixels as many shift to higher event multiplicities. The true charge sharing rates therefore give an indication of the amount of charge that is lost after applying the noise threshold. It is expected, as pixel sizes decrease and the true charge sharing rates increase (particularly of high multiplicity events), the noise threshold will cause more charge to be lost and negatively impact spectral resolution.



Figure 5.19: True proportion of charge sharing rates in the HF-CdZnTe detector calculated from simulated data when applying a noise threshold of 0 keV. (a) The total amount of charge sharing including all event types. The 3 keV simulated curve from figure 5.11b is shown for comparison. (b) The proportion of the individual event types at a noise threshold of 0 keV.

5.6 Discussion

Charge sharing in small-pixel Cd(Zn)Te detectors is significant and increases with detector thickness (figure 5.11). Even for soft X-rays, simulations of the HF-CdZnTe detector with no thermal or electronic noise, revealed that the majority of events still exhibit some charge sharing (figure 5.19a). The true charge sharing proportions, particularly at lower photon energies, is suppressed by the noise threshold. For applications such as in astronomy where each count is vital to achieve good signal-to-noise statistics, and good spectral resolution is necessary to identify emission lines, large proportions of charge sharing become an issue when the detector's spectral response to shared events suffers due to incomplete charge collection.

The HF-CdZnTe detector showed significantly improved energy resolution for the charge

sharing photopeaks compared to the CdTe detector (figure 5.8a). The better spectral response of shared events in the HF-CdZnTe detector is due to significantly less charge loss across the inter-pixel gap, revealed by the energy split analysis for the adjacent bip-ixels (figure 5.2) and quantified by determining the charge loss contribution to photopeak broadening, σ_c (figure 5.8b).

The reduced charge loss in shared events for the HF-CdZnTe detector is expected to primarily be due to the larger pixel contacts and therefore smaller 25 µm inter-pixel spacing (compared with 50 µm in the CdTe detector), resulting in improved charge collection in regions close to the pixel gaps. Simulations have shown that the electric field lines become distorted within the inter-pixel spacing close to the anode and have a weaker field strength [37, 150]. Carriers drifting in these regions are therefore more likely to become trapped and stop inducing a signal [39], resulting in charge loss. Smaller interpixel gaps [33, 38] minimise this effect as electric field distortion is less pronounced and fewer charges traverse inter-pixel regions. This is in line with our findings which show less charge loss in the detector with smaller pixel gaps (HF-CdZnTe).

The strong correlation between σ_c and interaction depth (figure 5.9b) suggests that hole carrier trapping influences the severity of charge loss in charge sharing events. At lower photon energies, due to shallower attenuation depths, the poor hole transport has a smaller impact on the energy resolution of shared events than at larger energies. The correlation of charge loss with depth of interaction due to the poor hole transport in high-Z semiconductors has also been reported in other works [143, 151]. The lower rate of σ_c with interaction depth (figure 5.9b) in the HF-CdZnTe over the CdTe might be a benefit of the improved hole transport, although a better comparison with standard CdZnTe material is required to confidently determine this. Abbene et al [36], who compared charge sharing and charge loss in 3×3 pixelated array detectors using 2 mm thick Redlen HF-CdZnTe material with 500 µm and 250 µm pixel pitch, both with 50 µm pixels gaps, found that charge loss for 59.5 keV photons worsened when the ratio between pixel gap and pixel pitch increased. Therefore, despite the improved hole transport in HF-CdZnTe, charge loss is predominately influenced by the pixel gap and pixel pitch size.

In detectors that can determine the interaction depth of events, through ASIC pixels capable of measuring both positive and negative polarity signals (e.g. STFC's PIXIE ASIC [152]) or otherwise, the correlation between the charge loss in shared events and interaction depth can be tested more vigorously. In a detector with this capability, discrimination techniques could be used to remove shared events with interaction positions close to the anode. This could further improve the energy resolution of high energy shared events, although at the cost of losing counts. Depth of interaction correction techniques could also be applied, and has already been done successfully to correct for charge loss and improve spectral performance in similar detectors by measuring the negative inducedcharge pulses [36,143].

The spectroscopic performance of the HF-CdZnTe detector compares favourably to the performance achieved using spectroscopic-grade CdZnTe from Redlen technologies [153], also coupled with the HEXITEC ASIC in a detector of 2 mm thickness and 250 µm pixel pitch. Using the spectroscopic-grade CdZnTe, the average FWHM of the 59.5 keV photopeak for the entire detector was 1.74 ± 0.39 keV for isolated events only, compared with 0.95 ± 0.07 keV achieved with the HF-CdZnTe detector here. Veale et al. [153] showed evidence of local variations in the electric field, linked to the build up of space charge due to the use of blocking contacts, which degraded spectroscopic performance.

The agreement between the experimentally determined charge sharing rates and simulation set to the applied external bias of -750 V (figure 5.11), suggests that the electric field strength within the HF-CdZnTe does not significantly suffer from local distortions and is uniform. Little spatial variation in the charge sharing proportions across the HF-CdZnTe detector support this finding (figure 5.12), as also previously reported in [21]. This is a likely explanation for the better isolated event photopeak performance of the HF-CdZnTe compared with the spectroscopic grade CdZnTe. The lack of local variations in the electric field is also evidence of better hole transport, as the improved electric field uniformity will be related to fewer carriers trapping.

At a 2 mm detector thickness, we have not observed any indication that the reduced electron lifetime in the HF-CdZnTe material has limited the spectroscopic performance. Whether the reduced electron transport will begin to limit performance in thicker HF-CdZnTe detectors, remains to be investigated.

5.7 Simulations of charge sharing in HF-CdZnTe detectors with pixel sizes for high-flux imaging

The demand for high Z sensors like CdZnTe at synchrotrons and XFELs was discussed in section 1.5. In addition to upgraded sensors, new ASIC designs are also required that can handle the capabilities of the improved light sources. DynamiX is a proposed chargeintegrating ASIC [154] which will have small pixels of $\leq 100 \mu$ m, a faster frame rate than HEXITEC of 1 MHz and a large dynamic range, needed for high-flux applications. Small pixels are preferred to provide the best possible spatial resolution for imaging and reduce saturation for individual pixels. However, this design choice will come with increased amounts of charge sharing. Since precise calibration of the detectors will be crucial for converting the recorded charge into the number of photons detected [70], an understanding of the magnitude of charge sharing and charge loss in these small pixel designs at the hard X-ray energies will be essential.

In this section, we used our detector model to simulate the rates of charge sharing in HF-CdZnTe detectors with thicknesses and pixel sizes that are of interest and consideration in detectors for high-flux imaging applications, and at hard X-ray energies that the nextgeneration XFELs and synchrotron light sources will achieve.

5.7.1 Simulation details

Simulations using the detector model were carried out with HF-CdZnTe sensors of 1.5 mm and 2 mm thickness under an applied bias voltages to achieve an electric field strength of 500 V mm⁻¹ for both thicknesses (-750 V and -1000 V respectively). For each sensor thickness, a detector response was simulated to X-rays of 15, 25, 30 and 60 keV at one count/frame. This set of simulations was repeated at each of the pixel pitches listed in table 5.8.

| Pixel pitch (μm) | Pixel contact size (μm) |
|-------------------------|------------------------------|
| 200×200 | 185×185 |
| 175×175 | 160×160 |
| 150×150 | 135×135 |
| 125×125 | 110×110 |
| 110×110 | 95	imes95 |
| 100×100 | 85×85 |
| 75×75 | 60×60 |
| 55×55 | 40×40 |

Table 5.8: Pixel sizes at which charge sharing was simulated. The pixel pitch and corresponding contact pad size of the pixelated anode (assuming an inter-pixel spacing of $15 \,\mu\text{m}$) are shown. The pixel contact size was used in the simulations.

An inter-pixel spacing of 15 µm for the pixelated anode was assumed for each pixel size. This is assumed to be the smallest the pixel gaps would be made for the Dynamix ASIC design (M.C. Veale, personal communication, 2020) at which the capacitive coupling between the readout electronics remains minimal [38]. The contact pad size of the pixelated anode that corresponds to each pixel pitch is listed in table 5.8. Although the weighting potential will vary in each of the simulated detector geometries due to differences in the pixel size to detector thickness ratio (w/L), each design is single carrier (electron) sensing. Using the electron cloud size to estimate charge sharing is therefore still an appropriate assumption. The weighting potential available with the closest w/L ratio for the pixel pitches in table 5.8 was used in the simulations, this was in all cases w/L = 0.125. A noise threshold of 3 keV was applied to the data during event reconstruction.

5.7.2 Results and discussion

Figure 5.20 shows the total proportion of charge sharing events predicted by the model as a function of detector pixel size for each of the simulated photon energies and sensor thicknesses. Figures 5.21 and 5.22 show the proportion of each individual event type for the 1.5 mm and 2.0 mm sensor respectively. For pixels below 100 µm, the number of events with m > 2 begins to increase rapidly. For the 2 mm thick sensor, when using a pixel size of 75 µm, all events are charge sharing events, whereas for the smaller sensor thickness, 20% of events are still isolated at 15 keV or 3% at 60 keV. Although in chargeintegrating operation under high-flux no isolated events will be obtained, when calibrating the detectors obtaining isolated events may prove useful. Dynamic gain switching [155], which is typically used in detectors for high-flux imaging [156], provides a way to achieve the large dynamic range requirements but also single photon resolution.



Figure 5.20: The total proportion of charge sharing events as a function of pixel size calculated from simulated data. (a) for the 1.5 mm thick sensor biased at -750 V. (b) for the 2.0 mm thick sensor biased at -1000 V.

Figure 5.23 shows the average event multiplicity as a function of pixel size. This reveals that as the pixel size decreases, the multiplicity of the events increases exponentially. The



Figure 5.21: The proportion of the individual event types as a function of pixel size for the 1.5 mm sensor. Event types of multiplicity 1 to 4 are shown separately, and all events with multiplicity greater than 4 are shown together.

thinner sensor of 1.5 mm, which is close to the fabrication limit for CdZnTe due to its brittle nature, decreases the average event multiplicity by $\sim 8\%$ compared to the the 2 mm thickness. Since the theoretical quantum efficiency is close to unity for the photon energies investigated for both sensors thicknesses, the 1.5 mm sensor would be the better choice to reduce charge sharing and thereby achieve better spatial resolution.

It is worth noting that the simulations were run at negligible photon flux (one count/frame), done in order to estimate the number of pixels over which individual photon events spread. Under the high-flux irradiation, 10^3 photon charge clouds can be in a pixel simultaneously. For a 25 keV photon, which generates ~6000 electron-hole pairs, this equates to 6×10^6 electrons in the detector pixel at the same time. All of these electrons will experience some repulsion from each other, and this may effect cloud size and therefore charge sharing rates. Although our model does not account for the interaction between different charge clouds, it does compute the contribution to cloud growth due to electron repulsion. To estimate the magnitude of this effect, we simulated the charge cloud size as a function of photon energy with and without electron repulsion switched on, shown in figure 5.24. At 60 keV, the electron repulsion accounts for ~20% of the charge clouds growth during



Figure 5.22: The proportion of the individual event types as a function of pixel size for the 2.0 mm sensor. Event types of multiplicity 1 to 4 are shown separately, and all events with multiplicity greater than 4 are shown together.



Figure 5.23: Average event multiplicity as a function of pixel size. Events with multiplicity 1 to 9 are considered. (a) for the 1.5 mm thick sensor biased at -750 V. (b) for the 2.0 mm thick sensor biased at -1000 V.

drift. It is therefore likely that the presence of multiple charge clouds will effect charge sharing rates. Studying this effect is of interest, but would require upgrades to the current detector model.



Figure 5.24: Average cloud growth during drift as a function of photon energy. Simulated by the model with and without the effect of electron repulsion on cloud growth. For a 2 mm HF-CdZnTe sensor biased with -1000 V.
Chapter 6

Ab initio simulations of bulk CdTe

6.1 Introduction

In previous chapters, we assessed the performance of CdTe and CdZnTe as a sensor material for radiation detection by using experimental data and a Monte Carlo detector model. In this chapter, we move on to the work performed to study CdTe and its alloys using the density functional theory (DFT) method.

The performance of these materials depends critically on their electrical properties, which are dominated by the presence of impurities due to the formation of defects or doping. Studying impurities is very challenging, if not impossible by experiment, and we therefore use DFT. The *ab initio* approach of DFT comes at significant computational cost. To study impurities, supercells (a system of a large number of atoms) are typically required and this further increases computational cost. Approximations are used to make the calculations feasible but as a consequence, the solutions are no longer exact. It is therefore essential to test the results from DFT, and the approximations made, against more accurate methods (e.g. all-electron calculations) and experimental measurements where available. In this chapter we present DFT calculations of bulk CdTe. This is the simple system upon which the more complex alloy supercell structures required to study defects (chapter 7) are built. The better understood system of bulk CdTe means more results from experiment and other theoretical calculations are available to check the accuracy of the structural and electronic properties of CdTe-based systems in our DFT calculations.

The use of pseudopotentials is one approach that can be taken to reduce computational cost (section 2.5.6). DFT calculations of CdTe in the literature [157–160] often employ the projector augmented wave method (PAW) [96]. We chose to use this approach so that we

could scale to larger systems of atoms to achieve the low alloying concentrations typical in CdZnTe sensors and to isolate defects.

