

## On the relative stability of orthorhombic and hcp phases of beryllium at high pressures

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2000 J. Phys.: Condens. Matter 12 8831

(<http://iopscience.iop.org/0953-8984/12/41/309>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.221

The article was downloaded on 16/05/2010 at 06:53

Please note that [terms and conditions apply](#).

## On the relative stability of orthorhombic and hcp phases of beryllium at high pressures

B Palanivel†, R S Rao, B K Godwal and S K Sikka

†High Pressure Physics Division, Bhabha Atomic Research Center, Mumbai 400 085, India

Received 28 June 2000, in final form 14 August 2000

**Abstract.** High-pressure electronic properties of Be have been investigated theoretically by means of *ab initio* electronic structure calculations. The calculations have been carried out by the semi-relativistic full-potential, linear muffin-tin orbital (FPLMTO) method, within the local density approximation. The crystal structure stability among the hcp, bcc and orthorhombic (distorted hcp) phases has been studied as a function of compression. The bcc structure is found to be energetically stable at pressures above 180 GPa. From the results of our calculations, the orthorhombic phase cannot occur as an intermediate phase between the ambient pressure hcp phase and the high-pressure bcc structure. Our work thus suggests the need for more accurate high-pressure x-ray data.

Beryllium is an important technological material of significant interest to basic research. Under ambient conditions it has a hexagonal closed-packed (hcp) structure. It transforms into a body-centred cubic (bcc) structure at 1538 K with a decrease in the molar volume of about 6% at ambient pressure (Martin and Moore 1959). The temperature of the hcp–bcc phase transition decreases with pressure, and the initial slope  $dT/dP$  of the phase boundary is about  $-60^\circ \text{GPa}^{-1}$  (Pistorius 1976). As a consequence of this negative slope, the stability region of the hcp phase in the  $P$ – $T$  space would reduce with an increase of pressure, and at room temperature and high pressure the hcp phase would eventually transform into the bcc phase.

The *in situ* x-ray diffraction measurements of Ming and Manghnani (1984) indicated a phase transformation in the pressure range of 8.6–14.5 GPa. In those measurements, only three additional superlattice reflections up to  $1.5 \text{ \AA}$  of the  $d$ -value were observed. The authors indexed all the observed peaks on an eight-atom supercell of the hcp structure, with a doubling of the lattice constant in the  $a$ – $b$  plane. However, they did not determine the atomic coordinates in the structure. Vijayakumar *et al* (1984) studied Be under high pressure using an electrical resistivity technique, and observed a small plateau in the resistance against pressure curve in the 5–5.5 GPa range. With an increase of pressure the resistance was again found to gradually decrease with a small hump, followed by a slight decrease (over a range of 0.5 GPa) at 12 GPa. This behaviour was in sharp contrast with that measured earlier by Marder (1963), who had noted a sharp resistance drop of 45% around 9.3 GPa, showing the drift of resistance with time, a characteristic of a first-order phase transition. Vijayakumar *et al* (1984) suggested a sluggish phase transition at 12 GPa, and also reinterpreted the x-ray data of Ming and Manghnani (1984) by indexing on a smaller orthorhombic (distorted hcp) cell in the space group  $P2_12_12_1$ ,

† Visiting scientist, present and permanent address: Department of Physics, Pondicherry Engineering College, Pondicherry 605104, India

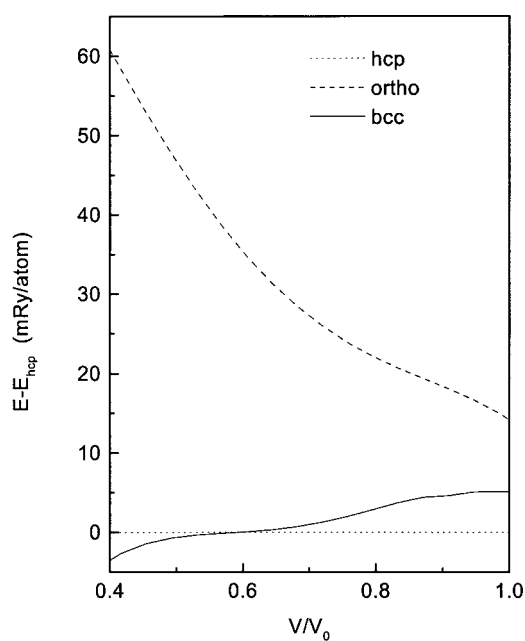
consisting of four atoms. As the parent hcp structure can be accommodated in the orthorhombic cell, the transition can be obtained continuously with a small volume change.

