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Theoretical study of the structural, electronic and vibrational properties of CdIn_2Te_4

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The structural, electronic and vibrational properties of the ordered-vacancy compound CdIn_2Te_4 have been studied theoretically in three phases. They are the tetragonal $\bar{1}\bar{4}$ and $\bar{1}\bar{4}2m$ phases, and a potential high-pressure $\text{Fd}\bar{3}m$ phase. We find that (i) the $\bar{1}\bar{4}$ and $\bar{1}\bar{4}2m$ are virtually identical in energy, (ii) a high pressure phase transition from either tetragonal phase to the $\text{Fd}\bar{3}m$ is unlikely, and (iii) the tetragonal phases are semiconducting with a direct band gap, while the $\text{Fd}\bar{3}m$ is metallic. We have calculated the Raman and IR modes for the $\bar{1}\bar{4}2m$ phase and compare with experiment.

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1. Introduction

Defect ternary compounds of the family $\text{A}^{\text{II}}\text{B}_2^{\text{III}}\text{C}_4^{\text{VI}}$ have been the subject of many experimental studies. This is motivated by potential applications in optical, electro-optical, acousto-optical, or thermoelectric [1,2] devices. This class of materials has also been studied theoretically. Because these structures have an ordered array of vacancies, theoretical studies have been performed to understand their effect. For example, Bernard *et al.* [3] and Marinelli *et al.* [4] have studied the structural and electronic properties of CdIn_2Se_4 . In this paper we study theoretically the related material CdIn_2Te_4 . CdIn_2Te_4 was first studied by Hahn *et al.* [5], and an example of a recent work is that of Santana *et al.* [6]. Its crystal structure, electronic, vibrational and high pressure properties have already been studied experimentally. There remains some controversy concerning the crystal structure. Hahn *et al.* [5] report the space group to be the $\bar{1}\bar{4}$, while Riede *et al.* [7] report $\bar{1}\bar{4}2m$. Experiments show CdIn_2Te_4 to be a semiconductor, and its vibrational properties have been measured on single crystal, polycrystalline samples and recently on thin films.

2. Crystal structures

We will compute equations of state for the two possible ground state structures $\bar{1}\bar{4}2m$ and $\bar{1}\bar{4}$, and the possible high pressure phase $\text{Fd}\bar{3}m$ structure. The $\bar{1}\bar{4}2m$ structure is body-centred tetragonal with one chemical formula unit per unit cell. Both Cd and In atoms are tetrahedrally coordinated by Te atoms. Each Te atom is in turn surrounded by two In atoms and one Cd atom. The metal vacancy is at the 2b site, and it is "tetrahedrally coordinated" by Te atoms. The $\bar{1}\bar{4}$ phase is similar to the $\bar{1}\bar{4}2m$ except for the layering of the metal (Cd and In) atoms. In the $\bar{1}\bar{4}2m$ phase, each metal atom occupies its own (001) layer, while in the $\bar{1}\bar{4}$ structure both metals can occupy the same layer. A possible high pressure phase is the spinel structure (MgAl_2O_4) structure of $\text{Fd}\bar{3}m$ symmetry. Here Cd is surrounded by the Te at a tetrahedral site, while In is at an octahedral site. The optimized fractional coordinates for the $\bar{1}\bar{4}$, $\bar{1}\bar{4}2m$ and

$\text{Fd}\bar{3}m$ structures are listed in Table II.

We use density functional theory in the local-density approximation with ultrasoft pseudopotentials and a plane-wave expansion of the eigenstates, as implemented in the Vienna *ab initio* simulation package (VASP) [8].

3. Results

Figure 1 shows the fit Birch-Murnaghan equation of state for each structure. The parameters extracted are listed in Table I, and are the minimum energy E_0 , the minimum volume V_0 , the bulk modulus K , and the first derivative of the bulk modulus K' . We find that the $\bar{1}\bar{4}$ phase and the $\bar{1}\bar{4}2m$ are virtually identical in energy. In a study by Berger *et al.* [9] on $\text{A}^{\text{II}}\text{B}_2^{\text{III}}\text{C}_4^{\text{VI}}$ materials it was found to be difficult to X-ray distinguish these two structures. In the work of [5], the $\bar{1}\bar{4}$ was favored to be the structure, while [7] favored the $\bar{1}\bar{4}2m$ structure. What theory adds to this uncertainty is that neither structure is favored energetically over the other. The experimental structure then is likely to be mixed or dependent on the synthesis conditions used.