The most commonly used approximate functionals in materials science, LDA and GGA, fail to reproduce the correct band gap of semiconductors due to the self-interaction error (SIE) (see section 2.5.5). Many methods exist which attempt to correct this problem. Hybrid functionals (e.g. HSE [161], PBE0 [162]) have been used to correct the band gap in CdTe as well as some thermodynamic and bonding properties [163]. Another method used is the GW approximation which applies a self-energy correction and has been shown to reproduce the experimental band gap of CdTe [164]. Unfortunately, these additions to DFT all come with significant increases to computational demand of one or two orders of magnitude and are often not suitable for calculations of large supercells. DFT+U is an alternative approach that has also been used to correct electronic properties, including the band gap, in CdTe by adding a localised potential term, U, to minimise the SIE [159,160]. This method is no more computationally intensive than standard DFT and has therefore been suggested for the study of defects in supercells [159].

In section 6.2, we present the pseudopotentials available in ABINIT and perform comprehensive tests with comparisons to all-electron calculations and experimental data in order to evaluate their suitability and efficiency for describing CdTe-based systems. In section 6.3, we describe the DFT+U method and the determination of the optimal values of U to correct the electronic properties of CdTe using the PAW method. These systems and checks provide the basis for the work described in chapter 7. Finally, in section 6.4, we demonstrate that the temperature dependence of the band gap in bulk CdTe can be calculated, showing that this is possible using first-principles.

6.2 Investigation of pseudopotentials: bulk CdTe

From the literature, we know that for non all-electron simulations of bulk CdTe, the PAW method is typically used [157–160]. Therefore, all pre-generated PAW datasets available in ABINIT for the atoms investigated in this work (Cd, Te and the alloying atoms used in chapter 7: Zn, Mn and Mg) were tested with calculations of bulk CdTe. Norm-conserving pseudopotentials (NCPPs), which are also available in ABINIT, were included in testing as well. NCPPs are simpler to use in ABINIT as fewer input parameters are required, and work with more advanced theoretical methods such as DFPT (section 6.4.2). NCPPs were therefore bench-marked to the PAW results to check both their suitability for simulating CdTe and to compare their performance (i.e. accuracy and

computational efficiency) to the PAW method. Details on all the PAW datasets and NCPPs and the approximations they use that were included in testing are listed in table 6.1. The ONCV_GGA pseudopotential is the only one which includes the Te *d*-electrons in the valence. For all other pseudopotentials, the Te *d*-electrons are placed in the core.

| Pseudopotential | E_{ma} | N. of valence electrons | | |
|--------------------------------------------|-------------|-------------------------|----|--|
| designation | - <i>xc</i> | Cd | Te | |
| JTH_LDA ^a | $PW92^1$ | 12 | 6 | |
| $\mathbf{KKM}_{\mathbf{LDA}^{b}}$ | PW92 | 12 | 6 | |
| $\mathrm{GBRV}_\mathrm{LDA}^c$ | $PZ81^2$ | 12 | 6 | |
| JTH_GGA | $PBE96^3$ | 12 | 6 | |
| $\mathrm{GBRV}_{-}\mathrm{GGA}$ | PBE96 | 12 | 6 | |
| TM_LDA^d | PW92 | 12 | 6 | |
| $\mathbf{FHI}_{\mathbf{L}}\mathbf{DA}^{e}$ | PW92 | 12 | 6 | |
| $\mathrm{HGH}_\mathrm{LDA}^f$ | PZ81 | 12 | 6 | |
| FHI_GGA | PBE96 | 12 | 6 | |
| HGH_GGA | PBE96 | 12 | 6 | |
| $\mathbf{ONCV_GGA}^g$ | PBE96 | 20 | 16 | |

Table 6.1: All PAW datasets (top section of table) and NCPPs (bottom section of table) tested with bulk CdTe simulations.

 a PAW dataset by F. Jollet, M.Torrent and N.Holzwarth (JTH) from 2018 [165] generated using the AtomPaw [166] software.

^b PAW dataset generated in this work (see Appendix B for details on generation).

^c Ultrasoft pseudopotentials (USPP) by K.Garrity, J.Bennet, K.Rabe and F. Vanderbilt (GBRV) [167] generated by Vanderbilt's USPP generator software and then converted to PAW datasets using the USPP2PAW software [168].

 d Troullier-Martins NCPP [169].

 e Fritz Haber Institute NCPP [170].

^f Hartwigsen Goedecker Hutter NCPP [171].

^g Optimized Norm-Conserving (ONCV) Vanderbilt pseudopotentials [172].

¹Perdew-Wang (1992) exchange-correlation (E_{xc}) functional [90].

²Perdew-Zunger (1981) E_{xc} functional [89].

³Perdew-Burke-Ernzerhof (1996) E_{xc} functional [91].

All simulations of CdTe described in this chapter are performed for a perfect bulk crystal using only two atoms. Since CdTe arranges in the zinc-blende (ZB) crystal structure, which consists of two FCC lattices (one for Cd and one for Te) shifted by 1/4 of the width of the unit cell, the nearest neighbour for each Cd atom will always be a Te atom and vice-versa. As such, a perfect bulk CdTe crystal can be approximated using a primitive cell of a single Cd and Te atom at crystallographic positions (0, 0, 0) and (1/4, 1/4, 1/4) respectively. Symmetry, applied by the primitive translation vectors, is then used to construct the infinite perfect CdTe crystal lattice within the periodic boundary condition (PBC). This is a relatively lightweight calculation, yet exact for a perfect bulk crystal of CdTe. This meant that testing of the pseudopotentials, which required many iterative

runs of varied inputs (section 6.2.1), was possible within feasible timescales.

6.2.1 Convergence checks

To test the available pseudopotentials (i.e. PAW datasets and NCPPs), convergence checks of the total energy (E_{tot}) of the bulk CdTe system in respect to E_{cut} and the **k**-grid (see section 2.5.6) were performed. The larger these parameters are, the more accurate the calculations. However, in the interest of computation time, a limit is set on their size, determined by the point at which convergence of E_{tot} is below a selected threshold. The convergence was measured by using the percentage difference between the current run and the run with the largest parameter sizes,

$$\left|\frac{E_{tot}(E_{cut}) - E_{conv}}{E_{conv}}\right| \times 100\% \tag{6.1}$$

where E_{conv} is the total energy from the calculation with the largest E_{cut} and k-grid inputs. We assumed the system to be converged when the total energy was within $10^{-3}\%$ of E_{conv} .



Figure 6.1: Convergence study for the plane wave cut-off energy parameter E_{cut} and size of the **k**-grid when using the JTH-LDA PAW dataset. Each curve represents the E_{cut} runs for a different **k**-grid density. The dotted horizontal lines show the best converged energy at $E_{cut} = 26$ H using the largest **k**-grid (28 **k**-points) and an energy 0.1 eV larger than this. The inset plot shows the percentage difference $(E_{tot}(E_{cut}) - E_{conv})/|E_{conv}| \times 100\%$, where E_{conv} is the converged energy at $E_{cut} = 26$ H with 28 **k**-points.

Figure 6.1 shows an example of a typical convergence check using the JTH_LDA PAW dataset, where each data point corresponds to the total energy obtained from a separate SCF calculation with a certain E_{cut} and **k**-grid size input. A tolerance of 10^{-12} on the potential residual was used in the SCF loops and Monkhorst-Pack grids [173] were used to sample the BZ with the input **k**-grid size. Using equation 6.1, the system was found to converge to within our defined threshold at the $4 \times 4 \times 4$ **k**-grid size with $E_{cut} = 19$ Ha (Figure 6.1 inset). The same convergence check was performed for each pseudopotential.

In all cases, the $4 \times 4 \times 4$ **k**-grid size was found to suffice to achieve convergence. The convergence with respect to E_{cut} showed greater dependence on the pseudopotential used - with each one compared and the convergence point shown in figure 6.2. The significantly larger values of E_{cut} required for three of the pseudopotentials are due to a greater number of valence electrons (ONCV_GGA) or very hard pseudopotentials (HGH).



Figure 6.2: Convergence of the total energy in respect to E_{cut} shown as the percentage difference to E_{conv} for all pseudopotentials. PAW datasets results shown as open markers with dotted lines, NCPP results by solid markers and lines. Triangle markers represent GGA and circles represent LDA.

6.2.2 Theoretical physical properties and comparison to literature

Using the parameters at which the bulk CdTe system is converged, calculations to determine the lattice constant, bulk modulus and band gap were performed using each pseudopotential. The calculated physical properties were compared to those available in the literature from all-electron codes and experiment.

The theoretical lattice constant was calculated by varying the volume of the unit cell through a series of SCF calculations and utilising the Broyden-Fletcher-Goldfarb-Shanno (BFGS) minimisation technique [174] to minimise the total energy of the crystal with respect to the volume of the unit cell. A tolerance of 5×10^{-5} Ha/Bohr was used on the forces along the crystal dimensions being relaxed. Below this threshold, structural relaxation was stopped and the lattice constant extracted from the relaxed crystal volume.

The total energy as a function of volume from the relaxation calculations when using the JTH_LDA PAW dataset is shown in figure 6.3a. The relaxed volume is at the minimum. The bulk modulus (B0) was obtained by fitting the equation of state (EOS) of a solid [175] to the data in figure 6.3a. From the EOS fit, the pressure on the crystal as a function of the volume is also obtained (6.3b). Using DFT it is therefore possible to determine the dependency of the physical properties on applied pressure, and this was investigated for bulk CdTe in [176].



Figure 6.3: (a) Equation of state (EOS) fit to multiple DFT calculations of different unit cell volume to determine the bulk modulus. (b) Pressure applied to CdTe crystal as a function of volume as obtained from EOS fit. The JTH_LDA PAW dataset was used for these results.

The relaxed lattice constant was then used in the calculations of the electronic structure. Using the electron density from the relaxed crystal structure, non-SCF calculations were performed to obtain the electron density of states (DOS) and electronic band structure. The band structure and total DOS obtained for the bulk CdTe system using the JTH_LDA PAW dataset is shown in figure 6.4. Figure 6.5 shows the contribution of the individual atoms and their electron states to the total DOS (i.e. local DOS). As expected, we see *d*-electrons in the Cd LDOS since these are included in the valence of the pseudopotentials but not for the Te atom. The direct band gap of CdTe can be seen at the Gamma segment (Γ) in the Brillioun Zone (BZ) **k**-space (figure 6.4a). The band gap energy was calculated for each pseudopotential by taking the difference in energy between the valence band maximum (VBM) and conduction band minimum (CBM) at the Gamma segment.



Figure 6.4: (a) Band structure and (b) total density of states (DOS) for bulk CdTe when using the JTH_LDA PAW dataset. The valence bands are shown in black and conduction bands in red. The units for the DOS are arbitrary as only the relative size and locations (in energy) of states are of interest. The energy zero is set to the VBM and a Gaussian broadening of 0.15 eV was used for the DOS.

Table 6.2 lists the physical properties obtained from calculations for each NCPP and PAW dataset. These are compared to literature results from all-electron calculations and experimental data obtained for bulk CdTe. Figure 6.6 shows the tabulated results graphically.

6.2.3 Discussion

All PAW datasets for both LDA and GGA were found to give accurate theoretical lattice constant and bulk modulus values within 0.25% compared to equivalent all-electron results. Consistent with the known shortcomings of the approximations, LDA underestimated the lattice constant and GGA overestimated. Relative to experimental data however, LDA was found to give better agreement to the structural properties than GGA. The theoretical lattice constant when using LDA is within ~1.0% of the experimental value. The band gaps found using GGA are within the range observed for all-electron results, whereas for



Figure 6.5: Local density of states (LDOS) for bulk CdTe using JTH_LDA PAW dataset. (a) total DOS from both atoms, (b) LDOS contribution from all ℓ -orbital electrons included in PAW valence from Cd atom, (c) LDOS contribution from all ℓ -orbital electrons included in PAW valence from Te atom. The energy zero is set to the VBM and a Gaussian broadening of 0.15 eV was used.

| Pseudopotential name | Lattice constant (\mathring{A}) | | Band gap (eV) | | B0 (GPa) | |
|-------------------------------|-----------------------------------|-------|---------------|-------|----------|-------|
| or literature | LDA | GGA | LDA | GGA | LDA | GGA |
| JTH | 6.413 | 6.621 | 0.605 | 0.583 | 46.14 | 35.39 |
| KKM | 6.415 | _ | 0.590 | _ | 46.65 | _ |
| GBRV | 6.423 | 6.631 | 0.581 | 0.559 | 46.89 | 35.60 |
| TM | 6.349 | _ | 0.629 | _ | 47.52 | _ |
| HGH | 6.428 | 6.631 | 0.595 | 0.544 | 45.36 | 35.93 |
| FHI | 6.421 | 6.647 | 0.467 | 0.429 | 45.51 | 35.24 |
| ONCV | _ | 6.623 | — | 0.576 | _ | 34.11 |
| Ouendadji et al. (AE) [176] | 6.421 | 6.631 | _ | 0.588 | 46.68 | 33.79 |
| Messaadia et al. (AE) [177] | 6.420 | _ | 0.601 | — | 45.53 | — |
| Khabita et al. (AE) [178] | 6.420 | 6.650 | 0.610 | 0.560 | 47.67 | 36.60 |
| Strauss et al. (Exp.) [179] | | 6.481 | 1. | 606 | 44 | 1.5 |

Table 6.2: Summary of structural and electronic properties found for each PAW dataset and NCPP used in this work, compared with all-electron (AE) and experimental results from the literature. The top two sections show the PAW and NCPP results respectively, followed by the AE results from WIEN2K DFT simulations and experimental measurements in the very bottom section.

LDA, only the JTH PAW gives exact agreement - with the others within $\sim 3\%$ of the allelectron results. As expected, the DFT calculated band gap significantly underestimates



Figure 6.6: Theoretical lattice constant (top), bulk modulus (middle) and band gap (bottom) obtained for a bulk CdTe system using the different pseudpotentials. AE results from table 6.2 are shown for comparison. Experimental results are not shown for band gap since standard DFT cannot reproduce this value. Black markers are NCPP results and red markers are PAW results.

the experimental value of 1.606 eV determined at 2 K [179].

