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Effect of spin–orbit coupling on the ground state structure of mercury

Vinayak Mishra^{a,*}, Jyoti Gyanchandani^b, Shashank Chaturvedi^{a,c}, S.K. Sikka^d^a Computational Analysis Division, Bhabha Atomic Research Centre, Visakhapatnam, AP 530012, India^b Material Science Division, Bhabha Atomic Research Centre, Mumbai 400085, India^c Computational Analysis Division, Bhabha Atomic Research Centre, Visakhapatnam, AP 530012, India^d Office of the Principle Scientific Adviser to the Government of India, New Delhi 110011, India

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ABSTRACT

Near zero kelvin ground state structure of mercury is the body centered tetragonal (BCT) structure (β Hg). However, in all previously reported density functional theory (DFT) calculations, either the rhombohedral or the HCP structure has been found to be the ground state structure. Based on the previous calculations it was predicted that the correct treatment of the SO effects would improve the result. We have performed FPLAPW calculations, with and without inclusion of the SO coupling, for determining the ground state structure. These calculations determine rhombohedral structure as the ground state structure instead of BCT structure. The calculations, without inclusion of SO effect, predict that the energies of rhombohedral and BCT structures are very close to each other but the energy of rhombohedral structure is lower than that of BCT structure at ambient as well as high pressure. On the contrary, the SO calculations predict that though at ambient conditions the rhombohedral structure is the stable structure but on applying a pressure of 3.2 GPa, the BCT structure becomes stable. Hence, instead of predicting the stability of BCT structure at zero pressure, the SO calculations predict its stability at 3.2 GPa. This small disagreement is expected when the energy differences between the structures are small.

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1. Introduction

At ambient pressure and room temperature, mercury is a liquid. It crystallizes into a simple rhombohedral structure (α Hg) with one atom in a unit cell, at 235 K [1–7]. The lattice constant of the rhombohedral structure is 3.005 Å and the angle between the primitive vectors of the rhombohedral structure is 70.53° [4]. BCT structure (β Hg) with c/a ratio 0.707 is the stable ground state structure below 79 K [7]. At room temperature, the liquid phase transforms to solid α Hg and α Hg transforms subsequently to the β Hg phase on applying pressure.

Experimental investigation of stable structure of Hg at ambient as well as at high pressures has been of interest for many years [5–8]. In the experimental studies, at room temperature, the sequence of liquid– α – β – γ – δ phase transitions has been suggested at 1.2, 3.7, 12 and 37 GPa respectively. The δ phase has an HCP structure. The structure of the γ phase was initially found to be an

orthorhombic structure in Ref. [6], but later on Takemura et al. found it to be a monoclinic arrangement [8].

Theoretical investigations of ground state structure and its properties has also been of interest [9–16]. Structural properties of Hg at high pressure are reported by Moriarty [9] and Jona and Marcus [10]. In the paper of Moriarty, the calculations are based on a model potential made up of volume-dependent but structure-independent pair interactions plus a volume dependent term. This model is not based on the density functional theory of Kohn–Sham [17,18]. Jona and Marcus [10] used a FPLAPW method based on DFT. However, in their work [10], the structural properties and EOS of only HCP phase of Mercury have been reported. Biering and Schwerdtfeger [11] performed DFT calculations using PAW pseudopotentials for studying the structural properties of mercury. However, they obtained rhombohedral structure as the ground state structure and the BCT structure became stable only at 6.5 GPa. They concluded that more accurate theoretical studies (including spin–orbit effects) are required for a complete description of mercury in the solid state [11].

Spin–orbit effects were included in the calculations of the structural properties of Hg performed by Mehl [14]. However, there were two discrepancies in Mehl's calculations. Firstly, the spin–orbit effects were included partially and secondly, less accurate LDA

* Corresponding author. Tel.: +91 891 2892 100.

E-mail addresses: v.mishra.11@gmail.com (V. Mishra), gjyoti@barc.gov.in (J. Gyanchandani), shashankvizag@gmail.com (S. Chaturvedi), sksikka@nic.in (S.K. Sikka).

version [19] was used for calculating exchange and correlation part. This study did not predict correct ground state structure. According to these calculations the hexagonal closed packed structure should be the ground state structure. In this paper [14] it is suggested that LDA version used in these calculations is not good and improvements of LDA as discussed in the paper would [20] provide part of the answer. It has also been suggested that the better treatment of the spin-orbit effects, with inclusion of local orbitals, may improve the results (as discussed in [21]).

According to the suggestions of Mehl [14], in our present calculations we have used an improved version of LDA [22] and therefore we do not get HCP structure as the ground state structure. We have also done better treatment of spin-orbit interaction with the inclusion of local orbitals as implemented in the WIEN 2K code [23] and therefore we get correct ground state structure with reasonably small disagreement with the experimental phase diagram.

2. Computational details

For heavy elements SO effects have been found to be important [24,25]. Hence, we have carried out calculations with and without inclusion of spin-orbit coupling. The calculations have been performed within the framework of density functional theory employing the full potential linearized augmented plane wave.