Range *et al.* [10] have found that the CdIn_2Te_4 undergoes a phase transition from the $\bar{1}\bar{4}$ to a NaCl-like phase. In the related material CdIn_2Se_4 , a phase transition from the tetragonal phase to a spinel-like has been observed to occur at 18Kbar [11]. Theoretical calculations place it at 10Kbar [4]. We find no "common tangents" between tetragonal phases and the cubic spinel phase of Figure 1. This indicates that an equilibrium phase transition from tetragonal to spinel is not possible.

The optimal external parameters are contained in Table I. The lattice parameters a_0 and c_0 for the $\bar{1}\bar{4}2m$ phase are 1.46% and 1.1% shorter than those reported in Ref. [12]. In the $\bar{1}\bar{4}$ phase, a_0 is 0.4% shorter than the reported by Ref. [5], while c_0 has negligible error.

The band structures for the spinel-like, $\bar{1}\bar{4}$, and $\bar{1}\bar{4}2m$ phases are shown in Figures 2 and 3a,b, respectively.

We find that the equilibrium tetragonal phases are semiconductors while the high energy spinel phase is metallic. The band gaps of the tetragonal phases are direct but small. The $\bar{\Gamma}$ point gaps are 0.75eV for $\bar{1}\bar{4}$, 0.5eV for $\bar{1}\bar{4}2m$. Their valence bands show portioning into subbands,

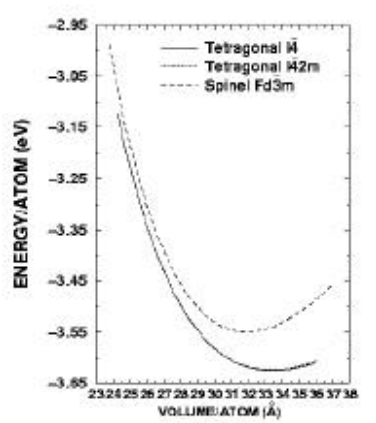


FIG. 1. Equation of State (energy per atom versus volume per atom) for the tetragonal phases $I\bar{4}$ and $I\bar{4}2m$, and the spinel-like $Fd\bar{3}m$ phase. The data are obtained from a Birch-Murnaghan fit of the LDA data. Table I summarizes the Birch-Murnaghan parameters.

TABLE I. (i) The parameters of the Birch-Murnaghan equation of state obtained from a fit of the LDA energy vs. volume data and the optimized external parameters. The internal coordinates were optimized at each volume. (ii) The optimized external parameters of each phase.

<i>Phase</i>	<i>E</i> ₀ (<i>eV/atom</i>)	<i>V</i> ₀ (<i>volume/atom</i>)	<i>K</i> (<i>Gpa</i>)	<i>K'</i>
I4̄2m	-3.624	33.290	31.762	6.134
I4̄	-3.625	33.401	30.490	6.301
Fd3̄m	-3.549	31.868	48.798	4.899

Phase	a ₀ (Å)	c ₀ (Å)	c ₀ /a ₀
I4̄2m	6.144	12.344	2.01
Ref.[1 2]	(6.231)	(12.481)	(2.003)
I4̄	6.167	12.299	1.99
Ref.[5]	(6.19)	12.30	(2.00)
Fd3̄m	12.13	12.13	1.00

with the narrow bands representing the filled d-orbital cadmium and indium states, which are included in the pseudopotential. Experimental results show that the $I\bar{4}$ phase has a direct band gap (1.22eV in [13]).

