First-principles study of the high-pressure hexagonal-close-packed phase of mercury

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Abstract
A recent experiment by Takemura *et al* (2005 *Proc. Joint 20th AIRAPT— 43rd EHPRG* (*Karlsruhe, June–July*)) on the pressure-induced hexagonal-close-packed phase of mercury, at pressures between 0.5 and 2 Mbar, has produced reliable data on lattice parameters, axial ratio and the equation of state. We have carried out first-principles calculations at 0 K of the structure parameters as functions of pressure by minimization of the Gibbs free energy. The agreement of the calculated lattice parameters and axial ratio with experiment is in the range of 1% for the lattice parameters and 2% for the axial ratio; the corresponding agreement for the equation of state is between 2 and 3%.

1. Introduction

The diamond anvil cell with x-ray diffraction has made possible reliable measurements on the pressure dependence of structures to high pressures. A few sets of data on lattice parameter values as functions of pressure are now available, including hexagonal-close-packed (hcp) Hg by Takemura [1], face-centred cubic (fcc) and hcp Al by Akahama *et al* [2] and body-centred cubic (bcc) and hcp Ba by Takemura [3]. Such data provide valuable tests of modern first-principles total-energy band-structure theory, since the physical properties of a system may change greatly but the same Hamiltonian free of adjustable parameters is applied over the entire pressure range. Also the fit of calculated to experimental data is a quantitative test of the procedure used to calculate equilibrium structure at each pressure, as well as a test of the energy-band calculation and of the data.

In this study of hcp Hg under pressure we have used a procedure to find equilibrium which minimizes the Gibbs free energy $G = E + pV$ ($E =$ energy per atom, $p =$ pressure, $V =$ volume per atom) at $T = 0$ K at constant pressure. This procedure has been called thermodynamically incorrect in two recent papers by Steinle-Neumann and Cohen [4] and by Sin'ko and Smirnov [5]. These authors mistakenly believe that it is not possible to define a Gibbs free energy for a system not in equilibrium. Our reply is that G for a crystal at $T = 0$ K and finite p provided by outside sources is well-defined, even for non-equilibrium states, and

moreover is minimized by the equilibrium structure at p. The fit at the 1% level of calculated lattice parameters $a(p)$ and $c(p)$ to measured values for hcp Hg, shown here, and for hcp Ba in [6], provide good support for the correctness of our procedure. In fact, a better fit than the 1% level found here should not be expected for rigid-lattice calculations like these, because even at low temperatures zero-point lattice vibrations produce lattice changes at the 1% level.

At ambient pressure mercury is liquid at room temperature; at $-38.9\,^\circ$C it solidifies into a rhombohedral structure ($a = 3.005$ Å at 227 K), and may exhibit a tetragonal phase at lower temperatures ($a = 3.995$ Å, $c = 2.825$ Å at 77 K), if this phase is 'formed at high pressure and retained when the pressure is removed' [7]. At room temperature, mercury solidifies if subjected to hydrostatic pressure, and exhibits a series of crystalline phases when the pressure is increased. At about 12 kbar the liquid solidifies into a rhombohedral structure (α-Hg); at 37 kbar it transforms into body-centred tetragonal (bct; β-Hg); at 120 kbar into orthorhombic (γ-Hg); and finally at 370 kbar into hcp (δ-Hg, lattice parameters a and c) [8]. This sequence is described concisely as follows (numbers are pressure values in kbar):

$$\text{liquid} \xrightarrow{12} \alpha\text{-Hg (rhomb.)} \xrightarrow{37} \beta\text{-Hg (bct)} \xrightarrow{120} \gamma\text{-Hg (orthorh.)} \xrightarrow{370} \delta\text{-Hg (hcp).}$$

The existence of a high-pressure phase of mercury in the hcp structure had been suspected in the 1986 study of a pressure-induced transition in CdHg alloys [9], and was confirmed theoretically by Moriarty in 1988 [10]. The first-principles generalized-pseudopotential calculations of Moriarty predicted a wide stability range for the δ phase up to at least 10 Mbar with a high but decreasing axial ratio c/a. This prediction was tested and confirmed experimentally up to at least 670 kbar by Schulte and Holzapfel [8].

Takemura *et al* [1] reported recently on a powder x-ray diffraction experiment on mercury from 0.5 to 2 Mbar in a diamond anvil cell. This experiment produced data on the pressure dependence of the lattice parameters a and c, their ratio c/a, the bulk modulus and its pressure derivative, and the equation of state.