On the theoretical side Be was studied by Perrot (1980) using the augmented plane wave (APW), linear muffin-tin orbital (LMTO) and *a priori* model potential methods for the total energy and pressure. Perrot (1980) found the results of the APW and LMTO methods in reasonable agreement with each other and in poor agreement with the calculations based on the model potential values. Boettger (1995) using linear combinations of the Gaussian-type orbitals filling function (LCGTO-FF) technique obtained equilibrium properties such as the lattice constants,  $c/a$  ratio, cohesive energy, bulk modulus and Poisson ratio to be in agreement with other theoretical methods. Using a linearized muffin-tin orbital method within the atomic sphere approximation (LMTO-ASA), McMahan (1982) predicted that the hcp–bcc transition would occur in Be below 200 GPa with a volume change of 1–2%. Moreover, assuming an exceptionally high value of Debye temperature for hcp Be in the calculations, McMahan suggested the possibility of this structural transition to occur at much lower pressures (around 20 GPa) as a result of the zero point contribution to the total energy. However the current experimental values of the Debye temperatures of hcp metals by Gopi Krishna and Sirdeshmukh (1998) reveal that its value for hcp Be is much lower, (897 K) and hence the hcp–bcc transition is unlikely to occur at pressures much lower than 200 GPa. In view of the accuracy limitations of the LMTO-ASA calculations, we have now carried out the first-principles total energy calculations by the more accurate full-potential, linear muffin-tin orbital method (FPLMTO), to resolve some of the above controversies. Our findings are reported below.

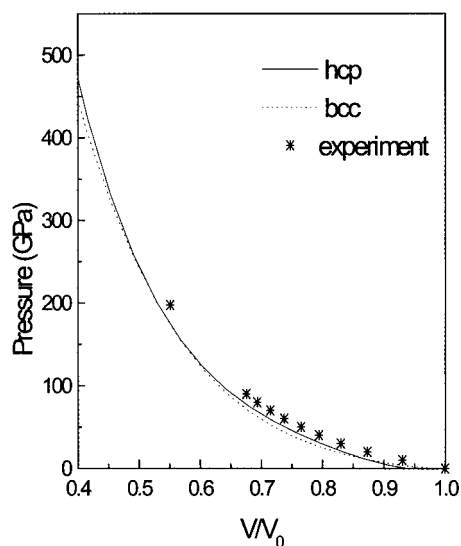
We employed Methfessel's version of the FPLMTO (Methfessel 1988). The LMTOs with  $l \leq 4$  of energies  $-0.01$ ,  $-1.0$  and  $-2.3$  Ry were chosen as basis functions. The scalar relativistic effects were included, and Hedin–Lundquist local density approximation (LDA) was employed (Hedin and Lundquist 1971). We used a common orthorhombic cell as the hcp and bcc structures can be accommodated in it. This choice of a common Brillouin zone (BZ) ensures the same  $k$ -points sampling in different structures. 152  $k$ -points were sampled in the irreducible part of the Brillouin zone. The four Be atoms corresponded to the 4c positions in the space group  $P2_12_12$ , and the position coordinates  $(3/4, 5/6, 3/4)$  gave the hcp structure, whereas the orthorhombic phase (Vijayakumar *et al* 1984) corresponded to the position  $(0.67, 0.82, 0.70)$ . Note that the atoms in the bcc structure corresponded to the  $(3/4, 3/4, 3/4)$  position with a change in the axial ratio of the orthorhombic cell to  $\sqrt{2}$  times the cubic lattice constant. In these calculations, we employed the  $c/a$  axial ratio in the hcp as well as distorted hcp structures at experimental values (Vijayakumar *et al* 1984). The total energies were evaluated in the hcp, bcc and orthorhombic (distorted hcp) structures, up to the pressure of about 450 GPa. In the hcp phase, our estimates show about a 2% contraction in the lattice constant (with a fixed axial ratio) as compared to the experimental data (Silversmith and Averbach 1970), which is within the limits of the LDA-based first-principles calculations.

Figure 1 shows the results from the total energy calculations at 0 K for the different structures. These results show that the hcp phase is more stable than the orthorhombic phase and the deviation in energy between them increases with increasing pressure. On the other hand, the bcc structure becomes more stable with respect to hcp structure above 180 GPa. These results on the structural stability of the bcc phase are consistent with earlier theoretical investigations on Be under compression (McMahan 1982).

To obtain the equation of state, we calculated the pressure at each volume from the contributions arising from the conduction electrons evaluated by the FPLMTO method, by fitting the total energies to a polynomial. We also included the pressure arising from the zero point vibrations (Godwal and Jeanloz 1989). The calculated 0 K equation of state for hcp Be (figure 2) is in good agreement with the reduced shock data up to 200 GPa (Marsh 1980, Nellis



**Figure 1.** Variation of the total energy (per atom) with the compression of Be in bcc (full curve) and orthorhombic (broken curve) structures, plotted with respect to that of hcp structure at each compression.  $V_0$  is the volume at ambient pressure.