The NCPP results for the physical quantities were found to be similar to the PAW results. The exceptions to this are the TM_LDA pseudopotential which underestimates the lattice constant by 1.1% and the both FHI pseudopotentials, which underestimate the band gap to a greater degree. The HGH and ONCV pseudopotentials provided the best predictions for the structural and electronic properties of CdTe. The inclusion of more valence electrons (ONCV) does not appear to improve the accuracy - we suggest it is not necessary to describe CdTe. In general, the NCPPs can be used to adequately simulate bulk CdTe. This check was necessary to determine their suitability before being used with DFPT to investigate the temperature dependence of the band gap (see section 6.4.2).

The PAW datasets were found to be more computationally efficient than the NCPPs, achieving total energy convergence at lower values of E_{cut} (figure 6.2). The JTH_LDA

PAW dataset converged at 19 Ha compared to 25 Ha for the best NCPP convergence result. In addition, the PAW datasets appear to converge more quickly as E_{cut} increases, with the JTH_LDA PAW dataset within 0.1 eV of the highest converged total energy at 14 Ha, compared with 23 Ha for the TM_LDA NCPP.

From this initial investigation, PAW datasets in ABINIT were found to be more suitable for CdTe simulations than the NCPPs, due to faster convergence with E_{cut} . For the larger systems of atoms required when investigating defects, the greater efficiency of PAW becomes significant. The JTH_LDA PAW dataset was chosen as the best performing pseudopotential and was consequently used for the work described in chapter 7. JTH PAW datasets exhibited the fastest convergence with E_{cut} and when using LDA, gave better overall agreement to all-electron and experimentally obtained values for structural and electronic properties than GGA.

6.3 DFT+U correction

Standard DFT calculations do not accurately predict the electronic properties of CdTe. This is evident by the significantly underestimated band gap and the observed weak coupling between the Te-5s and Cd-4d electron orbitals - apparent in the LDOS (figure 6.5). Experimentally observed photoemission spectra of CdTe [180] reveal strong s - d coupling. Wu et al. [159] have shown that the DFT+U approach can be used as a computationally low cost alternative with which to improve the prediction of the electronic properties of CdTe. DFT+U is a method in which a local potential (U) is used to correct the self-interaction error (SIE) in DFT. This is achieved by using a Hubbard-like model [181], as follows [182]:

$$E_{tot}^{DFT+U} = E_{tot}^{DFT} + \frac{U-J}{2} \sum_{\sigma} \left(n_{m,\sigma} - n_{m,\sigma}^2 \right),$$
(6.2)

where n is the orbital occupation number, m the orbital momentum and σ the spin index onto the electrons which the local potentials U (the strength of on-site Coulomb repulsion) and J (the strength of the exchange interaction) are added. Following Dudarev's method [183], the two potential terms can be combined into a single effective one, $U_{eff} = U - J$. This effective parameter U_{eff} is simply referred to as U in this work.

A universal value of U which corrects each property does not exist. Instead, the appropriate value of U depends on the property being corrected. Wu et al., using the VASP DFT code and associated PAW datasets, found that values of U=12.5 eV and 13.9 eV for LDA and GGA respectively were required to reproduce the experimental band gap. However, s - d coupling was found to match experiment at U = 7 eV. In this section, the U values required to correct the band gap and s - d coupling for the PAW datasets available in ABINIT with the DFT+U method are presented.

6.3.1 Determining the best value of U

Several approaches based on first-principle methods have been proposed to determine U [184]. In this work, we determined U empirically by searching for values that reproduce experimental results, as these are well known for CdTe. Since the average Coulombic potential described by the homogeneous electron gas does not accurately capture the strong Coulombic repulsion of highly localised electrons, the U potential was added to the 4*d*-Cd electrons as these are the most localised due to their large angular momentum. In order to prevent double counting of the potential for the localised electrons which is also still acted on by the homogeneous electron gas, a double-counting correction term (the full localised limit [185]) is subtracted from the Hamiltonian in the simulations.

The lattice constant, DOS and band gap were determined using each of the PAW datasets introduced in section 6.2 for calculations with different values of U (from 0 - 30 eV) applied. To verify the results obtained for the ABINIT PAW datasets, we performed the same study using two other sets of PAW datasets from different DFT software - Quantum Espresso (QE) and the Vienna Ab initio simulation package (VASP). The results from VASP meant a direct comparison to Wu et al. [159] was possible to validate the computational method. Convergence studies were performed against the same tolerances used in section ?? for the QE PAW datasets, whereas for VASP the converged values found in [159] were used to enable a direct comparison. Details on the QE and VASP PAW datasets and their converged parameter values are given in table 6.3.

Figure 6.7 shows the effect of the U potential on the band gap and lattice constant for each PAW dataset. The effect of U from our VASP calculations agrees with those from Wu et al. [159], supporting that the DFT+U calculations, which are set up the same way in each software, are being performed correctly. The relationship with U observed in VASP could not be reproduced using the other PAW datasets. Interestingly, the trend on the structural and electronic properties as a function of U vary significantly between the PAW datasets. This is most pronounced at large values of U, whereas for U < 5 eV, results from all PAW datasets are similar and within 15%.

| PAW dataset | Ema | N. of valence e^- | | ecut (Ha) | k -grid | |
|-------------------------------------------------------------------|---------------|-----------------------------------------|-----------------|---------------------------------------|------------------------------------------------|--|
| | Δxc | Cd | Te | (114) | M Brid | |
| $\begin{array}{c} {\rm QE_LDA}^{a} \\ {\rm QE_GGA} \end{array}$ | PZ81 PBE96 | 12 12 | $\frac{16}{16}$ | $\begin{array}{c} 25\\ 25\end{array}$ | $4 \times 4 \times 4$ $4 \times 4 \times 4$ | |
| $VASP_LDA^b$ $VASP_GGA$ | PZ81 PBE96 | $\begin{array}{c} 12 \\ 12 \end{array}$ | 6 6 | 13 13 | $8 \times 8 \times 8$ $8 \times 8 \times 8$ | |

Table 6.3: Details on the PAW datasets used with QE (first section in table) and VASP (second section in table). Values for the size of E_{cut} and k-grid parameters needed for convergence. For QE values were obtained using the tolerances set in this work and for VASP the values are taken from [159].

^a PAW dataset generated by A. Dal Corso [99] using "atomic" code.

 b PAW datasets v.54 from the VASP portal [186].



Figure 6.7: The band gap and unit cell lattice constant as a function of U for the ABINIT, QE and VASP PAW datasets. (a)-(b) results from LDA and (c)-(d) results from GGA. The solid black lines are the results from Wu et al. [159]. The horizontal dotted lines give the experimentally known values at close to 0K [179].

The experimental band gap could only be reproduced in ABINIT with the JTH PAW datasets, and at much larger U values of 27/30 eV for LDA/GGA than in the VASP case.

For the remaining PAW datasets, at U = 30 eV, the band gap remained below the experimental value of 1.6 eV at between 1.1 - 1.3 eV. These results show that although DFT+U improves the accuracy of the calculated CdTe band gap in all cases, the appropriate Uvalue depends on the PAW dataset being used and must be checked. Furthermore, it is possible that the experimental band gap can not even be reproduced for some PAW datasets - this seems likely for the QE PAW datasets (figure 6.7).

Although the U potential is applied to correct the electronic properties of CdTe, it also impacts the structural properties of the crystal and this must be checked too. This can be seen by the effect U has on the lattice constant. In all cases, except for VASP and QE, the lattice constant initially increases with U before reaching a maximum and then decreases with U. Whether the addition of U improves or worsens the predicted structural properties in comparison to experimental data, again depends on the PAW dataset used.



Figure 6.8: Total electron DOS and the local DOS for the Cd-4d and Te-5s electrons when using the JTH_LDA PAW dataset for (a) U = 0 eV, (b) U = 7 eV, (c) U = 27 eV. The dotted vertical lines indicate the energy positions of the two peaks and shoulder (9.5 eV) observed in the photoemission spectra of CdTe by Loeher et al [180]. The Valence states and conduction states are labelled by VB and CB respectively. The energy zero is set to the VBM when U = 0 eV.

The potential U applied to the Cd-4d electrons pushes the Cd-4d band down in energy, and this pulls down the VBM which results in the band gap opening up. This can be seen from the total and local DOS from calculations at U = 0, 7 and 27 eV, shown in figure 6.8. For standard LDA/GGA, the energy positions for the Cd-4d and Te-5s states are overestimated and show weak s - d coupling (figure 6.8a). The DOS therefore does not match the peaks recorded experimentally in photoemission spectra by Loeher et al. [180] nor exhibit strong s - d coupling [187]. By shifting the Cd-4d band with U = 7 eV when using the JTH_LDA PAW dataset, the DOS can be corrected to match experiment (figure 6.8a). The peaks at -11.5 and -9.5 eV show a significant contribution from both the Cd-4d and Te-5s electrons, revealing that strong s - d coupling also occurs after correction of the DOS energies. However, at this value of U the band gap is still underestimated. When the experimental band gap is reproduced at U = 27 eV, the DOS no longer matches experiment and only very weak s - d coupling is observed (figure 6.8c). Both electronic properties can therefore not be corrected with a single value of U. Table 6.4 shows the U potential needed to correct the band gap (when possible) or DOS for each PAW dataset.

| PAW name | U to correct band gap (eV) | | U to correct DOS (eV) | | |
|---------------|----------------------------|------|-----------------------|-----|--|
| 111., 1101110 | LDA | GGA | LDA | GGA | |
| JTH | 27 | 30 | 7 | 6 | |
| KKM | — | — | 8 | — | |
| GBRV | — | — | 9 | 8 | |
| QE | _ | — | 9 | 8 | |
| VASP | 12.5 | 13.9 | 7 | 6 | |

Table 6.4: The values of U determined to correct either the band gap or DOS to match experiment, for each PAW dataset. Note for some PAW datasets, the experimental band gap could not be reproduced over the investigated values of U.

6.4 Temperature dependence of the band gap

Wide-band gap semiconductors have the advantage that they can be operated over a large temperature range, including at room-temperature (~ 300 K). Nevertheless, as the band gap varies with temperature, detector performance will be impacted due to changes in noise generation and charge carrier excitation (see section 2.4.1). In this section, we calculate the temperature dependence of the band gap in bulk CdTe. The ability to calculate this relationship from first-principles will be useful in the study of potential higher order compounds for radiation detection for which experimental results are not always available.

The two main effects contributing to the temperature dependence of the band gap in semiconductors are the thermal expansion of the lattice, and the renormalization of the band energies due to the interaction between electrons and phonons [188]. The renormalization is a consequence of the zero-point vibrations [189] that arise from the electron-phonon coupling and is typically termed the Zero-Point Renormalization (ZPR). Using DFT+U, it was possible to calculate the effect of the expanding lattice on the experimental band gap - this is shown in section 6.4.1. Since the ZPR is a thermodynamic effect related to the phonon population which depends on the temperature, standard DFT, which performs calculations at zero Kelvin, cannot be used to calculate the ZPR. Instead, we used the density functional perturbation theory (DFPT) framework to calculate the ZPR - this is discussed in section 6.4.2.

6.4.1 Band gap dependence on thermal lattice expansion

The thermal expansion of the lattice as a function of temperature was calculated using

$$\Delta L = \alpha \cdot \Delta T \cdot L \tag{6.3}$$

where ΔL is the change in lattice constant resulting from a change in temperature, ΔT , for a lattice of length L at T = 0 K and α is the thermal expansion coefficient. Figure 6.9a shows the thermal expansion coefficient for CdTe measured experimentally at various temperatures between 2 and 700 K. The relaxed lattice constant obtained with the JTH_LDA PAW dataset and a local potential U = 27 eV was used with equation 6.3 to determine the lattice constant of bulk CdTe as a function of temperature - see figure 6.9b. Temperatures up to 380 K were investigated to cover the operating range for CdTe detectors. The DFT+U method with U = 27 eV was used in order to reproduce the experimental band gap at T = 0 K. Figure 6.9b shows that the change in lattice constant with temperature is small, with an absolute difference of ~0.006 Å or a relative change of ~0.1% between 0 and 380 K.

A DFT+U and band structure calculation was run for each lattice constants shown in figure 6.9b. The direct band gap at the gamma point was determined for every lattice constant input. Figure 6.10 shows the results from these calculations and represents the effect of the thermal expansion of the lattice on the band gap. The DFT calculated results are compared with Varshni's expression [192] for the temperature variation of the band gap energy in semiconductors, obtained by fits to experimental data by [193]. The comparison reveals that the thermal expansion effects in bulk CdTe contribute only a small amount to the temperature dependence of the band gap. At 300 K, thermal expansion accounts only for a band gap decrease of 0.0084 eV. This is in good agreement to the value of ~ 0.0090 eV found from analytical calculations [194].



Figure 6.9: (a) Thermal expansion coefficients for CdTe as measured experimentally by Smith et al. [190] and Williams et al. [191]. The markers indicate the temperatures at which the thermal expansion coefficients were measured. The lines illustrate the linear interpolation used between the measurements. (b) Lattice constant as a function of temperature due to thermal expansion.



Figure 6.10: Temperature dependence of the band gap due to the thermal expansion of the lattice. Compared with the experimental relationship between band gap and temperature, shown as the Varshni fit from [193].

6.4.2 Zero-point renormalization of the band gap due to electron-phonon coupling

The change in lattice dimensions due to thermal expansion was shown to have only a minimal affect on the temperature dependence of the band gap. This result highlights the importance of the interaction between electrons and phonons to describe the band gap relation with temperature for CdTe. To account for the thermally activated phonons, density-functional pertubation theory (DFPT) calculations were used. From the DFPT outputs, the zero-point renormalization (ZPR) as a function of temperature was then calculated using the electron-phonon interaction theory described by Allen, Heine and Cardona (AHC) [195] within the adiabatic approximation. A detailed description of the AHC theory and adiabatic approximation as implemented in ABINIT can be found in [196].

