Lattice parameters and equation of state of Cd and Hg at high pressure: A first-principles investigation

Vinayak Mishra [a,*], Jyoti Gyanchandani [b], Shashank Chaturvedi [a]

[a] Computational Analysis Division, Bhabha Atomic Research Centre, Visakhapatnam 530012, AP, India
[b] Material Science Division, Bhabha Atomic Research Centre, Mumbai 400085, India

ABSTRACT

First principles calculations have been performed to study high pressure behavior of Cd and Hg. Calculated results are consistent with the published experimental results. Anomaly has been found in the pressure dependence of the axial ratio c/a of hexagonal Cd, in the same pressure range in which it has been reported experimentally. BCT–monoclinic and monoclinic–HCP structural phase transitions have been found in the solid Hg at 11.4 and 35 GPa respectively. The transition pressures are in good agreement with the published experimental results. Calculated high pressure lattice constants and equation of state of both elements agree with the experimental results. Elastic constants of BCT and HCP phases of Hg have also been calculated to test the mechanical stability of these phases at various pressures, using Born stability criteria. FPLAPW total energy method has been used for these calculations.

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1. Introduction

Knowledge of high pressure behavior of lattice parameters of crystalline solids is necessary for determining their accurate equation of state (EOS). EOS of a material is the dependence of its pressure and energy on the density (volume) and the temperature. Interests in the study of lattice parameters of Cd have been for many years mainly because of two reasons. Firstly, it crystallizes in the hexagonal structure with c/a ratio of 1.89, which is significantly larger than the ideal value of 1.63 [1,2]. Secondly, high pressure dependence of the axial ratio c/a of hexagonal Cd shows anomalies [3–5]. Experimental measurements of the behavior of lattice parameters of group XII elements viz. Zn, Cd and Hg at high pressure were performed in [2–7]. Schulte and Hozapfel [2] measured the lattice parameters and EOS of Zn, Cd and Hg up to 75 GPa using diamond-anvil-cell by energy X-ray diffraction technique. In their experiments, several structural phase transitions were found in Hg at high pressure, however, any phase transition or anomaly was not observed in Cd. Takemura [3] performed angle dispersive powder X-ray diffraction experiments with methanol–ethanol–water mixture as a pressure medium to measure the lattice parameters of Zn and Cd up to 174 GPa. The anomalous behavior of the c/a ratio was observed in these experiments. However, there were only a few data points in the

pressure range where anomaly was suspected. Pratesi et al. [4] performed energy dispersive X-ray diffraction experiments, using silicon oil as a pressure medium, with the increased number of data points in the range of interest (0–16 GPa). They also observed anomalies in the pressure dependence of lattice parameters of Cd. Recently, Godwal et al. [5] performed angle dispersive X-ray diffraction experiment with better accuracy using argon as the pressure medium. The anomalies in the pressure dependence of the lattice parameters were confirmed in their experiments.

On the theoretical side, although several electronic structure calculations have been performed to understand the deviation of c/a ratio of Cd from ideal value [8–13], the anomalies in the pressure dependence of the c/a ratio of Cd are reported in a few papers [12,13] only. Godwal et al. [12] performed LMTO+ASA calculations of c/a at different compression, by finding the minimum of total energy versus c/a ratio at each volume. However, this method was less accurate as it could not find the minimum of total energy versus c/a ratio curve, without using a correction term [12]. Even after adding the correction term, it inaccurately predicted $c/a = 1.65$ at the equilibrium volume and required a shifting for correct predictions of c/a values [12] at high pressures. Qiu et al. [13] performed more accurate FPLAPW calculations of the lattice parameters of Cd at high pressure. However, in their calculations, they minimized the Gibbs free energy for obtaining the lattice parameters. This method was claimed to be a thermodynamically incorrect method [14,15]. In this paper, we have used FPLAPW method, and have minimized the total energy to obtain the axial ratio c/a. Minimizing total energy is a commonly used thermodynamic method to calculate the lattice parameters.

* Corresponding author.
E-mail addresses: vinayakm@barc.gov.in (V. Mishra),
chats@barc.gov.in (S. Chaturvedi).

Interests in the high pressure behavior of lattice parameters of mercury have also been for many years, as it undergoes multiple phase transitions when temperature or pressure is changed from the ambient conditions. Schulte and Hozapfel [16] constructed a phase diagram of Hg using the data obtained from their own experiments and literature. According to this phase diagram, it is liquid at atmospheric pressure and room temperature (300 K). It undergoes, liquid–α and α–β phase transitions, if the temperature is decreased from 300 K to 0 K. It crystallizes in a simple rhombohedral structure (α phase) when temperature is decreased to 233 K. Rhombohedral structure transforms to BCT structure (β phase) if the temperatures are further decreased to 0 K. Hence, at 0 K Hg crystallizes in the BCT structure. At 0 K it undergoes two phase transitions, namely, β–γ and γ–δ phase transitions, on applying pressure. These phase transitions occur at 12 GPa and 37 GPa respectively. δ phase is an HCP arrangement. γ phase was proposed to be an orthorhombic arrangement by Schulte and Hozapfel [2,16]. However, in a recently performed angle dispersive powder X-ray diffraction experiments, γ phase was found to be a monoclinic arrangement [6]. Very recently Yan et al. [17] performed the angular-dispersive X-ray diffraction experiment on the mercury decomposed from HgO. They found γ phase to be an orthorhombic arrangement, which was consistent with the results of Hozapfel et al. and inconsistent with the results of Takemura et al. [6]. However, these authors also stated that the discrepancy could be due to the poorer resolution in their experiments as compared to the experiments of Takemura et al. [6]. Most recently, Takemura et al. [18] carried out high pressure powder X-ray experiments on solid Hg up to 196 GPa. They found that c/a ratio of HCP Hg, which exists above 36 GPa, monotonously decreases with pressure similar to c/a of Cd. However, any anomaly was not found in the pressure dependence of the c/a axial ratio of HCP Hg.