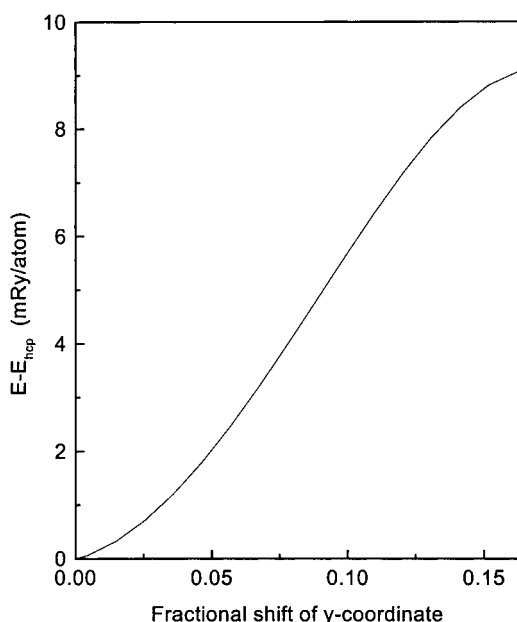


**Figure 2.** Curves of the equations of state of Be in the hcp and bcc structures. The reduced 0 K shock experimental data (Marsh 1980, Nellis *et al* 1988) have also been shown for comparison.

*et al* 1988). The equation of state curves of the hcp and bcc phases show little change from each other (see figure 2). We obtained a bulk modulus of 136 GPa, which is in good agreement with other theoretical estimates (in the range 126–131 GPa by Boettger (1995) and 110 GPa by McMahan (1982)), although experimental data show a lower value of 110 GPa.

The present calculations do not support the reported hcp–orthorhombic transition, based on the observed x-ray diffraction data between 8 and 12 GPa. (Ming and Manghni 1984, Vijayakumar *et al* 1984). Also, apart from the pressure-induced broadening of the bands, their structure with respect to the Fermi level remains the same under compression in the hcp phase. In particular, no electronic (Lifshitz 1960) transition is seen near 5.5 GPa (at which a small anomaly was observed in the resistivity data of Vijayakumar *et al* 1984) from the details of band structure results.

To see whether some other set of coordinates in the  $4c$  position of  $P2_12_12$  might give a lower energy, we calculated the total energies for some random sets of coordinates. The energy changes at 10 GPa for a typical variation in the  $y$ -coordinate from the hcp position are shown in figure 3, and are seen to correspond consistently to higher energy. Similar results were obtained for variations in other coordinates from the hcp position.



**Figure 3.** Variation in the total energy of Be at 10 GPa when the  $y$ -coordinate of the  $4c$  position of the space group  $P2_12_12$  is changed from that of the hcp position.

In order to obtain an understanding of the temperature effects on the relative stabilities, as the high-pressure experimental data were obtained at room temperatures, we adopted the method described below. The differences in the free energies ( $\Delta F$ ) between the two structures at a given volume could be written as

$$\Delta F = \Delta E_{cold} + \Delta E_{thermal} - T \Delta S$$

where  $\Delta E_{cold}$  and  $\Delta E_{thermal}$  are the cold and lattice thermal contributions to the total internal energies, respectively, and  $T \Delta S$  is the entropy contribution. The thermal and zero point contributions were evaluated following the methods adopted by Godwal and Jeanloz (1989). We employed the theoretically evaluated bulk moduli to estimate the Debye temperatures ( $\theta_D$ ) in various phases, and we obtained a value of 1270 K in the hcp phase, which is somewhat higher than the experimental value of 897 K. However, we employed the theoretically estimated value in this case, so as to have consistency in our relative estimates of the thermal and zero point

