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DFT investigation of elastic, mechanical, vibrational and thermodynamic properties of cadmium dichalcogenides

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ABSTRACT

Ab-initio calculations based on density functional theory (DFT) and ultrasoft pseudopotentials within both generalized gradient approximation (GGA) proposed by Perdew, Burke and Ernzernof (PBE) and local density approximation (LDA) as parametrised by Perdew and Zunger with the electron-ion interaction treated within Rappe Rabe Joannopoulos (rrkjus) pseudopotential, have been performed to investigate the structural, elastic, mechanical, dynamical and thermodynamic properties of Cadmium dichalcogenides (CdS_2, $CdSe_2$ and $CdTe_2$) in pyrite structure. The results of the equilibrium lattice constants and bulk moduli are in agreement with experimental and theoretical studies. Their elastic constants were calculated by fitting the computed stress-strain relationship linearly and their respective mechanical properties were then determined from the three independent elastic constants. The vibrational properties were predicted by calculating the phonon dispersion along high symmetry points using density functional perturbation theory (DFPT). The results obtained revealed that these compounds are ductile systems, they exhibit intra-ionic bonding, and are stable mechanically and dynamically in a pyrite structure. The temperature-dependent behaviours of some thermodynamic properties such as the internal energy, vibrational free energy, entropy and constant volume heat capacity for these compounds were also determined.

1. Introduction

Transition metal dichalcogenides have attracted so much attention from experimental and theoretical scientists due to their unique attributes. First, their structures are loosely packed together by relatively weak forces and as a result, allow foreign atoms to be readily intercalated [1–4], their d-orbitals interactions have the tendency of giving rise to new physical phenomena [5–7]. These materials are also known for their technological and scientific importance from being a good lubricant and as catalysts due to their qualities. They have also been exploited for photocatalytic [8] and photovoltaic [9] use, by virtue of their strong absorption in the solar spectrum region.

Cadmium dichalcogenides belonged to this transition metal dichalcogenides group and had been grown using wet electrodeposition technique, a method that has been proven to be efficient for large-scale deposition at low cost [10]. Roussets et al., 2008 [10] were able to show that $CdTe_2$ can easily be grown on CdTe and hence considered it as an alternative buffer layer to act as an ohmic contact between the absorber films and metallic contact for solar cell applications. Investigations on the stable crystal structure of Cadmium dichalcogenides among the crystal structure of most AB_2 compounds (Pyrite, Flourite, Marcasite and Trigonal) have been carried out and Cadmium dichalcogenides (CdX_2) where X = S, Se and Te) like most transitional metal dichalcogenides were observed to be more stable in a pyrite structure [11–13]. The structural and electronic properties of CdX_2 had been reported, their band structures were found to be semiconductive in nature with very flat conduction band and the sizes of the band gap were narrow and indirect [11,12,14]. They also have optical properties within the appropriate range for the photovoltaic application. $CdSe_2$ and $CdTe_2$, in particular, were proposed as promising materials for efficient absorption of the solar spectrum by virtue of their high absorption coefficients [11].

These attributes, properties and scientific importance of CdX_2 found in most works of literature are the motivations for the present study of the elastic, mechanical, vibrational and thermodynamic properties of CdX_2 using density functional theory within the local density and

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generalized gradient approximations (LDA and GGA).

2. Method of calculations

The calculation of structural properties for CdX_2 were performed in the framework of density functional theory (DFT) [15–17] within both generalized gradient approximation (GGA) and local density approximation (LDA) for the exchange-correlation energy. The projected augmented wave (PAW) as implemented in Quantum espresso code [18] were used for the GGA calculation with the parametrization by Perdew Burke and Ernzerhof (PBE) [19,20] while the LDA calculations as suggested by Perdew and Zunger [21] with the electron-ion interaction treated within Rappe Rabe Joannopoulos ultrasoft (rrkjus) pseudopotentials [22] were adopted for the three compounds. The pseudopotentials were taken from the database of the PSlibrary project [23]. The plane-wave energy cut-off of 35Ry and 50Ry were selected for the GGA-PBE and LDA calculations from the convergence plot, $8 \times 8 \times 8$ and $12 \times 12 \times 12$ Monkhorst-Pack [24] grid of kpoints were used respectively. The plane-wave energy cut-off and Brillouin zone sampling selected were enough to converge the total energies to within 10^{-6}eV for each self-consistent loop. For each system, an optimized lattice constant (a_0), bulk modulus (B) and the pressure derivative of the bulk modulus B' were calculated by fitting the total energy of the system at different volumes to the third order Birch-Murnaghan [25] equation of state. The values obtained for both PBE and LDA were used in the calculations of elastic constants for CdX_2. The elastic constants computed in this work employed the efficient stress-strain method proposed by Shang et al. [26]. Hooke's law is applied in calculating the stress after the application of a finite value of a given homogeneous strain of magnitude -0.0075, -0.0025, 0.0025 and 0.0075 to system [27].

