A theoretical study of native acceptors in $CdGeAs_2$

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Abstract. Native acceptor centres in CdGeAs$_2$ are studied using atomistic simulation techniques for which a new set of interatomic potential parameters consisting of two- and three-body terms is developed. Crystal lattice constants, elastic and low- and high-frequency dielectric constants are well reproduced in this atomistic model. The calculated formation energies for vacancies, interstitials and antisites in this material suggest that the intrinsic disorder is dominated by antisites in the cation sublattice followed by the Schottky and Frenkel defects. The acceptor centre identified by Hall-effect measurements and EPR is found to be related to the delocalized hole shared by the four As neighbours bound to CdGe. For this centre, calculations yield a binding energy of 0.13 eV in an agreement with the experimental value of 0.15 eV obtained by the Hall-effect measurements. Furthermore calculations provide the magnitude of the lattice distortion introduced by this acceptor centre in CdGeAs$_2$ which can be used for the analysis of ENDOR experiments.

1. Introduction

Cadmium germanium arsenide (CdGeAs$_2$) is an important material due to its suitability for nonlinear optical applications in the infrared region since it has the highest nonlinear optical coefficient, 236 pm V^{-1}, known for a phase matchable compound semiconductor. Additionally, it has a wide transparency region extending across the infrared from 2.4 to 18 μm [1–3]. The availability of large single crystals [4] of CdGeAs$_2$ has led to renewed efforts to utilize this material for frequency doubling (i.e. for second harmonic generation) carbon dioxide laser emission lines from 9.3 to 10.6 μm. The transparency of these crystals [4], although superior to that of earlier crystals [1] is still limited by the photo-ionization of native acceptors.

Nominally undoped Bridgman grown single crystals of CdGeAs$_2$ are found to be p-type. Hall effect measurements [5, 6] on the best available crystals indicate the presence of a single acceptor with an activation energy of 0.15 eV. On the other hand, Brudni *et al* [7], Halliburton *et al* [8] and Smith *et al* [9] utilizing respectively radiation damage techniques, EPR and thermal admittance spectroscopy measurements observe that there can be at least two native acceptors present in as-grown CdGeAs$_2$. Smith *et al* [9] have found that there is a level with an activation energy of 0.11–0.13 eV in agreement with Hall measurement on the same samples, and a second deeper acceptor with an activation energy of 0.346 eV.

It is the goal of this work to determine theoretically which native defects might give rise to these two acceptor centres in $CdGeAs_2$.

Theory has so far focused on calculating intrinsic properties such as the band structure [10, 11] and has not considered the chemistry of defects in this material. In this paper, we perform such a task considering vacancies, interstitials and antisites in $CdGeAs_2$. We use atomistic simulation methods based on the shell model to describe the crystalline lattice of $CdGeAs_2$ and will calculate formation energies of native defects and binding energies of the acceptor centres. We note here that this approach has been very successful in yielding reliable defect energies in a wide variety of materials including sixfold- and fourfold-coordinated structures [12]. Recent applications of the shell model include structural relaxation around dopants in sapphire [13], high-pressure phase transition in GaN [14] and defect energetics in $ZnGeP_2$ [15].

2. Perfect lattice

In the present atomistic description of a crystal, the lattice is considered to consist of ions interacting via a combination of electrostatics and interatomic potentials, while polarization is included by means of the shell model [16]. The total energy of a crystal is then taken to be a sum of two- and three-body interactions in the lattice. The (two-body) pairwise interaction term consists of the long-range Coulombic part and the short-range repulsive part and is given by

$$E_{ij} = (Q_i Q_j / R_{ij}) + V_{SR}(R_{ij}) \qquad (1)$$

where Q are charges and R_{ij} is the separation between ions. $V_{SR}(R_{ij})$ represents the short-range interaction between ions and is given by an analytical expression of the Born–Mayer form:

$$V_{SR}(R_{ij}) = A_{ij} \exp(-R_{ij}/\rho_{ij}) \qquad (2)$$

where A and ρ are the parameters obtained generally by empirical fitting methods.

Three-body interaction terms in our model are represented by the Axilrod–Teller [17] potentials:

$$E_{ijk} = k_{ijk}(1 + 3\cos\theta_i \cos\theta_j \cos\theta_k)/R_i^3 R_j^3 R_k^3 \qquad (3)$$

where k_{ijk} is a coefficient, θ_i is the ith angle and R_i is the side of the triangle formed by ions i, j and k in the lattice.