AHC calculations require the use of a \mathbf{q} -grid which is a set of phonon wavevectors (or \mathbf{q} -points) used to sample the Brillouin Zone. This is very similar to the \mathbf{k} -grid, except for phonons instead of electrons, and its size must also be converged on. The convergence of the \mathbf{q} -grid is performed on the ZPR and not the total energy, since this is the output from AHC calculations. We calculate the ZPR of only the VBM and CBM at the gamma point where the direct band gap of CdTe is located. For each \mathbf{q} -grid size, the ABINIT calculations performed to compute the ZPR were as follows:

- (i) A standard DFT SCF calculation using the relaxed theoretical lattice constant, converged parameters and centred on the gamma point to produce unperturbed ground-state eigenvalues and the electron density.
- (ii) A non-SFC DFT calculation to produce the wavefunctions at a homogeneous Monkhorst-Pack q-grid at the gamma point.
- (iii) A DFPT phonon calculation to determine the electron-phonon matrix elements at each q-point.
- (iv) The AHC adiabatic approximation calculation using the outputs from (i) (iii) to compute the ZPR at the VMB and CBM as a function of temperature from 0 380 K in steps of 20 K.

The AHC implementation in ABINIT was only compatible with NCPPs and not the PAW method. From the convergence checks (section 6.2), we selected the HGH pseudopotentials (both in LDA and GGA) to perform the AHC calculations. The TM and FHI pseudopotentials, although converging at significantly lower E_{cut} , poorly predicted the lattice constant and band gap respectively, when compared to PAW. The ONCV_GGA performed well but includes more electrons in the valence and was therefore dismissed due to the additional computational cost - phonon calculations are already very computationally intensive due to very dense **q**-grids required for convergence.

6.4.2.1. Zero-point renormalization convergence with q-grid

The ZPR converges very slowly with increasing **q**-grid [197]. Therefore a convergence threshold of $\pm 5\%$ of the densest **q**-grid was selected. This threshold was achieved for the ZPR of the VBM (ZPR_{VBM}) and CBM (ZPR_{CBM}) at a $30 \times 30 \times 30$ **q**-grid.

6.4.2.2. Band gap renormalization with temperature

The ZPR of the band gap (ZPR_q) is given by,

$$\operatorname{ZPR}_{q}(T) = \operatorname{ZPR}_{CMB}(T) - \operatorname{ZPR}_{VBM}(T)$$
(6.4)

which is a function of the temperature T. The $\text{ZPR}_g(T)$ is added to the band gap found for the HGH pseudopotentials (table 6.2) to obtain the temperature dependence of the band gap due to electron-phonon coupling. Since the band gap using NCPPs could not be corrected to the experimental gap, the relative change as a function of temperature when applying the ZPR_g contribution was computed - this is shown in figure 6.11 and compared to the experimentally determined Varshni fit.



Figure 6.11: Relative change in bandgap as a function of temperature for DFPT calculations when using each of the NCPPs, compared to a result from the literature [193].

The ZPR_g correction to the band gap dominates the temperature dependence of the band gap. The calculated trend as a function of temperature shows the same T^2 dependence at low temperatures and a linear T proportionality at higher temperatures as is observed from experiment for CdTe and typical for most semiconductors [198]. The ZPR calculated from the AHC theory slightly underestimates compared to experimentally obtained values - this can be seen from the ZPR_g at 0 K and the slope of the linear component of the temperature dependence (see table 6.5). We found the underestimate to be greater for the LDA compared to the GGA. However, some underestimation is expected as the lattice expansion effect on the band gap is not included and others have also reported [196, 199] an underestimation of the ZPR for LDA and GGA DFT calculations for different semiconductors.

The underestimate arising from DFT can be improved by using GW calculations instead [200] and, when further applying temperature induced lattice expansions, excellent agreement to experiment is obtained - as has been previously shown for diamond [199]. However, for many compound semiconductors, the GW correction is marginal and considering its large computational cost, can often be avoided [199]. We apply the relative change of the band gap due to the thermal expansion (Δgap_{lat}) with temperature (section 6.4.1) to our ZPR results (figure 6.11 and table 6.5). This improves the overall temperature dependence of the band gap we find for CdTe from DFT/DFPT calculations, particularly at higher temperatures.

| Data | $ZPR_g(T = 0 \text{ K}) \text{ (eV)}$ | $\partial E_g / \partial T \ (\%/K)$ | |
|---------|---------------------------------------|--------------------------------------|--------------------------|
| | | AHC | $AHC + \Delta gap_{lat}$ |
| HGH_LDA | -0.010 | -0.022 | -0.026 |
| HGH_GGA | -0.011 | -0.026 | -0.030 |
| Exp. | -0.014 [201] | - | 0.031 [193] |

Table 6.5: Zero-point renormalization of the band gap at zero Kelvin and gradient of the linear component of the temperature dependence at 'high temperatures' for bulk CdTe calculated using the HGH pseudopotentials for LDA and GGA. Theoretical values are compared to experimental measurements for which sources are given in the table.

6.5 Summary

In this chapter the DFT method was used to calculate physical and electronic properties of bulk CdTe from first-principles. The 2-atom bulk crystal provided a simple system to test the suitability of a number of different available pseudopotentials. We found that the JTH_LDA PAW pseudopotential provided the best balance between computational efficiency and accuracy when compared to all-electron results and experiment. This pseudopotential was therefore used in the work described in chapter 7 to study the alloys of

CdTe.

It was shown that the band gap could be corrected with the DFT+U method, but variations between PAW datasets meant this depended on the particular dataset used. Furthermore, the DOS and band gap could not be corrected with a single universal value of U applied to the localised Cd-4d electrons.

We showed that it is possible to determine the temperature dependence of the band gap for CdTe. This demonstrated the capability to calculate this dependence from first-principles for more complex CdTe-based systems for which experimental measurements do not exist. The change in band gap due to the thermal expansion of the lattice could be accurately calculated with DFT+U, but contributed only a small amount compared to the electron-phonon ZPR contribution. The ZPR influence on the band gap required the use of the DFPT framework to perform calculations of excited states, which is computationally very demanding.

Chapter 7

Study of the Cadmium Vacancy in $Cd_{1-x}A_x$ Te (A = Zn, Mn, Mg)

7.1 Introduction

Alloys other than CdZnTe from the II-VI compound semiconductor group have gained attention in recent years as possible low-cost alternatives to CdZnTe. Alloying CdTe with either Mn (Z = 25) or Mg (Z = 12) instead of Zn offers potential benefits that could see CdMnTe or CdMgTe become the workhorses of room temperature hard X-ray and gamma ray detection in the future [4]. More widespread use of CdZnTe has been stunted by the relatively high production cost of detector grade crystals. A large segregation coefficient of approximately 1.35 for Zn in CdTe [202] makes it difficult to grow large samples of CdZnTe that are compositionally homogeneous. This results in poor yield from growth [11,17,203], and requires crystal samples to be characterised and screened to determine the samples with purity suitable for use in detectors - thereby increasing costs. Mn [53] and Mg [204] have segregation coefficients near 1 in CdTe, which result in a more homogeneous distribution of the alloy and could ultimately lead to better yield and lower costs.

Other advantages over CdZnTe are that MnTe and MgTe have larger band gaps than ZnTe, such that a lower alloying concentration is needed to achieve the optimal band gap energy. This will reduce the probability of alloy scattering and improve the carrier $\mu\tau$ product [205], while also minimising inhomogeneities associated with alloying effects. CdMgTe has the additional advantage over the other two alloys that the lattice constants of CdTe (6.48 Å) and MgTe (6.44 Å) [206] are very similar, resulting in higher crystallinity by reducing the likelihood of extended defects.

Challenges in the use of these potential alloys for X-ray detection persist and have stalled their development and maturity. In CdMnTe, a higher bond-ionicity than in CdZnTe [207] leads to a greater tendency for crystallisation in the hexagonal structure, instead of the zinc-blende structure desired for its more suitable electrical properties. Due to the higher ionicity, more twinning compared to CdZnTe has also been observed [208]. In the case of CdMgTe, it often reacts exothermically, which poses a greater risk of explosion of ampoules during synthesis [54]. Both Mn and Mg ingots are currently not commercially available at ultra-high purity of 7N (99.99999%), which Cd, Zn and Te are. Lower purities introduce unwanted extrinsic defects. The lack of commercially available Mg ingots of >2N purity (99.99%) until only recently, is one of the primary reasons why CdMgTe has not been more widely considered as a possible candidate for X-ray detection until now.

Both CdMnTe and CdMgTe have not been as widely studied as CdZnTe in the application of detecting X-rays and gamma rays. More research has been dedicated to CdMnTe, with the first report of crystals grown for the purpose of radiation detection in 1999 [53]. Since then, large improvements have been made to both the resistivity and charge carrier properties [209–218], increasing spectroscopic performance. Some of the best of these quantities have been attained with Cd_{0.95}Mn_{0.05}Te doped with In and have a resistivity of ~10¹⁰ Ω cm⁻¹ and an electron $\mu\tau$ product of 3×10^{-3} cm²V⁻¹. This is comparable with, but not yet at the best levels obtained in CdZnTe ($\rho = 3\times10^{10} \Omega$ cm⁻¹, $\mu_e \tau_e = 1\times10^{-2}$ cm²V⁻¹ [110]). Very few investigations of CdMgTe grown for radiation detection have been performed [54, 219–221], but initial results are remarkably promising. The first reported development of CdMgTe for X-ray detection in 2013 [54] found about two orders of magnitude fewer Te-inclusions than in CdZnTe and CdMnTe, albeit relatively modest electron transport. Since then, a resistivity of $3.12\times10^{10} \Omega$ cm⁻¹ and $\mu_e\tau_e = 5.3\times10^{-3}$ cm²V⁻¹ has been achieved with In-doped Cd_{0.92}Mg_{0.08}Te crystals, and spectroscopic response at photon energies ranging from 60 - 662 keV has been demonstrated [219].

The resistivity and electron-hole transport, key parameters for good performance in semiconductor based radiation detectors, are strongly dependent on defect concentrations. The most abundant defect in Te-rich grown CdTe and its alloys, the Cadmium vacancy (V_{Cd}), is responsible for the p-type conductivity of these compounds since it acts as an acceptor [222]. Defects therefore also influence the resistivity. To continue the development of CdMnTe and CdMgTe detectors, a deeper understanding of their material properties and defects is needed. In this chapter, we focus on the V_{Cd} defect and calculate its formation energy as a function of alloying concentration for the three alloys discussed using supercell DFT simulations. To the best of our knowledge, these are the first reported calculations of defect formation energies in CdMnTe and CdMgTe, whereas calculations exist in the literature for CdTe and CdZnTe [12] - which we use for comparison and validation. Determination of the defect formation energies is also important for improving semiconductor defect concentration modelling using the generalised quasi-chemical approximation [223]. This was done in [219] for CdMgTe but using existing CdTe defect formation energies instead of the true values for CdMgTe.

In section 7.2 we briefly explain common defects in CdTe and its alloys. In section 7.3, details on calculating the defect formation energy and the DFT supercell simulations are given. In section 7.4, the V_{Cd} formation energy is calculated for a bulk supercell of CdTe and compared with the literature, and the convergence with supercell size and dependence on the local potential U is discussed. The energetically favourable crystallisation phases as a function of alloy concentration for each compound is presented in section 7.5. In sections 7.6 and 7.7, the physical properties and V_{Cd} formation energy for $Cd_{1-x}Zn_xTe$ and $Cd_{1-x}(Mn/Mg)_xTe$ systems are presented and discussed. Due to challenges with the magnetisation of Mn, some results for $Cd_{1-x}Mn_xTe$ are preliminary but still provide a useful insight. Finally, section 7.8 summarises the results.

7.2 Defects in CdTe

Regardless of the method used to grow CdTe and its alloys, the grown samples will contain defects to some degree. Extended defects such as dislocations, grain boundaries, twins and Te-inclusions can be relatively large in size $(>1 \,\mu\text{m})$ and have all been observed in as-grown CdTe-based crystals [11]. It is believed that these extended defects, and particularly the Te-inclusions, act as carrier trapping centres which negatively impact carrier lifetimes and therefore degrade charge collection efficiency [224]. Post-growth annealing procedures are typically adopted which significantly reduce the concentration of the extended defects [216, 225].

Native point defects will also be present in as-grown crystals and are more difficult to eliminate with post-growth annealing. There are three types of native defects: vacancies, interstitials and antisites [226]. The Te-rich conditions and the large vapour pressure of Cd typically used during CdTe growth result in crystals with a high concentration of defects on the cation sites [227]. Therefore, the most abundant point defects in CdTe and its alloys are the cadmium vacancy (V_{Cd}), where a Cd atom is missing from its site in the crystal lattice, and the tellurium antisite (Te_{Cd}), where a Te atom occupies a Cd site. V_{Cd} , unlike Te_{Cd} , is a mobile defect and its diffusion is believed to play a role in the formation of the Te-inclusions as V_{Cd} merge to form voids with Te atoms inside [228]. The V_{Cd} will also interact with Te_{Cd} to form complex defects such as $\text{Te}_{Cd} \cdot \text{V}_{Cd}$ and $\text{Te}_{Cd} \cdot (\text{V}_{Cd})^2$. All of these act as trapping centres. The V_{Cd} is also expected to accumulate more easily at dislocations and grain boundaries. Undoped CdTe based crystals can be both n-type or p-type conductors depending on if the V_{Cd} , which acts as an acceptor, or the Te_{Cd} , which acts as a donor, is more abundant. In Te-rich growth conditions, the V_{Cd} concentration is typically dominant and the material is p-type [222]. To compensate for the native defects and increase resistivity, intentional impurities are added which are usually In for p-type or Cl for n-type CdTe-based crystals [229].