The full phonon dispersion spectra and phonon density of states (phDOS) were computed using Density functional perturbation theory (DFPT) developed by Baroni et al. [28]. In this method, the dynamical matrices were calculated using *the* $4 \times 4 \times 4$ q-point grid, and fourier deconvolution of the dynamical matrices gives the inter-atomic force constants from which the phonon dispersion and phonon density of states were derived. The thermodynamic function such as Internal energy ΔE, vibrational part of Helmholtz free energy ΔF, specific heat capacity at constant volume C_V and entropy S were calculated from the PhDOS.

3. Results

Cadmium dichalcogenides have been convincingly proven from previous studies [10,12] that pyrite (Strukturbericht C_2, space group $Pa\bar{3}$) structure is their most stable structure. Therefore their structural, elastic, mechanical vibrational and thermodynamic properties in the pyrite structure have been reported using PBE and LDA methods.

3.1. Structural properties

The equilibrium lattice constants (a_0), bulk modulus (B), first pressure derivative of the bulk modulus (B') are reported in Table 1 and are compared with available theoretical and experimental studies. As usual, the experimental lattice constants suffer over and under estimation compared to the calculated lattice constants from PBE and LDA respectively. However, adopting the simple rule of thumb for these systems

$$a_0^{th} = \frac{a_0^{PBE} + a_0^{LDA}}{2} \tag{3.1.1}$$

The result accurately reproduces the experimental lattice constant to within 0.68%.

Table 1
The calculated equilibrium lattice constant, a_0(Å) bulk modulus, B (GPa) and pressure derivative of Bulk modulus, B' for CdX_2.

System	Sources	a_0(Å)		B (GPa)		B'	
		PBE	LDA	PBE	LDA	PBE	LDA
CdS_2	Our work	6.347	6.173	67.9	87.1	4.75	4.66
	Theory [11]	6.396	6.214	–	–	–	–
	Theory [14]	6.412	–	57.1	–	4.57	–
	Expt [12]	6.303		–		–	
$CdSe_2$	Our work	6.684	6.494	57.8	74.4	4.62	4.77
	Theory [11]	6.743	6.534	–	–	–	–
	Expt [12]	6.615		–		–	
$CdTe_2$	Our work	7.24	7.04	43.8	57.5	4.84	4.70
	Theory [11]	7.264	7.04	–	–	–	–
	Expt [10]	7.160		–		–	

3.2. Mechanical properties

The mechanical behaviours of CdX_2 compounds in the pyrite structure were determined from the three independent single-crystal elastic constants C_{11}, C_{12} and C_{44} presented in Table 2. The elastic moduli, Pugh and Poisson's ratios depicted in Table 3 were calculated from the Voigt-Reuss-Hill (VRH) approximation [29–31] shown in Eqs. (3.2.1)–(3.2.6) while Table 4 shows the mean value of PBE and LDA results:

$$B = \frac{C_{11} + 2C_{12}}{3} \tag{3.2.1}$$

$$G_V = \frac{C_{11} - C_{12} + 3C_{44}}{5} \tag{3.2.2}$$

$$G_R = \frac{5(C_{11} - C_{12})C_{44}}{4C_{44} + 3(C_{11} - C_{12})} \tag{3.2.3}$$

$$G = \frac{G_V + G_R}{2} \tag{3.2.4}$$

B and G are the Bulk and Shear moduli, G_V and G_R are Voigt's and Reuss's shear moduli respectively.

Hence, the Young modulus E and the Zener Anisotropy factor A are computed as follows [32]:

$$E = \frac{9GB}{3B + G} \tag{3.2.5}$$

$$A = \frac{2C_{44}}{C_{11} - C_{12}} \tag{3.2.6}$$

With the information above the mechanical stability of these cubic systems were examined as proposed by Born-Huang generalized elastic stability criteria [33,34] as shown in Eqs. (3.2.7)–(3.2.10)

$$C_{44} > 0 \tag{3.2.7}$$

$$\frac{C_{11} - C_{12}}{2} > 0 \tag{3.2.8}$$

$$B > 0 \tag{3.2.9}$$

$$C_{11} > 0 \tag{3.2.10}$$

Verifying the mechanical stability criteria, the elastic constants calculated from both PBE and LDA indicate that CdX_2 compounds are mechanically stable. The elastic stiffness is the extent to which an object can resists deformation in response to an applied force, and this is generally defined by the values of Bulk, Shear and Young Moduli. The obtained values predict that CdS_2 has the strongest resistance to deformation while $CdTe_2$ has the least resistance to deformation.

The computed Anisotropy factor (A) predicts the isotropic or anisotropic behaviour of these compounds. The values of their anisotropy factor A shown in Table 2 deviates from unity, thus indicates the