To describe the polarizability, we employ the shell-model description of the lattice atoms. In the shell model, each atom consists of a core of charge X, and a shell of charge Y, such that the total charge is the sum of the core and shell charges. The polarization is then simulated by the displacement of a shell from a core, the two being connected by a harmonic spring with a force constant K.

$CdGeAs_2$ crystallizes in the chalcopyrite phase [18, 19] with a tetragonal symmetry group of $I\bar{4}2d$. Chalcopyrites can be constructed [20] by first considering a superlattice of the (cubic) zincblende phase with $c/a = 2$, replacing each half of the cations by Cd and Ge ions respectively and finally introducing a small distortion along the z-axis leading to $c/a = 1.889$. As shown in figure 1, each atom is tetrahedrally coordinated in the lattice; cadmium or germanium cations have four near-neighbour arsenic anions while arsenic anions have two cadmium and two germanium cations as near neighbours. In the lattice, cations occupy special positions labelled as a and b with no positional degrees of freedom, while anions are placed in the d positions given by the internal parameter, x. The value of x varies
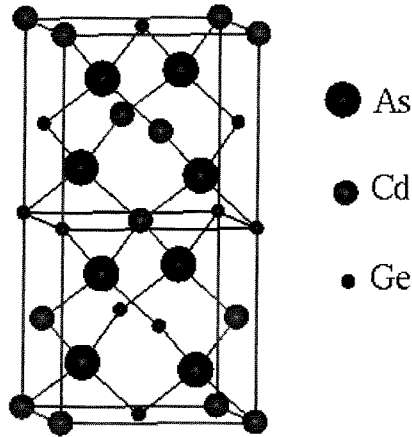
Figure 1. Crystal structure of CdGeAs$_2$.

from crystal to crystal and is related to tetragonal distortion (i.e. $2 - c/a$) in the lattice. For CdGeAs$_2$ the lattice parameters [19], a and c are 5.9432 Å and 11.2163 Å respectively at 298 K and the parameter x is 0.2785 leading to the interatomic distances of 2.629 Å for Cd–As and 2.430 Å for Ge–As.

In the chalcopyrite lattice, the tetrahedral coordination of atoms suggests that the covalent bonding (with sp^3-hybrid bonds) predominates. On the other hand, the composition of the cation sublattice indicates the presence of ionic character in the chemical bonding. In CdGeAs$_2$ a relatively large magnitude of tetragonal compression ($\approx$6 %) confirms that the chemical bonding is mixed. Based on the electronegativities of the constituent atoms, the Ge–As bond is expected to be less ionic than the Cd–As bond. Our atomistic model therefore do not assume either a fully covalent (i.e. Cd^{2-}Ge^{0}As$_2^+$) or fully ionic (i.e. Cd^{2+}Ge^{4+}As$_2^{3-}$) description of the lattice, but uses the empirical fitting method to determine the charges associated with Cd, Ge and As. Hence, the mixed (ionic–covalent) chemical bonding is taken into account by the use of the derived atomic charges along with the three-body terms included in the atomistic description of the material.

In our model, the two-body interaction term (2) therefore requires the determination of Q_{Cd}, Q_{Ge}, Q_{As} and V_{SR} (i.e. parameters A and ρ) for the Cd–As, Ge–As and As–As interactions in CdGeAs$_2$. Note that the short-range interactions between Cd–Cd and Ge–Ge are ignored as they become very small for large separations ($>$4.0 Å) in the lattice. We also need to determine the coefficient k_{AsGeAs} and k_{AsCdAs} for the three-body terms (3) along with the shell-model parameters Y_{As} and k_{As}. Both cations are considered as rigid ions in the lattice. All of these potential parameters are obtained by the empirical fitting method [21] which uses the experimentally known crystal properties such as crystal structure [18, 19], elastic [22] and dielectric [1, 23] constants of CdGeAs$_2$. Fitting and all calculations were performed using the program GULP [24].

Table 1 lists the model parameters representing the interatomic interactions in the lattice. The calculated crystal properties are compared with the experimental data in table 2. Accordingly, the potential model reproduces the lattice structure very well. The overall good agreement between the calculated and experimental properties for the perfect lattice indicates the reliability of the derived interatomic potential set for CdGeAs$_2$.

Table 1. Interatomic potential parameters of (2) and (3). The atomic charges are $+1.83e$, $+2.29e$ and $-2.06e$ for Cd, Ge and As, respectively. For As, the shell charge (Y) is $-2.22e$ and the spring constant (K) is 1.40 eV Å^{-2}.