contributions among the various phases. Our estimates of  $E_{thermal}$  for the hcp and orthorhombic phases at ambient pressure, and at  $V/V_0 = 0.88$  (i.e. about 10 GPa pressure, around which the x-ray diffraction data were indexed on an orthorhombic cell), are shown in detail in table 1. The calculated values of table 1 give  $[(E_C + E_{thermal})_{ortho} - (E_C + E_{thermal})_{hcp}] = 16.7$  mRy/atom. If we had used the experimental value for  $\theta_D$ ,  $E_{thermal}$  in the hcp phase would have been less by about 2 mRy/atom and, as per the comparison made below, would further lead to increase the stability of the hcp phase. Also note that in magnesium, which belongs to the same group of the periodic table as Be, it has been shown that the deviations from the classical value of the thermal energy have a negligible impact on the hcp–bcc phase line. Regarding the entropy contribution, an order of magnitude estimate can be obtained from the  $\Delta S$  value between hcp and bcc phases evaluated by Willaime and Massobrio (1989). They estimated this term, by molecular dynamics simulations, to be  $0.143k_B$  per atom, almost independent of temperature. As the orthorhombic structure can be treated as a distortion of the hcp towards the bcc structure, the use of  $\Delta S_{hcp \rightarrow bcc}$  would provide an upper bound for the intermediate orthorhombic structure. Hence at room temperature, the free energy difference due to entropy is about 0.3 mRy/atom. This is more than an order of magnitude smaller than the  $\Delta(E_C + E_{thermal})$  estimated above. Thus the existence of the intermediate orthorhombic phase between the hcp and bcc structures around the 10 GPa pressure range is not supported by our calculations. Note that  $\Delta E_{cold}$ , as evaluated by our FPLMTO calculations, is more than 15 mRy/atom higher in energy for the orthorhombic phase as compared to the hcp or bcc phases, and the difference keeps increasing with higher compression (see figure 1). With such a large structural energy difference, it is unlikely that the improvements such as the generalized gradient approximation (Perdew *et al* 1996, 1999) to the exchange–correlation terms in the total energy would alter the present conclusions. However, as the resistance measurements (Marder 1963, Vijayakumar *et al* 1984) had shown some abrupt or sluggish changes with pressure, some other structure not explored in the present work could be a possible cause.

**Table 1.** Comparison of the various energy terms contributing to free energy at ambient pressure and at 10 GPa for the hcp and orthorhombic phases.

Parameter	Ambient pressure		$V/V_0 = 0.88$ (i.e. 10 GPa)	
	hcp	orthorhombic	hcp	orthorhombic
Grüneisen parameter ( $\gamma$ )	2.1	1.1	1.93	1.05
Debye temperature ( $\theta_D$ ) (K)	1270	1160	1640	1260
Zero point energy ( $E_{zero}$ ) (mRy/atom)	9.04	8.28	11.60	9.01
Lattice thermal energy ( $E_{lattice}$ ) (mRy/atom)	1.60	1.58	0.54	0.81
$\Delta E_C$ with respect to hcp (mRy/atom)	0	14.3	0	19.0
$E_{thermal} = E_{zero} + E_{lattice}$ (mRy/atom)	10.64	9.86	12.14	9.82

The present studies point out the need for more accurate experimental data under pressure for Be. The availability of intense synchrotron x-ray sources, coupled with an angle dispersive x-ray diffraction facility and incorporating an imaging plate as an area detector, can provide the necessary data for the low- $Z$  element Be. It may also be instructive to study the structural properties of Be under compression by constant pressure *ab initio* molecular dynamics simulations, avoiding tedious structural search by trial and error, in order to look for the possible intermediate phase between hcp and bcc structures.

**References**

- Boettger C J 1995 *Int. J. Quant. Chem.* **29** 197
- Godwal B K *et al* 2000 to be published
- Gopi Krishna N and Sirdeshmukh D B 1998 *Acta Crystallogr. A* **54** 513
- Hedin L and Lundquist B I 1971 *J. Phys. C: Solid State Phys.* **4** 2064
- Lifshitz I M 1960 *Zh. Eksp. Teor. Phys.* **38** 1569 (Engl. transl. 1960 *Sov. Phys. JETP* **11** 1130)
- Marder A R 1963 *Science* **142** 664
- Marsh S P (ed) 1980 *LASL Shock Hugoniot Data* (Berkeley, CA: University of California Press)
- Martin A J and Moore A 1959 *J. Less Common Metals* **1** 85
- McMahan A K 1982 *AIP Conf. Proc.* **78** 340
- Methfessel M 1988 *Phys. Rev. B* **38** 1537
- Ming L C and Manghnani M H 1984 *J. Phys. F: Met. Phys.* **14** L1
- Nellis W J *et al* 1988 *Phys. Rev. Lett.* **60** 1414
- Perdew J P, Burke K and Ernzerhof M 1996 *Phys. Rev. Lett.* **77** 3865
- Perdew J P, Kurth S, Zupan A and Blaha P 1999 *Phys. Rev. Lett.* **82** 2544
- Perrot F 1980 *Phys. Rev. B* **21** 3167
- Pistorius C W F T 1976 *Progress in Solid State Chemistry* vol 1, ed J O McCaldin and G Somorja (New York: Pergamon)
- Silversmith D J and Averbach B L 1970 *Phys. Rev. B* **1** 567
- Vijayakumar V, Godwal B K, Vohra Y K, Sikka S K and Chidambaram R 1984 *J. Phys. F: Met. Phys.* **14** 165
- Willaime F and Massobrio C 1989 *Phys. Rev. Lett.* **63** 2244