The frequencies and symmetries of the vibrational modes for the $I\bar{4}2m$ phase are shown in Table III. We choose this phase because there is experimental IR and Raman data. Group theory predicts the 18 optical modes of the $I\bar{4}2m$ phase at $\mathbf{k} = \mathbf{0}$ to be associated with 5 irreducible representations in the combination $2A_1 + 1A_2 + 2B_1 + 3B_2 + 5E$. We determined the phonon spectra at $\mathbf{k} = \mathbf{0}$ by means of the *direct approach* and the *symmetry properties* of the force-constant matrix [14]. Riede *et al.* [7] studied the infrared and Raman spectrum of a polycrystalline $I\bar{4}2m$ sample of $CdIn_2Te_4$. We found a good agreement with their results except for the assignment of the high frequency

portion of the spectrum. The major differences are: a B_2 mode at infrared reflectivity $\bar{\nu}_{TO}=151\text{cm}^{-1}$, $\bar{\nu}_{LO}=156\text{cm}^{-1}$ that we indexed here as E at 157.28cm^{-1} , and a E mode at $\bar{\nu}_{TO}=169\text{cm}^{-1}$, $\bar{\nu}_{LO}=183\text{cm}^{-1}$ that we indexed here as B_1 at 180.30cm^{-1} .

TABLE II. The optimized internal coordinates of the tetragonal $I\bar{4}$ phase; the tetragonal $I\bar{4}2m$ phase and the normal spinel $Fd\bar{3}m$ phase.

Phase	Element	Site
$I\bar{4}$	Cd	$2a(0,0,0)$; etc.
	In	$2b\left(0,0,\frac{1}{2}\right)$; etc.
	In	$2c\left(0,\frac{1}{2},\frac{1}{4}\right)$; etc.
	Te	$8i(x,y,z),(\bar{x},\bar{y},z),(y,\bar{x},\bar{z}),(\bar{y},x,\bar{z})$; etc. Calculated: $x = 0.2819$, $y = 0.2202$, $z = 0.1399$ Expt. [5] $x = 0.26$, $y = 0.24$, $z = 0.13$
$I\bar{4}2m$	Cd	$2a(0,0,0)$; etc.
	In	$4d\left(0,\frac{1}{2},\frac{1}{4}\right)\left(0,\frac{1}{2},\frac{3}{4}\right)$; etc
	Te	$8i(x,x,z),(\bar{x},\bar{x},z),(x,\bar{x},\bar{z}),(\bar{x},x,\bar{z})$; etc. $x = 0.2817$, $z = 0.1098$
$Fd\bar{3}m$	Cd	$8a\left(\frac{1}{8},\frac{1}{8},\frac{1}{8}\right),\left(\frac{7}{8},\frac{3}{8},\frac{3}{8}\right)$; etc
	In	$16d\left(\frac{1}{2},\frac{1}{2},\frac{1}{2}\right)\left(\frac{1}{4},\frac{3}{4},0\right)\left(\frac{3}{4},0,\frac{1}{4}\right)\left(0,\frac{1}{4},\frac{3}{4}\right)$; etc
	Te	$32e(x,x,x),(x+\frac{1}{2},\bar{x}+\frac{3}{4},\bar{x}+\frac{1}{4})$ $(x+\frac{3}{4},x+\frac{1}{4},\bar{x}+\frac{1}{2}),(\bar{x}+\frac{1}{4},\bar{x}+\frac{1}{2},x+\frac{3}{4})$ $(\bar{x}+\frac{1}{2},x+\frac{3}{4},x+\frac{1}{4}),(\bar{x}+\frac{3}{4},\bar{x}+\frac{1}{4},x+\frac{1}{2})$ $(\bar{x},\bar{x},\bar{x}),(\bar{x}+\frac{1}{4},x+\frac{1}{2},\bar{x}+\frac{3}{4})$; etc. $x=0.2582$