	A_{ij} (eV)	ρ_{ij} (Å)	k_{ijk} (eV Å^{-9})
Cd–As	329.5	0.4826	
Ge–As	531.6	0.4119	
As–As	32 228.9	0.3131	
Cd–As–As			272.4
Ge–As–As			−277.5

Table 2. Calculated and experimental bulk properties of CdGeAs$_2$.

		This work	Experiment
Structure	a (Å)	5.951	5.9432 [19]
	c (Å)	11.221	11.2163
	c/a	1.886	1.887
	x_{As}	0.279	0.2785
Lattice energy/unit cell (eV)			
	E_L	−134.6	—
Elastic constants (10^{11} dyn cm^{-2})			
	C_{11}	9.70	9.45 [22]
	C_{12}	4.47	5.96
	C_{13}	5.45	5.97
	C_{33}	8.95	8.34
	C_{44}	4.26	4.21
	C_{66}	3.42	4.08
Dielectric constants			
	ϵ_0^{11}	14.75	14.8 [23]
	ϵ_0^{33}	15.43	15.4
	ϵ_∞^{11}	10.17	10.06 [1]
	ϵ_∞^{33}	10.93	11.04

3. Native defects

Defect energies of several plausible types of ionic and electronic native acceptor defect have been calculated using the Mott–Littleton methodology [25, 26] in which the lattice is divided into a series of different regions around the defect by concentric spherical boundaries. Immediately surrounding the defect is region 1 in which all ions are treated explicitly and fully optimized. Beyond this is region 2a in which all atoms are still explicitly considered, but the relaxation effects are much smaller and can be treated more approximately. The validity of the successive approximations made in the above multiregion method improves as the radii of the regions increase. Therefore it is important to check the convergence of the results with region size. In the present work a region 1 containing approximately 350 atoms was found to be sufficient to converge the absolute defect energy to better than 0.01 eV, though relative energies will be far more converged than this. We also note here that provide the defects are charge neutral overall and the qualities of fitting to the structural properties are the same, then to the first order the defect energies should not depend too strongly on the charges used in the model. If defect-induced displacements in the lattice are large then the particular shape of the anharmonic region of the potential energy curve

will become more important thereby yielding a strong dependence of defect energies on the charges. However, given that we know the ions in CdGeAs$_2$ do not have integral charges, the use of partial charges is therefore expected to give a better account of this anharmonic region in defect calculations.

The Schottky defects in the lattice are formed by moving the constituent ions to the surface from their bulk sites whereas the Frenkel defects are pairs of the vacancy and interstitial of the same type of ion. In calculations an interstitial was simulated as an addition of atom to the empty interstitial position in the lattice. The Schottky, Frenkel and antisite formation energies (table 3) were obtained from defect energy calculations of vacancies, interstitials and antisites in the lattice. In CdGeAs$_2$ the Schottky defect is $(V_{Cd} + V_{Ge} + 2V_{As})$, the Frenkel defect pairs are $(V_{Cd} + Cd_i)$, $(V_{Ge} + Ge_i)$ and $(V_{As} + As_i)$ and the antisite pairs are $(Cd_{Ge} + Ge_{Cd})$, $(Cd_{As} + As_{Cd})$ and $(Ge_{As} + As_{Ge})$. As shown in table 3, the lowest formation energy turns out to be for the $(Cd_{Ge} + Ge_{Cd})$ antisite pair which is followed by the Schottky and Frenkel pairs of Cd and Ge. The large formation energies for the antisite pairs $(Cd_{As} + As_{Cd})$ and $(Ge_{As} + As_{Ge})$ would seem to preclude their occurrence as intrinsic point defects in CdGeAs$_2$. This ordering of formation energy is what we expected since the magnitude of formation energy depends mainly on the extent of distortion introduced by individual defects in the lattice. In the present case, antisite disorder in the cation sublattice introduces least distortion in the lattice compared to that introduced by either vacancies, interstitials and antisites involving both cation and anion sublattices†. We note here that (tetrahedral) covalent radii of Cd, Ge and As ions are 1.405, 1.225 and 1.225 Å respectively [27].

Table 3. Native defect formation energies in CdGeAs$_2$.

	Formation energy (per defect) (eV)
Schottky pair	
$(V_{Cd} + V_{Ge} + 2V_{As})$	1.88
Frenkel pair	
$(V_{Cd} + Cd_i)$	2.39
$(V_{Ge} + Ge_i)$	2.82
$(V_{As} + As_i)$	5.07
Antisite pair	
$(Cd_{Ge} + Ge_{Cd})$	0.28
$(Cd_{As} + As_{Cd})$	12.1
$(Ge_{As} + As_{Ge})$	13.1

The magnitude of the formation energy for the $(Cd_{Ge} + Ge_{Cd})$ antisites is small (≈ 0.3 eV) suggesting that appreciable disorder would occur in the cation sublattice at higher temperatures. This is in accord with what has been reported for CdGeAs$_2$ which has a high-temperature disordered zincblende phase. In this phase, Cd and Ge occupy cation sites randomly in contrast to the ordered chalcopyrite phase where Cd and Ge occupy alternating cation sites. Upon cooling to room temperature, the lattice is then expected to retain some of the disorder in the cation sublattice.