Between the alloys described here, CdZnTe is the most well studied system. The role of Zn is better understood and it is now widely accepted that the best composition for radiation detection is around Cd_{0.9}Zn_{0.1}Te [11,228] - in agreement with what we estimated for the HF-CdZnTe material in section 4.7.3. A progressive tendency towards p-type conductivity with increasing Zn content has been interpreted as an increase of V_{Cd} and reduction of Te_{Cd} [228]. This is in accordance with the changes in the defect formation energies as a function of Zn content - determined from DFT calculations [12]. Since the V_{Cd} is mobile, this defect can diffuse out of the crystal during post-growth annealing and a CdZnTe crystal with lower defect concentration than in CdTe is obtained. Chu et al [228] showed that 10% is the optimal Zn content, compromising between a higher concentration of complex defects at lower Zn due to more Te_{Cd}, and a greater amount of Te-inclusions observed at larger Zn content due to very high levels of V_{Cd}. The effects of Mn and Mg in CdTe on defect concentrations is less well understood, and consequently the optimal alloying concentration in Cd_{1-x}Mn_xTe and Cd_{1-x}Mg_xTe is not yet established.

7.3 Computational details

We used supercell geometries which is a common approach in computational studies of point defects [230]. Supercells are needed to minimise artificial long-range interactions between the defects due to the periodic boundary condition (PBC) - as these interactions are known to affect the calculated defect formation energies [231]. In our case, a large number of atoms had the additional benefit of achieving the low alloying concentrations of most interest for radiation detection and allowing the randomisation of the alloy atom positions. Unless noted otherwise, all calculations were performed with 64 atom supercells consisting of $2 \times 2 \times 2$ unit cells in the zinc-blende phase with randomised positions of n alloy atoms A (A = Zn, Mn or Mg) on the cation sub-lattice. For the V_{Cd}, the formation energy ΔH_f was calculated as [230],

$$\Delta H_f = E_{tot}(Cd_{31-n}A_nTe_{32}:V_{Cd}) - E_{tot}(Cd_{32-n}A_nTe_{32}) + \mu_{Cd} + q(E_F + E_V)$$
(7.1)

where E_{tot} is the total energy of the supercell, firstly containing the V_{Cd} , and secondly without the defect but in the same alloy configuration. q is the charge associated with the defect and E_F the Fermi energy referenced to the valence band maximum energy E_V . We only calculated the defect formation energy for the neutral (q = 0) V_{Cd} , so the last term in equation 7.1 is zero.

The cadmium chemical potential, μ_{Cd} , accounts for the energy loss due to the missing cation replaced by the vacancy. The range of possible values for μ_{Cd} is defined by whether Cd-rich or Te-rich growth conditions are used. Since crystals grown under Te excess result in better carrier transport [232], we calculated the defect formation energies in Te-rich conditions only. To determine the corresponding μ_{Cd} , we first calculated the tellurium chemical potential (μ_{Te}). This was obtained from a bulk Te calculation using a unit cell with 3 atoms in a trigonal lattice, a $8 \times 8 \times 5$ k-grid and E_{cut} of 20 Ha structurally relaxed below 5×10^{-5} Ha/Bohr (convergence on the total energy was performed using the tolerances defined in section 6.2.1). The Te-rich μ_{Cd} was then obtained using

$$\mu_{Cd} = E_{tot}^{\text{CdTe}} - \mu_{Te} \tag{7.2}$$

where E_{tot}^{CdTe} is the total energy of bulk CdTe (2 atoms) and μ_{Te} is the energy of a single Te atom in bulk Te.

The JTH_LDA PAW pseudopotentials were used for all atoms in the supercell calculations, unless stated otherwise. The pseudopotentials for the alloy atoms Zn, Mn and Mg contained the $3d^{10}4s^2$ (12e⁻), $3s^23p^63d^64s^1$ (15e⁻) and $2s^22p^63s^2$ (10e⁻) electrons in the valence, respectively, with the remaining electrons approximated in the core.

For the 64 atom supercells, a Monkhorst–Pack **k**-grid of $2 \times 2 \times 2$ and E_{cut} of 15 Ha was used. These values are lower than the converged parameters found in section 6.2.1 (**k**-grid = $4 \times 4 \times 4$, $E_{cut} = 20$ Ha). A less dense **k**-grid is needed for supercells because as the volume in real space increases, the volume of the Brillioun zone (BZ) decreases proportionally resulting in greater **k**-point sampling. For verification, convergence of the V_{Cd} formation energy in bulk CdTe was checked with the higher converged parameters, which only led to a 0.1% difference. This is much smaller than the differences arising from supercell size convergence (section 7.4) or alloy positions (section 7.6) - the lower input parameters were therefore used in the interest of computation time. Both the volume and atomic positions of the supercells were structurally relaxed until stresses below 1×10^{-3} Ha/Bohr were reached. For each ternary alloy concentration, 10 runs with different random alloy positions were performed. Structural relaxation was found to significantly influence the defect formation energies (up to 30% differences were observed when the structure with the defect was not relaxed). Supercell calculations which did not relax below the stress tolerances were therefore disregarded.

CdMnTe is a dilute magnetic semiconductor (DMS) due to the introduction of the Mn atoms, and has been predicted to exhibit either ferromagnetic or antiferromagnetic [233] behaviour. MnTe has a Curie temperature of 323 K [234], so the alloy is expected to still exhibit its magnetic properties at room temperature. We therefore performed spin-polarized DFT calculations of ferromagnetic CdMnTe and added magnetic moments of 4 μ_B to each Mn atom [233]. The magnetic moment on each atom was allowed to change during the ground-state calculations.

7.4 Bulk CdTe supercell calculations

In bulk calculations of CdTe using a 64 atom supercell, the obtained lattice constant (6.413 Å) and band gap (0.607 eV) were the same as for the primitive 2 atom cell CdTe calculations (section 6.2.2). This was checked to confirm that the bulk supercell used to create the ternary alloys and host the Cd vacancy was set up correctly.

The artificial electrostatic interaction between defects across the PBC is only completely eliminated in the limit of an infinitely large supercell. For charged defects, the Makov-Payne correction [235] is often applied to small finite supercells to account for this effect. Since we are only concerned with the neutral V_{Cd} , we had to determine the convergence of the defect formation energy with supercell size and extrapolate to an infinitely large supercell, as shown in figure 7.1. This is the most accurate approach to calculating the defect formation energy in the absence of artificial electrostatic energies, albeit also very tedious and computationally demanding. Details on the computational resources and times for each supercell size from 8 to 512 atoms are shown in table 7.1. We therefore only performed this calculation for the defect in bulk CdTe and not its alloys.

The extrapolated fit to an infinitely large supercell was done using only the cubic supercells (figure 7.1). We found that for the non-cubic supercells (32 atoms and 128 atoms), the defect formation energy diverged from the expected linear convergence trend. This is likely



Figure 7.1: Convergence of the formation energy for neutral V_{Cd} with supercell size. The magenta horizontal line indicates the defect formation energy for an infinitely large supercell determined from extrapolation.

because the defect is not equidistant in all directions to the defects repeated in the PBC. We therefore conclude that non-cubic supercells should be avoided when calculating point defects. The extrapolated V_{Cd} formation energy for an infinitely large supercell was found to be 1.72 eV. This is within 0.12 eV in comparison to the 64 atom supercell calculation. Since this difference is less than the variation of the defect formation energy seen across multiple works in the literature (table 7.2), we considered the 64 atom supercell to be the best compromise between accuracy and performance for the alloys studied.

| Supercell size (N. of atoms) | Wall time (hrs) | CPUs used | CPU time (hrs) |
|------------------------------|-----------------|-----------|----------------|
| 8 | 0.02 | 8 | 0.15 |
| 32 | 0.20 | 25 | 4.93 |
| 64 | 0.64 | 50 | 31.93 |
| 128 | 5.91 | 110 | 649.64 |
| 216 | 61.50 | 100 | 5929.21 |
| 512 | 101.20 | 216 | 20338.05 |

Table 7.1: Details on computational time and resources required for simulations of supercell systems with increasing number of atoms. For the 8 atom supercell the BZ was sampled with a larger **k**-grid of $4 \times 4 \times 4$ and for the 512 atom supercell the BZ was only sampled at the gamma point (1 **k**-point). All other supercells used a **k**-grid of $2 \times 2 \times 2$. The wall time is the real elapsed time, whereas CPU time is the effective computation time considering the number of CPUs used.

The V_{Cd} formation energy in bulk CdTe obtained in this work was compared to the value found in other works, shown in table 7.2. Since the type of approximation used is known

to influence the bond length, and we observed that changes in lattice constant effect the formation energy (section 7.6.2), we also calculated the V_{Cd} formation energy using the JTH_GGA PAW pseudopotential. The formation energy obtained when using GGA is similar (<0.1 eV) to when using LDA with a variation less than that across the literature or due to supercell size convergence. Therefore, for all further calculations only the LDA pseudopotential was used. Additional validation and dependency of the exchangecorrelation functional was performed using the QE code. Overall, our formation energy values agree well with those found in the literature and are not significantly dependent on the approximation used. Different, randomised positions of the V_{Cd} were found to have no effect on the defect formation energy.

| Approximation (E_{re}) | $\Delta H_f (eV)$ | | |
|--------------------------|-----------------------------|-----------------------------------------------------------------------------|--|
| | This work | Other work | |
| LDA | $\frac{1.60^{a}}{1.58^{b}}$ | $\begin{array}{c} 1.67 \ [12] \\ 1.58 \ [236] \\ 1.85 \ [237] \end{array}$ | |
| GGA | 1.66^{a} | $\begin{array}{c} 1.53 \ [237] \\ 1.52 \ [238] \\ 1.91 \ [239] \end{array}$ | |

Table 7.2: Formation energy for neutral V_{Cd} as calculated in this work with comparison to equivalent values obtained by others. No U potential was used in the calculation of these values. ^{*a*}ABINIT

^bQUANTUM ESPRESSO (QE)

We also investigated the dependence of the V_{Cd} formation energy on the U potential applied to Cd-4d electrons within the DFT+U framework, shown in figure 7.2. For U >12 eV, it was not possible to relax the 64 atom supercell containing the defect below the tolerances. The magnitude of U necessary to correct the band gap to the experimental value (U = 27 eV), could therefore not be used. At U = 12 eV, the V_{Cd} formation energy increased by ~20%. Since the band gap could not be corrected, we opted to remove U from all calculations to ensure that the calculated formation energies are in closer agreement to the other works in the literature (table 7.2).



Figure 7.2: Formation energy of the neutral V_{Cd} in a 64 atom supercell of bulk CdTe as a function of local potential U on the 4d-Cd electrons within the DFT+U method.

7.5 Phase transitions of the ternary compounds

The phase in which the ternary alloys form depends on the ground-state structural preferences of the binary tellurides and the alloy concentration. CdTe, ZnTe, MnTe and MgTe can all crystallise in either the zinc-blende (ZB) phase (space group $F\bar{4}3m$), wurtzite (W) phase ($P6_3mc$) or the NiAs-type (NiAs) phase ($P6_3mmc$). The unit cell for each of these phases is shown schematically in the top row of figure 7.3.

CdTe and ZnTe are both most stable in the ZB structure. CdZnTe should therefore favour the ZB phase regardless of the Zn concentration. The situation is more complex when alloying with Mn or Mg because MgTe is experimentally reported to favour the wurtzite (W) phase ($P6_3mc$) [240] and MnTe the NiAs-type (NiAs) structure ($P6_3mmc$) [241]. Yang et al. [242] have shown from first principles that CdZnTe, as expected, is stable in ZB at all Zn concentrations and that $Cd_{1-x}Mg_x$ Te transitions into W at x = 0.80 and NiAs at x = 0.90 Mg. It is important to understand the phase transitions as this influences the likelihood of crystallisation in a particular phase depending on alloy composition. A change in phase will correspond to changes in structural and electrical properties, for example the binary tellurides in the NiAs structure all possess indirect band gaps. We calculated the most stable phase as a function of alloy concentrations corresponding to



Figure 7.3: Conventional crystal lattice or phase of a single unit cell for (a) the zinc-blende (ZB), (b) the wurtzite (W) and (c) the NiAs-type (NiAs) structures. Structures in the top row show atoms at the edges of the unit cell and bonded atoms in adjacent unit cells due to the PBC. Structures in the bottom row show only the atoms belonging completely to a single unit cell and correspond to the unit cells used in calculations. The Te atoms are gold, the Cd atoms magenta and Cd-Te bonds are represented by the grey bars. The size of the atoms corresponds to their ionic radius.

the phase transitions of CdMnTe have not yet been reported on.

The phase transitions were calculated using 8 atom supercells, which allowed alloy compositions of $\mathbf{x} = 0.0, 0.25, 0.5, 0.75$ and 1.0. Since no defects were introduced in these calculations, the use of smaller supercells was possible. At each concentration x, the ground-state total energy of the system was calculated for each alloy in the ZB, W and NiAs phases. The bottom row in figure 7.3 shows the number of atoms and their positions in the single unit cells used in the calculations for each phase. For the W and NiAs structures, $2\times1\times1$ supercells were required to obtain 8 atoms. The use of smaller supercells also meant a very high convergence of the total energy $(10^{-4}\% \text{ of } E_{conv}$ using equation 6.1, necessary due to small differences in energy between phases), could be achieved. An E_{cut} of 30 Ha and a $6\times6\times6$ k-grid were required to reach this convergence with the exception of the Cd_{1-x}Mn_xTe NiAs structures where a $9\times9\times7$ k-grid was needed. By calculating the difference in total energy, ΔE , of the W and NiAs structures in respect to the ZB structure, the phase transitions as a function of alloy concentration were examined - shown in figure 7.4.