2. Procedure and results on hcp mercury

Here we compare our first-principles total-energy calculations on δ-Hg with the experimental data of Takemura *et al*. We have used the WIEN2k computer program developed by Blaha and co-workers [11], based on the full-potential linearized augmented plane-wave (FPLAPW) method for computation of the electronic structure of solids from the Kohn–Sham equations of density functional theory [12, 13] in the generalized gradient approximation (GGA).

The parameters used in the WIEN program were: muffin-tin radius RMT = 2.3 bohr; plane-wave cut-off RK_{max} = 8.0; largest vector in the charge-density Fourier expansion GMAX = 16 bohr^{-1}; k-point sampling in the Brillouin zone of 28 000 points (about 1500 in the irreducible wedge IBZ); criterion for energy convergence 1×10^{-6} Ryd.

The calculations used our well-tested procedure [14] of minimizing the Gibbs free energy G at zero temperature for a number of pressures in the range from 0.4 to 2 Mbar. We calculate G at a given p along the epitaxial Bain path (EBP), which is defined so that $(\partial G/\partial c)_a = 0$ at any given a [14]. Then at a minimum of G along the EBP, G has a minimum for two variations of a and c, and hence must be a minimum for all variations of a and c around equilibrium. In figure 1 we show this detail of the electronic calculation by plotting $G(c/a)$ along the EBP for three values of p. The shift of equilibrium to smaller c/a as p increases is shown. The values of a and c separately are known at each point of the EBP. More details about the procedure are given in [15].

The calculated values of $a(p)$ and $c(p)$ are presented in graphic form in figure 2 together with the measured values. Figure 3 depicts the calculated axial ratio c/a versus p and
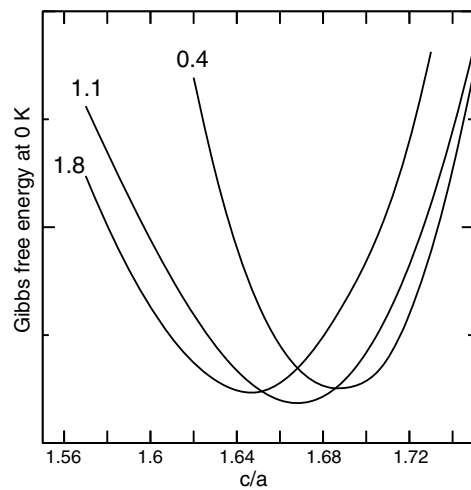
Figure 1. Epitaxial Bain paths for Hg. Gibbs free energy G at 0 K as a function of axial ratio c/a at three different pressures: 0.4, 1.1 and 1.8 Mbar, as marked. The ordinate axis, in units of $G + 39322$ Ryd, ranges for 0.4 Mbar from -1.2853 to -1.2848), for 1.1 Mbar from -0.782 to -0.780 and for 1.8 Mbar from -0.342 to -0.339.
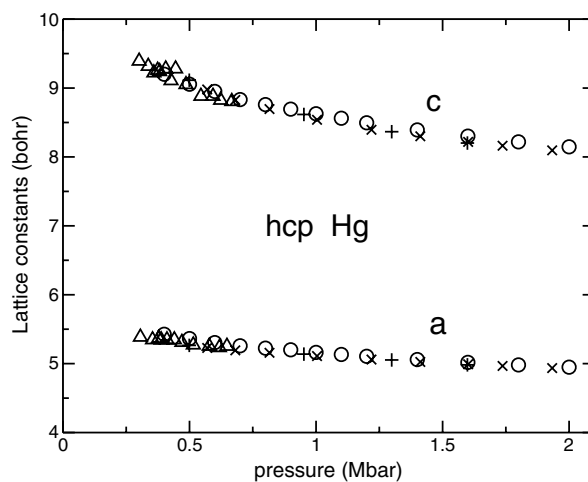

Figure 2. Lattice parameters a and c of hcp Hg as functions of pressure: crosses and plusses, Takemura *et al* experiments [1]; open triangles, Schulte and Holzapfel experiment [8]; open circles, this work.

figure 4 shows the calculated equation of state $V(p)$. In each figure the experimental results of Takemura *et al* [1] and of Schulte and Holzapfel [8] are shown. The agreement with experiment varies for a from 1.5 to 0.6% at low and high pressures, respectively: for c from 0.4 to 0.8%, for c/a from 2.4 to 0.5% and for the volume/atom from 2 to 3%.