† A detailed list of individual defect energies and lattice coordinates can be obtained from the authors (pandey@mtu.edu).

4. Native acceptors

A native acceptor centre in CdGeAs$_2$ may involve either cation vacancy (V$_{Cd}$ or V$_{Ge}$) or antisite (Cd$_{Ge}$) based on the effective charge considerations and can stabilize a hole on near-neighbour As ions with the binding energy given by

$$\Delta E = E_A + E_h - E_{h+A} \qquad (4)$$

where E_{h+A} refers to the energy of the hole–acceptor complex, E_h is the energy of the hole and E_A is the energy of the acceptor in the lattice. For the bound hole, ΔE is taken to be positive.

The hole–acceptor complex in CdGeAs$_2$ can be classified according to the degree of delocalization of the hole states in the lattice. For example, a complete delocalization refers to sharing of a hole by all of the four As neighbours of the acceptor (i.e. four-centre case). Alternatively, a hole next to the acceptor centre may be shared by a pair of As neighbours (i.e. two-centre case) or localized on one of the As ions (i.e. one-centre case) in the lattice. The presence of hole–acceptor complexes in as-grown CdGeAs$_2$ has been revealed by Hall-effect measurements [5, 6, 28], electron paramagnetic resonance (EPR) [8], and thermal admittance spectroscopy [9]. We note here that a direct comparison can be made between ΔE and the acceptor binding energy obtained from the Hall-effect measurements.

Our approach to calculation of ΔE is similar to that used in an earlier study [15] of ZnGeP$_2$ where we assumed that the presence of a hole in the lattice reduces the (shell) charge thereby only modifying long-range Coulombic interactions between ions. The short-range interaction parameters (2) are taken to be the same as obtained for the perfect lattice. This assumption is likely to overestimate the one-centre hole binding energy slightly since it provides a more accurate treatment of the delocalized hole (four-centre case) relative to the localized hole (one-centre case). Furthermore, we expect, to a first approximation, cancellation of the hole self-interaction energies in (4) for the four-centre case since dE is the difference of two terms involving the delocalized hole.

Calculations based on the Mott–Littleton methodology (described in section 3) are performed to obtain defect energies for (4) to calculate ΔE. These include, for example, antisite (E_A), delocalized hole (E_h) and antisite next to the delocalized hole (E_{h+A}) in the lattice. All defect coordinates are fully optimized in these calculations. The calculated binding energies (ΔE) are given in table 4. Accordingly, a striking distinction is found in the binding energies of acceptors associated with either vacancies or antisites for different hole localization regions. The hole tends to be localized near a cation vacancy, i.e., the more the hole is localized, the larger is the binding energy. But the trend is exactly opposite for antisites where a larger binding energy is found to be associated with the delocalized hole. It is well known that the localization of a hole in the lattice is a result of interplay between lattice distortion and polarization. In CdGeAs$_2$, the distinct behaviour of hole localization can therefore be

Table 4. The calculated binding energies (ΔE (eV) of (4)) of native acceptors in CdGeAs$_2$.

Acceptor centre[a]	1-centre	2-centre	4-centre
Hole near V$_{Cd}$	0.49	0.26	0.15
Hole near V$_{Ge}$	0.80	0.67	0.59
Hole near Cd$_{Ge}$	0.04	0.12	0.13

[a] Localization of a hole on an As, two As and four As neighbours to the cation site is represented by one-centre, two-centre and four-centre cases respectively.

understood in terms of the distortion and polarization introduced by these defects in the surrounding lattice. For example, a V_{Cd} has an effective charge of $-1.8e$ in comparison to the effective charge of $-0.5e$ associated with Cd_{Ge}. The difference in effective charges along with the fact that a Cd atom is much larger than the Ge atom results in an inward relaxation ($\approx$6%) of As neighbours for V_{Cd} in contrast to an outward relaxation ($\approx$5%) of As neighbours for Cd_{Ge}. Based on simple electrostatic arguments, the localized hole (i.e. one-centre case) is therefore expected to have a larger binding energy for V_{Cd} than that for Cd_{Ge}.