Figure 7.4: Difference in total energy per 2 atoms for the studied ternary alloys of CdTe in the wurtzite (W) and NiAs-type (NiAs) structures with respect to the zinc-blende (ZB) structure as a function of the alloy composition x, where x is equal to (a) Zn, (b) Mg and (c) Mn. The intersect between the difference curve (blue for W or turquoise for NiAs) and the ZB ref (red horizontal line at y = 0) indicate the alloy composition at which a phase transition from ZB to the respective structure is predicted.

The phase stability of CdZnTe and CdMgTe observed from our calculations are in good agreement with Yang et al. [242]. Figure 7.4a shows that the CdZnTe alloy favours the ZB phase at all Zn concentrations. From figure 7.4b we see that $Cd_{1-x}Mg_x$ Te transitions from the ZB to W phase at x = 0.74 and from W to NiAs at x = 0.90. Although, experimentally, MgTe is usually observed in the wurtzite structure, theoretically the NiAs structure is predicted to be its true thermodynamic ground-state [242]. Indeed, in an experiment at relatively low pressures, a W to NiAs transition for MgTe has been observed [243], supporting theory. It is suggested that the W structure is possibly a high-temperature metastable phase. In the case of $Cd_{1-x}Mn_x$ Te, figure 7.4c reveals that the alloy undergoes a phase transition from the ZB to NiAs structure at x = 0.56. A phase transition from ZB to W structure is calculated at x = 0.63, however, at this composition the NiAs structure is already more stable, and it is therefore less likely to be observed. The NiAs phase is significantly more energetically favourable than ZB or W for MnTe.

Buried wurtzite phases have been observed in the lattice of an otherwise zinc-blende structure of CdTe and may be responsible for a degradation of the electrical properties [244]. Given the small ΔE (figure 7.4) between the ZB and W phases at all compositions for each alloy, it is possible that buried wurtzite phases may occur in any of the alloyed compounds during crystal growth. For the CdMnTe alloy, the calculations suggest that buried NiAs phases are also possible, increasing the overall likelihood of crystallisation in the hexagonal structure. This is in agreement with experiment where CdMnTe shows the greatest tendency to crystallise in the hexagonal structure and has the highest bondionicity of the three alloys [207]. Buried phase transitions, if associated with a reduction in electrical properties such a poorer carrier lifetimes, will pose challenges in the growth of homogeneous crystals for high performance radiation detection. Using X-ray diffraction, the co-existence of ZB, W and NiAs phases has been confirmed in $Zn_{1-x}Mn_xTe$ at x > 0.8[245]. Our theoretical results suggest this co-existence is also likely in $Cd_{1-x}Mn_xTe$.

7.6 $Cd_{1-x}Zn_xTe$ supercell calculations

7.6.1 Physical properties

Figure 7.5a shows the average lattice constant for $Cd_{1-x}Zn_xTe$. Zn concentrations, x, ranging from 0 to 1 in steps of ~0.1 were used in addition to concentrations of x = 0.03 and x = 0.06 to include the smaller alloy compositions of interest in CdMnTe and CdMgTe radiation detectors. A complete range of alloy content using a relatively small step size meant the relationship of the calculated parameter between the two binary tellurides could be observed accurately. The change in lattice constant with Zn was observed to obey Vegard's law [246] and is therefore linear. Different positions of the Zn atoms had little effect on the relaxed lattice parameter. The decrease in the lattice parameter is due to decreasing bond lengths between the cation and Te atoms, as revealed by figure 7.5b.

The direct band gap at the gamma point in the BZ was calculated at each Zn concentration using one of the relaxed supercell runs, shown in figure 7.6. The relationship between the band gap and alloy concentration, x, can be represented by the polynomial,

$$E_q(x) = (1-x)E_q^{\text{CdTe}} + xE_q^{\text{ZnTe}} + bx(1-x)$$
(7.3)

where E_g^{CdTe} and E_g^{ZnTe} are the band gaps of CdTe and ZnTe respectively and b is the quadratic bowing parameter. The magnitude of the curvature away from a linear relationship is described by the bowing parameter. The fit of equation 7.3 to the calculated band gaps is shown in figure 7.6. We observe a downward bowing which is in agreement with experiment [247] and other *ab initio* works [248]. The bowing magnitude of b = 0.36 is an underestimate due to the DFT band gap problem (see section 2.5.5), with its true value at ~0.65 [247]. The impact of downward bowing means a higher Zn content is needed to achieve the ideal band gap for low resistivity CdZnTe.

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Figure 7.5: (a) Average lattice constant (from the three dimensions of the supercell) of $Cd_{1-x}Zn_x$ Te as a function of Zn concentration x for the unit cell. Each black marker represents a separate supercell calculation with randomised positions of the Zn atoms on the cation sub-lattice. The green curve is the average from all of the separate calculations. (b) Average bond length between atom pair. Each blue and red marker represents a separate supercell calculation. The horizontal blue and red lines indicate the respective bond length in the host binary telluride, which corresponds to the ideal strain-free value.



Figure 7.6: Band gap energy of $Cd_{1-x}Zn_xTe$ as a function of alloy concentration x.

7.6.2 V_{Cd} formation energy

The formation energy of the cadmium vacancy as a function of Zn content obtained from each of the 10 random alloy compositions of the CdZnTe supercell calculations are shown in figure 7.7. The average V_{Cd} formation energy calculated shows a downwards trend as the Zn concentration rises, before slightly increasing from x = 0.9 until the binary telluride ZnTe is reached. Note that at x = 1.0 the defect is in fact a Zn vacancy. The decreasing formation energy means formation of the V_{Cd} becomes more favourable as the Zn content increases. This is in agreement with the findings from *ab initio* calculations of CdZnTe performed by Carvalho et al. [12], and explains the trend towards p-type conductivity in CdZnTe since the V_{Cd} acts as an acceptor. The relationship is thought to deviate from linearity because of frozen-in stress fields introduced from the Zn-Te and Cd-Te bond lengths being above and below their strain-free values respectively (figure 7.5b) [12]. The energy necessary to form the defect is affected in the direct neighbourhood of the stress fields.



Figure 7.7: Formation energy of V_{Cd} defect in Te-rich $Cd_{1-x}Zn_xTe$ as a function of alloy concentration x. Each black marker represents a separate supercell calculation with random positions of the Zn atoms on the cation sub-lattice.

The V_{Cd} formation energy obtained from the 10 different random alloy compositions varies from 0.05 eV to 0.3 eV (depending on the Zn concentration). The variability of the formation energy with different Zn positions is largest when the number of possible arrangements of Zn and Cd on the cation sub-lattice is greatest, this corresponds to x = 0.5. To investigate the dependency of the V_{Cd} formation energy with alloy composition further, we performed a total of 30 calculations of the $Cd_{0.5}Zn_{0.5}Te$ alloy with random Zn positions. Additionally, we performed calculations of the x = 0.5 alloy with controlled positions of the Zn atoms relative to the V_{Cd} , these were: (NN) where the Zn atoms occupy all the nearest-neighbour sites, (FN) where the Zn atoms occupy the furthest possible neighbouring sites and (AN) where the Zn and Cd atoms are alternating neighbours i.e. one Zn atom, one Cd atom, etc. The correlation between the V_{Cd} formation energy with a number of different physical parameters obtained from each of these calculations is shown in figure 7.8.

From figure 7.8a, we see that the V_{Cd} formation energy is not simply due to the changes in energy from the different configurations of the bulk alloy structures. From figures 7.8a-b we also observe that the grouping of Zn atoms on NN sites and FN sites is less energetically favoured compared to a more mixed distribution (AN) of the Zn and Cd atoms. This suggests that the Zn atoms are less likely to group together in the dilute alloy and that V_{Cd} vacancies will avoid proximity to only Zn atoms.

No clear correlation between the defect formation energy and the Zn-Te or Cd-Te bond lengths was found (figures 7.8c-d). The tetrahedral geometry of the V_{Cd} and its four nearest neighbour Te atoms shows the strongest correlation (R = 0.93) with defect formation energy (figure 7.8e). We quantified this geometry by calculating the average length of the four dangling bonds left by the V_{Cd} to the Te atoms, which we define as the V_{Cd} -Te bond length. The positive correlation indicates that alloy configurations with higher V_{Cd} formation energies are associated with a larger V_{Cd} -Te bond length. This is likely linked to the volume of the supercell containing the defect (figure 7.8f) and the change in volume between the supercell with and without the defect (figure 7.8g). This implies that the V_{Cd} formation energy is dependent on the volume/lattice constant of the alloy configuration - with the formation of the defect becoming more favourable as the lattice constant decreases i.e. with compression. This also explains the general downwards trend of the V_{Cd} formation energy (figure 7.7) with Zn content as the average lattice constant is decreasing.

We also performed 30 calculations of random Zn positions in the $Cd_{0.5}Zn_{0.5}Te$ alloy without allowing the volume or atomic positions to relax. In this case, the standard deviation of the calculated V_{Cd} formation energies was 0.01 eV compared with 0.09 eV when the alloys were structurally relaxed (figure 7.8h). This suggests that the variability of the formation energy is less dependent on the interactions of the Zn atoms with the host lattice and defect, and more dependent on the strain the Zn atoms exert on the supercell volume. Which Zn positions in the alloy result in small or large changes in volume is less clear, as the controlled Zn positions NN, FN and AN did not explain the changes in volume or formation energy.



Figure 7.8: (a)-(g) Correlation plots between the formation energy for the V_{Cd} defect and different properties as obtained from 30 different calculations of the $Cd_{0.5}Zn_{0.5}Te$ 64-atom supercell structure with randomised Zn positions. The R-value for each relationship was fit to the red markers only. The blue markers correspond to controlled Zn positions where Zn atoms where placed at Next-nearest neighbour (NN) sites, furthest neighbours (FN) sites, or alternating between Cd and Zn neighbours (AN) to the position of the cadmium vacancy. (h) Gaussian function fit to distribution of 30 $Cd_{0.5}Zn_{0.5}Te$ formation energies obtained when supercell was relaxed versus when not relaxed.
7.7 $Cd_{1-x}(Mn/Mg)_x$ Te supercell calculations

7.7.1 Physical properties

Figure 7.9 shows the lattice constant and bond lengths as a function of alloy concentration for both CdMgTe and CdMnTe. Structural relaxation below the stress tolerances of these alloys, in particular for CdMnTe, was more difficult. This is likely linked to their greater tendency to crystallise in the W or NiAs phase, making it more difficult for the structure to minimise to its ground-state energy in the ZB phase. As a result, the number of supercell calculations with random alloy positions completed per concentration is less than 10.

When alloying with Mg, we observe only a small change in lattice constant from 6.41 \mathring{A} to 6.37 \mathring{A} between CdTe and MgTe respectively (figure 7.9a). The lattice constant decreases linearly with Mg content following Vegard's law until x = 0.9, at which point the gradient suddenly becomes steeper. This corresponds with the concentration at which we determined that CdMgTe undergoes a phase transition from W into NiAs. Similarly, for CdMnTe, a change in slope for the same relationship (figure 7.9c) is observed at x > 0.5 which corresponds to its phase transition into NiAs at x = 0.56. At alloy concentrations where the structures favour the NiAs phase, for which the CdMnTe ground-state energy is significantly lower than in the other phases (figure 7.4c), the relaxation algorithm struggles to minimise the energy in the ZB phase, resulting in a deviation of the lattice constant from Vegard's law. Other theoretical studies of Cd_{1-x}Mn_xTe [249,250] did not report such a strong deviation from Vegard's law, though it should be noted that larger x intervals of 0.25 were used (compared with our smaller steps of x = 0.1). In [250], the lattice constant at x = 0.75 was also observed to be below the linear relationship and the authors consequently report a downward bowing of the lattice constant.

Table 7.3 shows the total magnetic moment, the magnetic moment over all interstitial sites and the average magnetic moment on each atomic species for $Cd_{1-x}Mn_xTe$. Partially occupied Mn-3d states produce the permanent magnetic moments on the Mn atoms, which have a free space charge of 5 μ_B [233]. From our calculations we observe that the magnetic moments of the Mn atoms in CdTe are reduced to $\sim 4 \mu_B$ and produce small local moments on the otherwise non-magnetic Cd and Te atoms at all compositions. The total magnetic moment per Mn atom is however equal to 5 μ_B up to x = 0.5, after which it begins to decrease as the alloy approaches MnTe (likely due to a decrease of the Te-site moments). These findings are in agreement with other theoretical studies of ferromagnetic CdMnTe [233, 250–252]. The reduction of the Mn magnetic moment from its free space value has

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Figure 7.9: Average lattice constant and bond lengths as a function of alloy concentration x for (a-b) $Cd_{1-x}Mg_xTe$ and (c-d) $Cd_{1-x}Mn_xTe$ alloys. The markers represent a separate supercell calculation with random positions of the alloy atom on the cation sub-lattice. The horizontal blue and red lines in the bond length plots indicate the respective bond length in the host binary telluride, which corresponds to the ideal strain-free value.

been shown to be due to strong hybridisation between the Mn-d and Te-p electrons [233]. Te and Cd atoms at nearest-neighbour (NN) sites to the Mn atoms have moments above the average. For Cd_{0.9}Mn_{0.1}Te, the local moments on the NN Cd and Te sites to the Mn atoms are 0.012 μ_B and 0.027 μ_B compared with the average magnitudes of 0.009 μ_B and 0.013 μ_B respectively. The average magnetic moment and NN moment converge at x = 0.6 for both the Cd and Te sites.