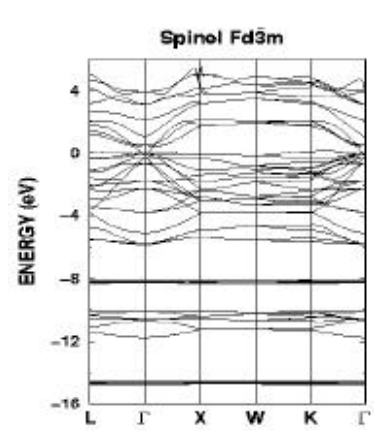


Fig. 2. Band structure for the normal spinel phase at the minimum energy volume, V_0 , (see Table I). The high-symmetry points are: $L=\frac{2\delta}{a}\left(\frac{1}{2},\frac{1}{2},\frac{1}{2}\right)$, $\Gamma=(0,0,0)$, $X=\frac{2\delta}{a}(1,0,0)$,

$$W=\frac{2\delta}{a}\left(1,\frac{1}{2},0\right), K=\frac{2\delta}{a}\left(\frac{3}{4},\frac{3}{4},0\right).$$

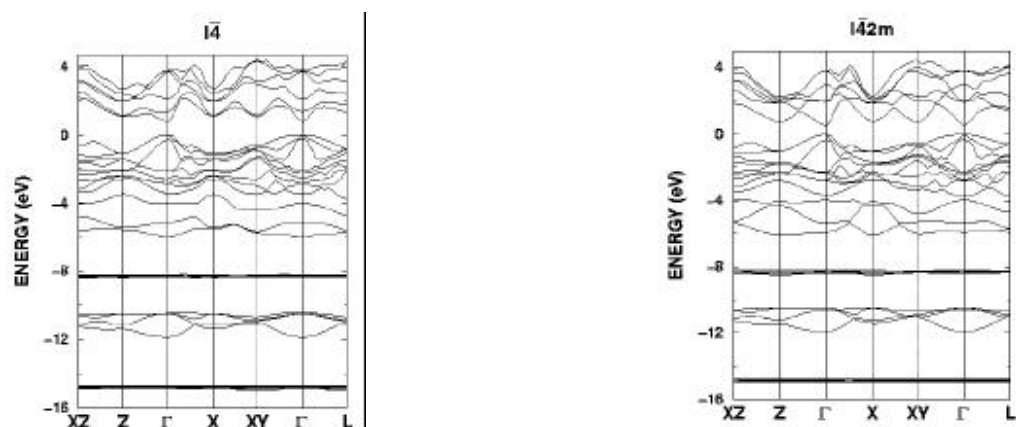


Fig. 3. Band structure for the tetragonal phases at the minimum energy volume, V_0 , for each one (see Table I). The top of the valence band is at 0.0eV. (a) $I\bar{4}$ and (b) $I\bar{4}2m$ phases. The high-symmetry points are: $XZ = \frac{\delta}{a} \left(1, 0, \frac{a}{c} \right)$, $Z = \frac{2\delta}{a} \left(0, 0, \frac{c}{a} \right)$, $\Gamma = (0, 0, 0)$.

$$X = \frac{2\delta}{a} (1, 0, 0), \quad XY = \frac{\delta}{a} (1, 1, 0), \quad \text{and} \quad L = \frac{\delta}{a} \left(1, 1, \frac{c}{a} \right).$$

TABLE III. Raman and infrared active modes for CdIn_2Te_4 ($I\bar{4}2m$) at the Γ point ($\mathbf{k} = 0$).

$\nu(\text{cm}^{-1})$	Symmetry	Raman	IR
49.12	E	✓	✓
63.94	B_1	✓	
68.24	B_2	✓	✓
68.40	E	✓	✓
99.85	A_1	✓	
126.46	A_2		
129.67	B_2	✓	✓
132.66	A_1	✓	
146.82	E	✓	✓
156.50	E	✓	✓
157.28	E	✓	✓
170.91	B_1	✓	
180.30	B_2	✓	✓

4. Conclusions

We find that the tetragonal $I\bar{4}$ and $I\bar{4}2m$ phases have virtually identical total energies and similar structural and electronic properties. The total energy results suggest that both phases are likely, and that details of the synthesis route may favor one phase over the other, or that mixed phases exist. We find that a tetragonal to a spinel phase transition is unlikely by an equilibrium transformation under pressure. The spinel phase is found to be metallic, while the $I\bar{4}$ and $I\bar{4}2m$ phases are semiconductors with a direct Γ band gaps. A comparison of the vibrational spectrum of $I\bar{4}2m$ shows agreement with experimental results except for a high frequency symmetry assignment.

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