On the theoretical side, several attempts have been made to understand the ground state structure of mercury [19–24]. However, only a few attempts have been made to study its high pressure behavior [25–27]. At high pressure, first theoretical study was performed by Moriarty [25], however, a model potential was used in his calculations which was not based on the density functional theory. Also, γ phase was not included in his calculations. Jona and Marcus [26] have accurately calculated high pressure lattice parameters and equation of state (EOS) of the δ (HCP) phase of mercury using FPLAPW method. Their results show good agreement with the published experimental results, however, β and γ phases were not included in their calculations. Biering and Schwerdtfeger [27] have performed DFT calculations for all the solid phases of mercury. They have, however, used pseudo-potential based DFT method. Also, their calculations did not converge for the γ phase near equilibrium volume [27]. Moreover, their calculations were focused to high pressure transitions only, theoretical results of high pressure lattice parameters of any phase of Hg have not been given. In addition, they concluded that since energies of different phases of mercury are very close to each other, therefore, more accurate calculations are required. In this paper we have performed more accurate calculations using FPLAPW method to obtain the phase transition pressures, high pressure lattice parameters and EOS. We have also calculated the density of states (DOS) of all phases at various pressures, in order to check the connection between an energetically stable phase and its DOS. In addition, we have calculated the elastic constants of β and δ phases to check the mechanical stability of these phases at various pressures.

2. Computational details

Present calculations have been performed within the framework of density functional theory employing full potential linearized augmented plane wave (FPLAPW) method, as implemented in the WIEN 2k code [28]. PBE-GGA [29] exchange correlation potential have been used for Cd. It is known from the previous work [30] that local density approximation (LDA) gives better results for Hg in comparison to generalized gradient approximation (GGA). Lattice constant of the rhombohedral Hg calculated using the LDA is close to the experimental value, it deviates only by 1.1% from the experimental lattice constant, whereas, the GGA results overestimate the lattice constant by 17.8% [30]. Therefore, we have used PW-LDA [31] for Hg. 5000 k-points were taken for Hg to sample the irreducible Brillouin zone. It is necessary to take larger number of k-points in order to study the anomalous behavior of the pressure dependence of c/a, therefore, we have taken 40 000 k-points for Cd.

All other input parameters required by FPLAPW method were same for Cd and Hg. The basis function was expanded up to $R_{MT}K_{max} = 10$, where R_{MT} is the muffin tin radius and K_{max} is the plane wave cut off parameter. Different R_{MT}'s may lead to different energies even if the total energy calculations are performed for the same structure and the volume. Such volume dependent energies of different structures cannot be compared for determining the energetic stability of the structures. Therefore, in our calculations, we have used same R_{MT} (2.2 bohr) for all the structures. 5d, 6s and 6p electrons were treated as valence states while the 4f, 5s and 5p electrons were treated as semi-core states. The self-consistent cycle was run until the energy convergence criterion of 10^{-5} Ry was reached.

3. Results and discussion

3.1. Lattice parameters of Cd

In order to find the c/a ratio as function of compression or volume (V), we have performed total energy calculations by varying c/a ratio, for each volume. In Fig. 1, we have plotted total energy with respect to c/a for six selected volumes. In our calculations, c/a ratio was varied from 1.56 to 2.24 for each volume. However, in order to distinguish the minimum of these selected (E–c/a) curves, results are shown for smaller range of c/a, in Fig. 1. The c/a ratio, which gives the minimum energy at a given volume, is the optimized c/a ratio for that volume and the minimum energy is the total energy $E(V)$ at that volume. Once the volume dependence of c/a is known, then the volume dependence of lattice parameters c and a can be obtained by using following
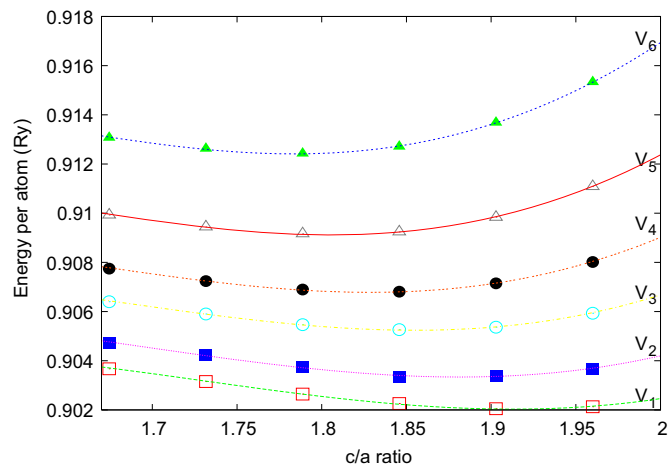

Fig. 1. Energy versus c/a ratio for HCP Cd. $V_1 = 22.88$ A^3, $V_2 = 22.32$ A^3, $V_3 = 21.76$ A^3, $V_4 = 21.21$ A^3, $V_5 = 20.65$ A^3, and $V_6 = 20.1$ A^3. The curves of V_1 and V_2 volumes are shifted below by 2 mRy and 1 mRy respectively for clear visibility.