The electronic band structure has been calculated using the relaxed supercell geometries, with both CdMgTe and CdMnTe in the ZB phase showing a direct band gap at all alloy concentrations. Figure 7.10 shows the direct band gap energy as a function of alloy

| Mn concentration x | Cd | Mn | Te | Interstitial | Total per Mn atom |
|----------------------|--------|--------|--------|--------------|-------------------|
| 0.03125 | 0.0032 | 3.9508 | 0.0046 | 0.8021 | 4.9999 |
| 0.0625 | 0.0069 | 3.9411 | 0.0094 | 1.6082 | 4.9999 |
| 0.09375 | 0.0092 | 3.9775 | 0.0132 | 2.3769 | 5.0000 |
| 0.3125 | 0.0310 | 4.0171 | 0.0408 | 7.8419 | 5.0000 |
| 0.5 | 0.0479 | 4.0518 | 0.0607 | 12.4573 | 4.9999 |
| 0.6875 | 0.0612 | 3.9933 | 0.0560 | 15.7432 | 4.8182 |
| 0.90625 | 0.0718 | 3.9406 | 0.0480 | 19.0197 | 4.6569 |
| 1.0 | 0 | 3.8335 | 0.0289 | 18.8171 | 4.4505 |

Table 7.3: Magnetic moments on the different atomic sites as a function of Mn concentration in CdMnTe. The moments are given in units of Bohr magneton (μ_B). The magnetic moment on the atomic sites is the average value from all the atoms of that species in the structure. The interstitial moment is a total of all interstitial sites in the crystal. The total magnetic moment for the different alloys includes the moments from all atomic and interstitial sites and is normalised by the number of Mn atoms in the alloy.

concentration for CdMgTe. The relationship is mostly linear with only a small degree of downwards bowing (b = 0.20), revealed by the fit to equation 7.3. The smaller bowing parameter in CdMgTe compared with CdZnTe means that the required alloy content to achieve the optimal band gap for radiation detection is further reduced, in addition to the advantage of the already larger band gap of MgTe than ZnTe. Overall, this results in a greater rate of increase of the band gap when adding Mg (~0.015 eV/Mn%) compared to when alloying with Zn (~0.003 eV/Zn%). Experimental measurements of the band gap of Cd_{1-x}Mg_xTe with Mg content [253] suggest either a linear function or very slight band bowing and are therefore consistent with our theoretical result (figure 7.10).

In spin-polarized calculations, two separate band structures exist for the spin-up and spindown configurations. This implies that two different band gaps are possible for CdMnTe, as shown in figure 7.11. A fit to the data with equation 7.3 was performed for the spin-up case but not to the spin-down case because the data does not show a quadratic relationship. The spin-down band gap increases monotonically with Mn content, whereas the spin-up band gap shows very significant downwards bowing to the extent that the gap size decreases up to $x \approx 0.4$. For the latter gap, this is not the expected behaviour as the CdMnTe band gap is known from experimental measurements [254] to increase with Mn concentration. In another first-principles study of CdMnTe [249], the authors found both the spin-up and spin-down band gaps (where the spin-down was also the larger gap as in our calculations) to increase with Mn content with slight downwards and upwards bowing respectively. In their calculations, the CdTe band gap was corrected to its experimental value within the DFT+U framework by adding U to both d- and p-electrons. At the time of investigation, U could only be added to the d-electrons in ABINIT. We therefore could not attempt to



Figure 7.10: Band gap energy of $Cd_{1-x}Mg_xTe$ as a function of alloy concentration x.



Figure 7.11: Band gap energy of $Cd_{1-x}Mn_x$ Te as a function of alloy concentration x for the spin-up (a) and spin-down (b) case.

test if the band gap relation with Mn required correction of the SIE.

7.7.2 V_{Cd} formation energy

The formation energies for the V_{Cd} in $Cd_{1-x}Mg_xTe$ and in $Cd_{1-x}Mn_xTe$ as a function of x are shown in figure 7.12. Note that fewer than 10 calculations were obtained per concentration due to the relaxation threshold not being met. A larger number of samples per concentration for these alloys proved less important than for CdZnTe due to the greater absolute change in defect formation energy with x, meaning variations from the random positions of the alloy atoms was less significant.



Figure 7.12: Formation energy of V_{Cd} defect in (a) $Cd_{1-x}Mg_xTe$ and (b) $Cd_{1-x}Mn_xTe$ as a function of alloy concentration x. Each black marker represents a separate supercell calculation with randomised positions of the alloy atoms on the cation sub-lattice.

When alloying CdTe with Mg, we find that the V_{Cd} formation energy increases linearly with Mg content at a rate of ~0.01 eV/Mg%. This implies that the addition of Mg should reduce the p-type conductivity and improve resistivity. A higher barrier for V_{Cd} formation in CdMgTe is also consistent with experimental observations that showed orders of magnitude lower concentrations of Te-inclusions than in CdZnTe and CdMnTe [54], where the formation of the V_{Cd} becomes more likely with the addition of the respective alloy.

The increase in defect formation energy is thought to be linked to an increase in ionic bonds, which tend to be more difficult to break than covalent bonds. Mg has the lowest electronegativity of the alloy atoms considered, meaning the difference in electronegativity between Mg and the Te is greatest, and this is known to result in larger proportions of ionic bonding. In addition to this, since the lattice constant and bond length between CdTe and MgTe are very similar (figure 7.9a-b), a significant decrease in volume (which we have shown reduces the formation energy of V_{Cd}) does not occur. This is also believed to be the reason for the linear relationship, because frozen-in stress fields due to bond lengths deviating from their strain-free value are minimised. The variation in defect formation energy from the few random Mg configurations obtained at x = 0.5, shows the same relationship as observed for CdZnTe - where greater compression of the volume is linked with a lower formation energy of the V_{Cd} .

The defect formation energies in the $Cd_{1-x}Mn_xTe$ system were determined using nonmagnetic calculations. This approach was taken because in the spin-polarized ferromagnetic calculations, we could not determine how to eliminate the energies introduced by the magnetic moments on the Cd, Te and interstitial sites in order to obtain only the energy associated with the formation of the defect. Since the moments should cancel between the bulk and defect-containing structures, the non-magnetic calculations were assumed to provide a good estimate when calculating the defect formation energy. From figure 7.12b we see that the V_{Cd} formation energy decreases with Mn content. This decrease is very drastic when Mn is first introduced at concentrations from x = 0 - 0.0625, before stabilising and decreasing more gradually as the binary telluride MnTe is approached. A negative formation energy implies that large numbers of this defect will form spontaneously under equilibrium conditions during crystal growth. Our results indicate that this occurs at Mn concentrations greater than 10%. The lower barrier to V_{Cd} formation in CdMnTe, along with the higher V_{Cd} formation energy in CdMgTe, could explain the comparatively greater Te-inclusion sizes and concentration observed in as-grown CdMnTe crystals from IR microscope images [255].

The significant decrease in volume with increasing Mn content (figure 7.9c) explains, in part, the reduction of the V_{Cd} formation energy. The stresses induced from the Mn-Te bond lengths in $Cd_{1-x}Mn_x$ Te that are larger than their strain free value in MnTe (figure 7.9d), will contribute to the divergence from linearity and are possibly pushing the formation energy further down. The drop in formation energy at $x \approx 0.6$ could correspond with the sudden decrease in lattice constant of the CdMnTe structure due to its phase transition from ZB into NiAs-type. However, the reason behind the significant rapid decrease in V_{Cd} formation energy at very low Mn concentrations, is not clear.

7.8 Summary

Alloying CdTe with Mn or Mg instead of Zn has the potential to allow for more compositionally homogeneous crystal growth and lower production costs. However, little is currently known about the behaviour of the native defects in response to Mn and Mg alloy atoms. In this chapter, we calculated from first-principles, the physical properties of $Cd_{1-x}A_x$ Te (A = Zn, Mn, Mg) and determined the formation energy of the cadmium vacancy defect in each of these compounds as a function of the alloy concentration x.

We showed that $Cd_{1-x}Mn_x$ Te undergoes a transition from ZB to NiAs-type at x = 0.56. CdZnTe showed no transitions and CdMgTe transitioned from ZB to W at x = 0.74 and from W to NiAs at x = 0.90. Our findings help explain the greater tendency observed in CdMnTe to crystallise in hexagonal phases. Furthermore, the phase transitions appeared to cause a deviation from Vegard's law for the lattice constant in ZB alloys approaching the respective binary telluride MgTe or MnTe.

The supercell method with 64 atoms was used to calculate the V_{Cd} formation energies. We found that non-cubic supercells do not eliminate the artificial interaction between defects in the PBC linearly, and should therefore be avoided in the calculations of defect formation energies. The three alloy atoms when mixed with CdTe all have significantly different impacts on the V_{Cd} formation energy. Our results suggest different primary factors behind the change in V_{Cd} formation energy with alloy concentration for each ternary compound. We showed a positive correlation between the volume and V_{Cd} formation energy, which explains the decreasing formation energy with increasing Zn content. This correlation could not explain the larger absolute changes in the V_{Cd} formation energy with Mn or Mg content. We believe that the V_{Cd} formation energy increases in CdMgTe due to more ionic bonding between Mg-Te than Cd-Te, and that minimal frozen-in stress fields due to a similar lattice constant of MgTe and CdTe are responsible for a linear relationship. For $Cd_{1-x}Mn_xTe$, we calculated negative V_{Cd} formation energies at x > 10%, which could help explain the greater concentrations of Te-inclusions observed in as-grown CdMnTe crystals. The significant decrease in formation energy could not however be explained by the change in volume alone when adding Mn.

From our results, CdMgTe shows promise as a potential CdTe-based alloy for radiation detection. The increasing V_{Cd} formation energy should reduce p-type conductivity and the large band gap of MgTe combined with a low bowing parameter mean a smaller Mg content is needed than Zn content to achieve room temperature operation. CdMnTe may pose greater challenges due to a higher tendency to crystallise in the NiAs phase and low V_{Cd} formation energies. However, due to the difficulty of performing calculations with the magnetic Mn atoms, the band gap and V_{Cd} formation energy in CdMnTe require further investigation. Furthermore, for a more complete picture, the formation energies of the Te_{Cd} defect in these alloys also need to be calculated. These future investigations are discussed in more detail in section 8.2.

Chapter 8

Summary, conclusions and future work

8.1 Summary and conclusions

In this thesis we have investigated CdTe-based radiation detectors using experimental, Monte Carlo and *ab initio* methods. The high Z number and wide band gap of CdTe make it an attractive semiconductor for the detection of hard X-rays (> 20 keV) and room temperature operation. This has applications in several fields such as nuclear medicine, X-ray astronomy and the probing of materials by imaging at high-flux facilities like synchrotrons and XFELs. To fully take advantage of the demands in these applications, the performance in CdTe-based detectors must be preserved in designs with small pixels to achieve spatial resolution requirements or greater sensor thicknesses to achieve good efficiencies at high photon energies.

From experiment, we measured the spectral performance of a novel high-flux capable CdZnTe (HF-CdZnTe) detector compared with a gold-standard CdTe detector covering the soft to hard X-ray energy regime (6-140 kev). We calculated the spectral resolution of both isolated and charge sharing events and were able to quantify the factors such as charge loss and sensor fluorescence influencing their energy response. We demonstrated that by using a fully spectroscopic Monte Carlo (MC) detector model, the rate of charge sharing between pixels could be predicted with good accuracy. By comparing experimental and MC simulated data, we were able to estimate a number of useful quantities such as the size of the electron charge clouds, the strength of the electric field and the Zn concentration in the HF-CdZnTe material. By performing density functional theory (DFT) calculations, we

studied alloys of CdTe that are of interest for radiation detection from first-principles (*ab initio*). We calculated the formation energy of the cadmium vacancy (V_{Cd}) in Cd_{1-x}Zn_xTe, Cd_{1-x}Mn_xTe and Cd_{1-x}Mg_xTe as a function of alloy concentration x as well as the physical properties of the different alloy compositions.

In chapter 3 we calibrated the 2 mm thick HF-CdZnTe detector hybridised with the HEXITEC ASIC using X-rays and gamma-rays emitted from radioisotope sources. This included a per-pixel energy calibration, determination of a global noise threshold and a faulty pixel map. The event reconstruction algorithm used throughout the thesis to produce spectra and images from raw experimental and simulated data was also described. We found that for non-charge sharing events the HF-CdZnTe detector had an average pixel spectral performance (0.85 ± 0.16 keV at 59.5 keV) close to that of the gold-standard 1 mm thick CdTe detector (0.81 ± 0.20 keV). From the energy resolution and photon counting performance of each individual pixel, we were able to assess the uniformity of the crystals. The HF-CdZnTe detector did not appear to exhibit any extended crystalline defects, although scratches to the electrode influenced uniformity. In the CdTe detector, bulk defects which reduced the energy resolution and counting performance were observed. In both detectors we observed pixels in which the spectral performance degraded with increasing photon energy, which we attributed to the presence of Te-inclusions.

In chapter 4 we described in detail the development of the Monte Carlo Cd(Zn)Te detector model to simulate the spectroscopic response to X-rays. The purpose of the model was to help explain the response of the Cd(Zn)Te detectors, particularly the charge sharing effect, and predict performance in future detector designs. We obtained good agreement between the experimentally measured radioisotope spectra and simulated ones. By comparing the size of the sensor fluorescence peaks in HF-CdZnTe detector response to those in simulated responses of $Cd_{1-x}Zn_xTe$ detectors with different Zn fractions x, we were able to estimate the Zn content in the HF-CdZnTe material at x = 0.10 - 0.15.

In chapter 5 we investigated the charge sharing effect in the pixelated detectors using measurements and MC simulated detector responses. The energy resolutions of charge sharing events with multiplicity m = 2 and m = 4 were calculated and shown to be significantly worse than m = 1 events due to charge losses associated with the pixel gaps. The smaller gaps of 25 µm reduced charge loss in the HF-CdZnTe detector such that for m = 2 events an energy resolution of 1.63 ± 0.08 keV at 59.5 keV was achieved, from a best possible value of 1.30 ± 0.11 keV keV.