3. Discussion

Rigid-lattice first-principles calculations of structural parameters as functions of pressure based on density functional theory with the GGA should not be expected to agree with experiment
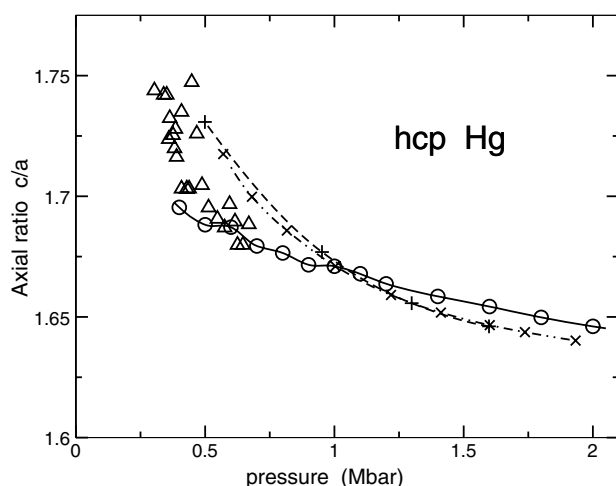
Figure 3. Axial ratio c/a of hcp Hg as a function of pressure: crosses and plusses, Takemura *et al* experiments [1]; open triangles, Schulte and Holzapfel experiment [8]; open circles, this work.
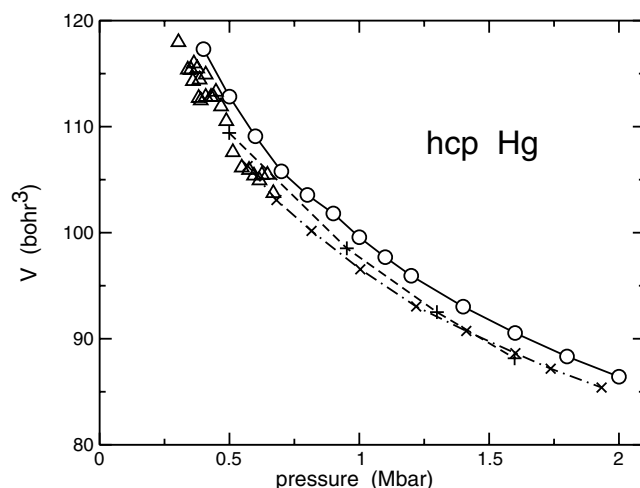

Figure 4. Equation of state of hcp Hg: crosses and plusses, Takemura *et al* experiments [1]; open triangles, Schulte and Holzapfel experiment [8]; open circles, this work.

better than at the 1% level for at least two reasons: (1) the GGA can overestimate equilibrium lattice parameters in the 1% range; (2) lattice vibrations, even at temperatures near 0 K, can produce changes in lattice parameters in the 1% range, e.g., the phonon spectra calculations of Quong and Liu [16] show that the zero-point vibrations increase the lattice parameters from the rigid-lattice values by 1.3% in bcc Li, by 0.4% in bcc Na and by 0.1% in fcc Al.

Determination of phase-transition pressures from rigid-lattice calculations is less accurate than determination of the lattice vectors. The transition pressures correspond to the intersection of $G(p)$ functions for the two phases involved. The $G(p)$ values are much more sensitive to the effects of lattice vibrations than the lattice vectors. Thus from Debye theory the energy of zero-point vibrations (ZPE) is proportional to the Debye theta Θ_D and $\Theta_D \propto V^{-\gamma_G} \propto a^{-3\gamma_G}$, where γ_G is the Grüneisen parameter with values typically between 1.5 and 2. Hence Θ_D, ZPE

and the change δG of G due to ZPE vary as a^{-5} or a^{-6}. This sensitivity of G to changes in a, which is different in different phases whose ZPE are different, can move the intersection point of $G(p)$ curves substantially, particularly if the $G(p)$ curves are nearly parallel, as is common. The transition pressures in [10] served to separate the phases of Hg, but are not accurate because the effects of lattice vibrations were not considered and also because the intersections of energy curves rather than free-energy curves were used to find the transition pressures.

A measure of the improvement in the accuracy of band calculations since the calculations in [10] were made is provided by comparison of the values of structural parameters of hcp Hg from [10] and here. The values of $a(p)$ and $c(p)$ separately are not given in [10], but figure 3(c) gives $(c/a)(p)$. The value of c/a at $p = 0$ is 25% higher than found here and in the experiment, and the value at $p = 0.5$ Mbar is 10% higher than here. Although [10] is a first-principles calculation, it used a model potential made up of structure-independent but volume-dependent pair interactions plus a volume-dependent term now replaced by the Kohn–Sham plus GGA potential.

Acknowledgment

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