The FP-LAPW method is implemented in the WIEN 2K code [23]. As discussed in [16], the local density approximation gives better results for Hg in comparison with a generalized gradient approximation, therefore, we have calculated exchange and correlation effects using Perdew-Wang local density approximation [22]. We expanded the basis function up to $R_{\text{MT}}K_{\text{max}} = 10$, R_{MT} is the muffin tin radius and K_{max} is the plane wave cut-off parameter. The value of R_{MT} was chosen to be 2.0 bohr. The self-consistent cycle was run until the energy convergence criterion of 10^{-5} Ry was reached. 5000 k - points were taken in the calculations.

The second variational procedure has been used to include the spin-orbit coupling as implemented in the WIEN 2K code [26]. In this procedure eigenvalues and eigenvectors are calculated using the scalar relativistic wavefunctions. In our calculations we have taken the second variation energy cut off E_{cut} as 8.0 Ry. To decrease the dependency of the results on the values of E_{cut} and R_{MT} , an additional basis function, namely a relativistic local orbital (LO) with a $p_{1/2}$ radial wavefunction, has been included in the SO calculations. These radial wavefunctions improve the basis.

3. Results and discussion

Calculated ground state properties are presented in Table 1. The equilibrium volume V_0 is determined by calculating the total

energy for several volumes and then by fitting E versus V data to the Birch-Murnaghan equation of state [27]. Bulk modulus B and the pressure derivative of the bulk modulus B' are also obtained by the BM fitting. Reported values obtained from experimental investigations and other theoretical calculations are also given in Table 1 for comparison. We find reasonably good agreement between calculated values and reported experimental and other theoretical values of these properties from the literature.

Small deviations may be due to the reason that our calculations have been performed at zero kelvin whereas the experimental measurements are at higher temperatures. The bulk modulus of the rhombohedral structure calculated by us differs from that calculated in Ref. [11], because in the calculations of Bierung et al. [11], the ground state properties for α Hg were obtained by fitting the Murnaghan equation of state to only the data points that converged to the actual α Hg structure, whereas in our calculations we have used those E versus V data points for which a and θ were optimized. In Ref. [7] the experimental values of B and V_0 of BCT structure have been obtained by the fitting of large scattered data at room temperature and high pressure (> 3.7 GPa). This could be the reason for the disagreement of our calculated data with the experimental data of Ref. [7] for the BCT structure. However, a V_0 value of BCT structure in our calculations is in good agreement with the reported experimental value in Ref. [14].

Now we describe the results of the optimization of the lattice parameters. Calculation of the volume-dependent energy of a cubic system is straightforward – it can be done by changing the unit cell size i.e. lattice constant a . However, for crystal structures such as rhombohedral, BCT and HCP, changing only the cell size a is not sufficient. For example, in HCP and BCT structures, c and a may change by different percentages with a change in volume. Therefore we must accurately calculate the c/a ratio for these structures at each volume. This is done by determining the c/a ratio that minimizes the system energy at a given volume V . We have done the lattice parameter optimization for the volumes 125.63, 133.48, 141.33, 149.18, 157.03, 164.88 and 172.74 bohr³. In Fig. 1, we have shown the energy of BCT structure as a function of c/a ratio for three volumes viz 141.33, 149.18 and 157.03 bohr³. We can see that the minimum of the energy versus c/a ratio is approximately at $c/a=0.707$, for the volume 149.18 bohr³ (which is close to the equilibrium volume of 150.31 bohr³). The experimental c/a value at equilibrium volume for the BCT structure is 0.707. Hence, our result is in good agreement with experiment. Moreover, for $c/a=1$, the BCT structure becomes BCC. Since at all volumes the energy reaches a minimum much below this value of c/a , we can say that the BCC structure will not be energetically stable for Hg at any volume.

Similarly, in a rhombohedral structure, two parameters which may change with the volume are the lattice constant a and the angle between the lattice vectors θ . For each volume, we have

Table 1
Ground state properties of α Hg (Rhomb.) and β Hg (BCT).

Method	V (Å ³)	B (GPa)	B'	Lattice parameters (a, c in Å and θ in deg.)
Rhomb.				
Without SO	22.97	31.30	9.58	$a=2.929, \theta=75.036$
With SO	23.03	31.27	7.9992	$a=2.8884, \theta=79.55$
PAW-LDA [12] (without SO)	23.14	25.9	11.1	$a=2.947, \theta=74.21$
Experiment	22.99 [1]	38.2 [9]		$a=3.005, \theta=70.53$ [4]
BCT				
Without SO	22.27	52.86	6.98	$a=3.973, c=2.821$
With SO	21.97	54.13	7.71	$a=3.9813, c=2.7716$
PAW-LDA [12] (without SO)	22.60	52.3	4.2	$a=4.022, c=2.793$
Experiment	24.0 [7], 22.54 [14]	36 [7]		$a=3.995 \pm 0.004, c=2.825 \pm 0.003$ [2]

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