As shown in table 4 the calculated binding energies for various acceptor centres vary from 0.04 to 0.80 eV. Note that the energy gap for this material is only 0.57 eV at room temperature. For Hall effect measurements on the best available crystals [5, 6], a value of 0.15 eV is obtained for the acceptor binding energy. The acceptor centre revealed in the Hall-effect measurements is therefore likely to be associated with the delocalized hole (i.e. four-centre case) in the vicinity of Cd_{Ge} for which calculations yield the binding energy of about 0.13 eV. The acceptor centre involving V_{Cd} was not chosen as one would expect the deepest level, 0.49 eV, to be its populated level (table 4). We note here that a detailed electronic structure study of these defect complexes is planned to confirm the proposed assignment of the acceptor centres in CdGeAs$_2$.

In fact, our prediction regarding the nature of the dominant acceptors is confirmed by the EPR measurements. Halliburton *et al* [8] have proposed that the dominant EPR signal may be due to the acceptor centre consisting of either a cation vacancy or antisite cation with the unpaired spin shared by the four neighbouring As ions. This is consistent with our selection of the shallow acceptor as the cation antisite, Cd_{Ge}. Our further analysis of the calculated results find that the near neighbours of V_{Cd} relax inward by 0.08 Å in contrast to the outward relaxation of near neighbours of Cd_{Ge} of about 0.19 Å from their regular lattice sites (table 5). It is to be noted here that the magnitude of the lattice distortion introduced by acceptors can be used in the analysis of (future) magnetic resonance studies to ascertain more precisely the nature of the EPR-active centre.

Table 5. The calculated lattice distortion introduced by native acceptors in CdGeAs$_2$.

Acceptor centre	Near-neighbour separation[a] (Å)		
	1-centre	2-centre	4-centre
Hole near V_{Cd}	2.38	2.50	2.56
Hole near V_{Ge}	2.26	2.37	2.41
Hole near Cd_{Ge}	2.97	2.71	2.62

[a] The near-neighbour separations in the perfect lattice are 2.43 and 2.63 Å for Ge–As and Cd–As, respectively.

Recent capacitance–voltage measurements using thermal admittance spectroscopy [9] have reported the presence of two acceptor levels in p-CdGeAs$_2$ with binding energies of 0.11–0.13 eV and of 0.346 eV. The first acceptor level is the same one revealed by Hall effect measurements yielding binding energies of 0.10–0.12 eV for these exact same samples [5] which are fairly heavily doped. This value corresponds to the delocalized hole (i.e. four-centre case) bound to the Cd_{Ge} as previously discussed. Based on comparison of the binding energy of the second acceptor with the calculated binding energies (table 5), we predict that the deeper acceptor is associated with the localized hole bound to V_{Cd}, as this centre's deepest level will be populated. The other possibilities can be ruled out as they have binding energies which exceed the band gap of CdGeAs$_2$.

5. Summary

A set of interatomic potentials consisting of two- and three-body potential parameters coupled with the shell-model description of the lattice is developed for $CdGeAs_2$ reproducing its structural, elastic and dielectric properties successfully. Native defect formation energies show that antisites in the cation sublattice will dominate the intrinsic disorder in this material. The dominant acceptor centre controlling the optical properties of this material and revealed in the EPR and Hall-effect measurements is likely to be a hole shared by four neighbouring As ions in the vicinity of Cd_{Ge}. The deeper level is probably due to the a hole localized on one As ion and bound to V_{Cd}.

Although $ZnGeP_2$ and $CdGeAs_2$ belong to the same chalcopyrite family, the nature of dominant acceptors in these materials is predicted to be different. Defect calculations corroborating the Hall effect and magnetic resonance studies find that the zinc vacancy, not the zinc antisite (Zn_{Ge}), is associated with the dominant acceptor centre in $ZnGeP_2$. This is not the case in $CdGeAs_2$ where a cadmium antisite (Cd_{Ge}) is predicted to be associated with the dominant acceptor in the lattice. We believe that this difference may well be due to defect-induced lattice distortion which plays a key role in stabilizing the hole states in the lattice. Based on the size argument, native acceptors associated with zinc antisites (Zn_{Ge}) are not expected to introduce significant lattice distortion in $ZnGeP_2$ since both Zn and Ge have the same tetrahedral radius [27] of 1.23 Å. On the other hand, the tetrahedral radius of Cd is about 1.41 Å. Therefore, the size difference of about 15% between Cd and Ge would be expected to cause significant distortion by a cadmium antisite (Cd_{Ge}) in the $CdGeAs_2$ lattice.

Acknowledgments

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