By calculating the charge loss as a function of photopeak energy for charge sharing events,

we showed a positive correlation between charge loss to the pixel gaps and photon interaction depth. As a result, we argued that improved hole transport (as in the case of the HF-CdZnTe material) will reduce incomplete charge collection in the pixel gaps and improve the energy resolution of shared events, but discussed that a better detector comparison was necessary to confirm this conclusion [144]. In a recent study, the authors compared a high-flux HF-CdZnTe detector with a low-flux (i.e. standard) LF-CdZnTe detector directly and showed that the charge losses in the gaps are in fact not related to the transport properties of the carriers [256]. Instead, the improved spectral performance of charge sharing events in the HF-CdZnTe detector over standard CdZnTe is due to less distorted electric field profiles near the inter-pixel gaps. By comparing experimental charge sharing rates with simulated ones, we showed that the electric field strength in the HF-CdZnTe is not degraded from its applied value (like in the CdTe detector) and likely uniform. In addition to its use for high-flux measurements, the HF-CdZnTe material offers improved energy resolutions for charge sharing events due to a better electric field profile.

The MC detector model was able to accurately predict the rates of individual event types of multiplicity m = 1 - 4. From this agreement, we showed that the electron charge cloud arriving at the anode in the HF-CdZnTe detector has a relatively fixed average diameter of ~108 µm for X-rays from 1 - 120 keV. Using simulation we could therefore show that, in the absence of a noise threshold, the majority of events (even for soft Xrays) undergo charge sharing. We also predicted charge sharing rates in very small pixel designs in consideration for high-flux applications. Although K-shell fluorescence from the Cd and Te atoms was found to significantly increase charge sharing rates, fluorescence shared events showed better energy resolution. The MC model was shown to have the capability to predict the distribution of charge in shared events like diagonal bipixels and tripixels, and can therefore assist in the development of current charge loss correction techniques [42,46].

In chapter 6 we performed DFT calculations of the relatively simple bulk CdTe system on which the more complex alloys we studied are built. By testing a range of pseudopotentials, we determined that using the local density approximation (LDA) with the Projector augmented-wave (PAW) method provided the most computationally efficient and accurate description of CdTe in our DFT calculations. The DFT+U approach was tested as a low computational cost approach to correct the band gap underestimation, but it was found that this could not be done without pushing some electron states to non-physical energies at which relaxation of the more complex alloys was not possible. We also calculated from first-principles the temperature dependency of the CdTe band gap by considering the effects of the lattice expansion and electron-phonon interactions.

In chapter 7 we used DFT supercell structures to investigate the effect alloying CdTe with Zn, Mn and Mg has on the crystal's physical properties and formation energy of the native cadmium vacancy (V_{Cd}) defect. We found that the V_{Cd} formation energy behaves very differently when introducing Mn or Mg compared to Zn. The greater barrier for the formation of the V_{Cd} when adding Mg, combined with a minimal band gap bowing parameter, are positive first signs for the application of CdMgTe in radiation detectors. Although we were able to show a decreasing V_{Cd} formation energy when alloying with Mn, which could explain the high concentrations of Te-inclusions observed in as-grown CdMnTe crystals, simulation challenges related to CdMnTe being a dilute magnetic semiconductor meant we could not yet draw more confident conclusions. We calculated that $Cd_{1-x}Mg_xTe$ and $Cd_{1-x}Mn_xTe$ undergo phase transitions from a zinc-blende structure to a hexagonal one at x = 0.74 and x = 0.56 respectively. This is a further complication of these potential alloys in comparison to CdZnTe, which does not undergo any theoretical phase transitions.

Using experiment and Monte Carlo simulations we have been able to give some insight into the performance and issue of charge sharing in Cd(Zn)Te detectors, including for a novel high-flux capable HF-CdZnTe material. Using *ab initio* methods, we were able to investigate some of the physical properties related to detector performance in Cd_{1-x}Mn_xTe and Cd_{1-x}Mg_xTe alloys, which are in early stages of detector development.

8.2 Future work

Given that common thicknesses of CdZnTe detectors can be sensitive up to 1 MeV photons, it would be of interest to repeat many of the experimental and simulated calculations performed at greater incoming photon energies. Radioistoposes such as ⁶⁷Ga, ¹³¹I and ¹³⁷Cs could be used to generate line energies at 185, 365, 662 keV respectively. The Monte Carlo detector model could be tested at these higher energies, including comparisons of charge sharing rates and the size of multi-pixel events observed, as well as the influence of Compton scattering on the detector response, which will be more pronounced at these energies. The correlation between charge loss in shared events with depth of interaction could also be investigated more rigorously at these energies, in particular the levelling-off with energy that we observed. This correlation could also be tested by using a dual polarity ASIC which can discriminate events based on their interaction depth, or by collimated diagonal illumination such that depending on the interaction position along the abscissa, the depth is known. Charge sharing events of different interaction depth could then be compared at the same line energy. This should reveal a better energy resolution for shared events with interactions near the cathode, and could give some more insights into the electric field profile.

The Monte Carlo detector model was developed in Python from the ground up where each component (photon generation, photon attenuation, charge transport) is modular and can be run separately. It is therefore relatively straightforward to make changes to the model. A number of assumptions and simplifications were made particularly to the charge transport stage of the model. To improve the accuracy of charge sharing predictions and possibly even simulate charge loss in the inter-pixel regions, 3D electric field and weighting potential maps output from third party software could be used. This would require using numerical solutions to the Schockley-Ramo theorem as opposed to the Hecht equation. Instead of computing the electron charge cloud as a whole, the path and charge induction of each electron and hole carrier could be computed. Trapping and de-trapping probabilities of the carriers during drift could also be applied. Such an implementation will come at significant computational cost and may require development of the charge transport component in a low-level programming language instead. However, such additions would make the model more widely applicable to different detector designs (e.g. geometry, read out structure).

In regards to the DFT calculations, future work could expand on a number of areas. The band gap temperature dependence for alloys of CdTe for which experimental results are not available, such as CdMgTe, could be calculated. This could be done using the method presented for CdTe, although may only be computationally feasible using small supercells, at which low alloying concentrations can not be achieved. The calculations of the band gap and V_{Cd} formation energy in $Cd_{1-x}Mn_xTe$ also require more investigation to determine the dependency of the quantities on the magnetisation. Calculations performed on the alloys could be expanded to $Cd_{1-x}Zn_xTe_{1-y}Se_y$ which is receiving attention as a potential successor to CdZnTe due to a higher yield of high-quality material [55]. Preliminary work was done to calculate the formation energy of the Te-antisite Te_{Cd} to obtain a more complete picture of the defect concentrations expected in the alloys, especially as Te_{Cd} can act to compensate the V_{Cd} as a donor. This can be expanded to the lesser common defects on anion sites, interstitial positions and even the native complex defects. By calculating the ionisation levels, whether the defects act as acceptors or donors and are shallow or deep states, can also be determined from first-principles.

Appendix A

Noise saturated frames in the CdTe detector

Analysis of data collected with the CdTe detector when biased to -500 V revealed that during some acquisitions, multiple frames were completely saturated with noise - i.e. the majority of pixels in a frame recorded a count above the noise threshold. Figure A.1a shows the number of pixels which recorded an event above a noise threshold of 3 keV for each frame of a one hour dark acquisition. Figure A.1b shows the average energy in each of those frames. The noise saturated frames are clearly visible, with many recording above 6000 counts/frame (> 93% frame occupancy).

Noise saturated frames were observed to occur both during dark acquisitions and when a source was used. The percentage of frames in an observation which were saturated by noise was also found to vary significantly between each observation in which the noisy frames appeared. Details on some of the acquisitions which showed noise saturated frames are listed in table A.1. It could not be determined why these noise frames occurred during some observations but not during others, nor what influenced the frequency at which the noise frames occurred when they did. Furthermore, the average energy of the noise in saturated frames also varied between acquisitions (table A.1). By inspecting individual frames, the noise was observed to always follow a particular sequence across frames (related to how it was read out by the rolling readout) when saturation occurred.

The readout of noise across frames when saturation occurred is shown in figure A.2. Single frame images before, during and after a noise saturation event are shown sequentially in panels (a) to (e). Panel (f) shows the small section of figure A.1 relating to the frames shown in figures A.2a-e. The pixels recording counts in the top left corner and along



Figure A.1: Number of counts per frame (a) and average energy of the noise counts within the frame (b) for each frame of the dark acquisition taken on the 30/01/2019 with the CdTe detector.

| Source | Acquisition date | Duration (s) | Proportion of noisy frames (%) | Mean energy of noise (keV) |
|---------------------|------------------|-----------------|-----------------------------------|-------------------------------|
| Dark | 12/12/2018 | 3600 | 6.75 | - |
| Dark | 30/01/2019 | 3600 | 0.25 | 3.95 |
| Dark | 05/02/2019 | 7200 | 57.73 | - |
| $^{109}\mathrm{Cd}$ | 15/05/2019 | 1800 | 0.06 | 5.88 |
| $^{109}\mathrm{Cd}$ | 16/05/2019 | 1800 | 10.17 | 3.76 |
| $^{241}\mathrm{Am}$ | 16/05/2019 | 3600 | 0.15 | 3.79 |

Table A.1: A list of observations with the CdTe detector in which the noisy frames were observed. Details on the magnitude of the noise is shown. For two of the observations, the event list files were no longer available in order to calculate the mean energy of the noise.

the bottom edge in each frame are hot pixels, likely associated with a crystal defect or physical damage to the crystal at that location. The noise saturation events were observed to always begin at the top of the detector where the corner defect is located (panel (b) in figure A.2). The frame following this contains the most noise, often saturating completely from top to bottom with noise (panel (c)). Before the noise would completely disappear, noise is recorded in the bottom rows of a frame (panel (d)). The rolling readout moves from rows 0 to 80 (from bottom to top in the frame images). The sequence in which the noise is read out across frames therefore suggests that the noise saturation is linked with the corner defect hot pixels.



Figure A.2: (a)-(e) A sequence of single frames immediately before and after a noise event showing the location and energy of the noise counts recorded for the dark acquisition on the 30/01/2019 for the CdTe detector. (f) A snapshot of figure A.1a around the noise peak for which the sequence is shown. The noise threshold of 3 keV is applied to these frames.

Noise saturation frames were also observed in multiple Cd(Zn)Te detectors used with the HEXITEC system at RAL STFC (M.D. Wilson, personal communication, 2019). In total 10 of 17 detectors (including the one in this work) investigated showed severe noise saturation. In all cases that noise saturation frames were detected, a defect at either the detector edge or corner was present and similar movement of the noise originating from the defect as shown in figure A.2 was observed. When no defect in the form of hot pixels could be observed, noise saturation frames did not occur. In some cases reducing the bias voltage (from 500 to 300 V mm⁻¹) caused both the hot pixels and noise saturation frames to disappear. A possible explanation for the noise saturated frames is that large leakage currents from defect hot pixels increase the power consumption which in turn increases the leakage current across the whole detector.

As a result of this work identifying the noise saturation issue, the HEXITEC user interface software was updated by RAL STFC (M.D. Wilson, personal communication, 2021) to remove rows in a frame which recorded more than 40 counts and report to the user the total number of rows removed. The removal of noise was done by rows instead of frames to minimise the amount of data discarded. The bonding process of the detector to the ASIC has also been modified such that during bonding nothing touches the detector edges, reducing the likelihood of edge damage. The HF-CdZnTe detector was bonded after these changes and no noise saturation has been detected in this detector.

Appendix B

Generating the KKM_LDA PAW pseudopotential

Before the JTH_LDA PAW datasets from 2018 which are used in Chapters 6 and 7 were available, we used the 2016 versions [257]. Unfortunately, the Cd PAW dataset introduced a non-physical electron state, which we determined to originate from the Cd-5s orbital by inspecting the LDOS (figure B.1). By using the AtomPaw software and following the guidelines by Torrent & Holzwarth [258] on how to generate a PAW dataset, we removed the non-physical state by producing a new PAW dataset, referred to as KKM_LDA, based on the original.

Figure B.2 shows the partial wave, projector functions and logarithmic derivatives for each valence electron orbital for the Cd atom of the original PAW dataset. We only needed to modify the s-orbital inputs to the PAW dataset, and left the p- and d-orbitals the same as in the original. Specifically, the projector functions had to be reduced, which was done by increasing the reference energy for the second partial wave basis for the s-orbital electrons from 1 Ry to 3 Ry. The changes this had to the quantities of the PAW dataset are shown by the dotted lines in figure B.2.

The calculated band structure and total DOS (figure B.3) using the newly generated KKM_LDA PAW dataset reveal that the non-physical state from the Cd-5s electrons has been removed.



Figure B.1: Calculated total and LDOS for CdTe using the JTH_LDA 2016 PAW dataset. The Fermi energy has been set to 0 eV and is indicated by the grey dotted line.



Figure B.2: Partial waves (ϕ_i) , pseudized partial waves $(\tilde{\phi}_i)$, projector functions (ρ_i) and log derivatives for the Cd atom JTH_LDA 2016 PAW dataset. Each column of subplots corresponds to one of the angular momenta of the Cd valence electrons going $\ell = 0,1,2$ from left to right. The first two rows of subplots correspond to the first and second partial waves basis. The third row of subplots show the logarithmic derivative computed for the exact atomic problem against computation with the PAW dataset. The dotted lines in the first column ($\ell = 0$) of subplots are for the newly generated KKM_LDA PAW dataset.



Figure B.3: Band structure and total DOS for CdTe calculations when using the KKM_LDA PAW dataset.

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