Equations of state for barium in high-pressure phases

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Abstract
The universal equation of state with an arbitrary reference point presented by the author (Fang Zheng-Hua 1998 *Phys. Rev.* B **50** 16 238) is applied successfully to the analysis of the experimental compression data of barium in different structural phases (I, II, and V). The comparison given in this paper shows that this equation suits for the isothermal compression behaviour of barium in the high-pressure phases (II and V) better than the Birch–Murnaghan equation. The applicability of equations of state for solids in high-pressure phases is also discussed.

1. Introduction

In 1994, Takemura [1] investigated the crystal structures of barium over a wide pressure range at room temperature using x-ray diffraction techniques. He reported that at room temperature barium has one bcc phase I and two hcp phases, II and V, under pressures of up to 90 GPa. The experimental compression data of barium in these phases were also presented.

Later, Zeng *et al* [2] studied theoretically the structural features of barium in terms of electronic structure calculations and Nelmes *et al* [3] studied experimentally the structure of phase IV of barium that was not solved in [1]. The fact that Takemura [1] found no suitable equation of state for all the phases of barium has attracted little attention till now.

In [1], the pressure and volume data of each phase were fitted with the Birch–Murnaghan equation of state in the following form [4]:

$$P = \tfrac{3}{2} B_0 (x^{-7} - x^{-5})[1 + \tfrac{3}{4}(B_0' - 4)(x^{-2} - 1)] \tag{1}$$

where P is the pressure, $x = (V/V_0)^{1/3}$, V is the volume, and V_0 is the volume at zero pressure, B_0 and B_0' are, respectively, the isothermal bulk modulus and its first pressure derivative, both at zero pressure. Equation (1) has been widely used in geophysics and high-pressure physics [5,6]. However, Takemura [1] found that the fits were not always satisfactory and that the Birch–Murnaghan equation of state failed to fit the experimental compression data of phase II. So, instead of equation (1), a polynomial equation in the following form for phase II was used:

$$P = B_0(1 - V/V_0)[1 + \tfrac{1}{2}(1 + B_0')(1 - V/V_0)]. \tag{2}$$

Large errors inherent in the extrapolation of the equations of state of the high-pressure phases to zero pressure are shown. In order to get good convergence Takemura had to take a fixed value for B_0' in the fits for phases II and V, which is physically non-natural.

Equations (1) and (2) as well as most other isothermal equations of state, such as the universal equation of state (UEOS) [7], and the Murnaghan equation of state [8], have a common feature: the free parameters, B_0 and B_0' correspond to the zero-pressure thermodynamic quantities of the solid under study, which implies that in these equations of state the reference point is fixed at zero pressure. Therefore, when applying these equations to a solid in the low-pressure phase, i.e. phase I, there are only two adjustable parameters, B_0 and B_0' to be determined for the normal volume V_0 of the solid which can be measured directly. However, there is a restriction on applying these equations to a solid in high-pressure phases because the zero-pressure volume of the solid in high-pressure phases is actually not in existence and so it cannot be determined.

Recently, in a brief report [9] the author pointed out that there are two defects in applying the UEOS or other equations with the same zero-pressure boundary condition as that of the analysis of the experimental data for the isothermal compression of solids in high-pressure phases. One defect is that the fitting parameters in the equation have actually little physical meaning because these parameters correspond to the thermodynamic quantities for a non-existent state; the other defect is that the fitting parameters are increased from the original two (B_0 and B_0') to three (B_0, B_0', and V_0) (unless B_0', is fixed in advance, as was done in [1]). In order to eliminate the above defects, the author [9] presented the UEOS with an arbitrary reference point as follows:

$$P - P_r = \frac{3Br(1-y)}{y^2} \exp\left[\frac{3}{2}(B_r' - 1)(1-y)\right] \tag{3}$$

where the subscript r denotes the reference point, $y = (V/V_r)^{1/3}$. Equation (3) has been applied successfully to the isothermal compression of ten metal halides as well as cerium all in high-pressure phases [9]. However, since the test presented in [9] involves only the first structural phase transition for these solids. i.e. phase II, whether equation (3) suits for more structural phases of a solid, as in cases of barium, still needs to be tested. In this paper the validity of equation (3) for barium at different structural phases will be examined and the applicability of equations of state for a solid in high-pressure phases will be discussed further. In view of the fact that hitherto there is no suitable equation of state reported in the literature for barium in all structural phases, the test as well as the discussion are of interest.

The paper is organized as follows. In section 2 the test on the validity of equation (3) for barium will be presented and the comparison with equations (1) and (2) are also given. The discussion on the applicability of equations of state for a solid in high-pressure phases will be given in section 3. The conclusions are given in section 4.

2. Test and comparison

When applying equation (3) to the analysis of the experimental isothermal compression data of barium in each phase, we may simply fix the reference point (P_r, V_r) at the low-pressure end of the phase under study. Because the reference volume V_r can be measured directly [1], there are only two adjustable parameters, i.e. the isothermal bulk modulus B_r, and its first pressure derivative B_r' both at the reference point (P_r, V_r), to be determined in equation (3). The values of B_r and B_r' obtained by the fitting to the experimental data [1] of barium in each phase with equation (3) are all listed in table 1. In order to examine the validity of equation (3), we calculated the curves of pressure versus volume compression V/V_0 for barium at these phases

Table 1. Data for barium at the reference points (P_r, V_r) in phase I, II and V. Where V_0 denotes the normal volume, i.e. the volume of phase I at atmospheric pressure.

Phase	P_r (GPa)	V_r/V_0	B_r (GPa)	B'_r	EOS
I	0	1.0000	7.6	3.5	(3)
			7.7	3.4	(1) [1]
II	5.9	0.6479	11.7	5.1	(3)
V	48	0.3302	145.9	9.5	(3)
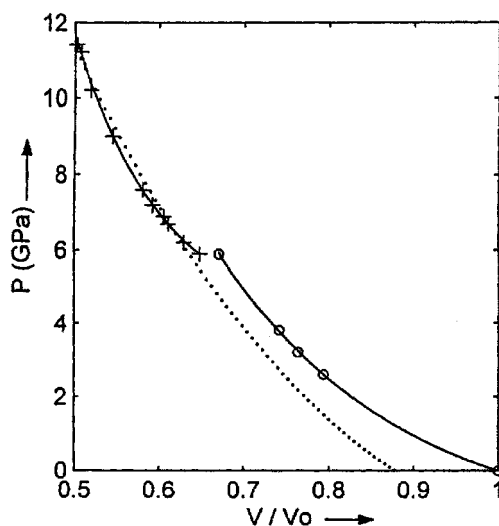
Figure 1. The pressure–volume ratio for barium in phases I and II ——: equation (3) for phases 1 and 2, respectively; ······: equation (2) for phase II. The symbols ○ and + denote, respectively, the experimental points [1] for phases I and II. The curve given by equation (1) for phase I coincides with that given by equation (3).

using the values of the input parameters listed in table 1. For convenience of comparison, the corresponding experimental data [1] as well as the results given by equations (1) and (2) using the values of the free parameters reported by Takemura [1] are all shown in figures 1 and 2.

Since the normal volume V_0 i.e. the volume of barium in phase I at atmospheric pressure is known, the compression of barium at different phases are all transferred into the normal volume compression V/V_0, as presented in figures 1 and 2. In the case of phase I, $V_r = V_0$ and $P_r = 0$, equation (3) is equal to the UEOS given by Vinet *et al* [7] and the volume compression V/V_0 is directly given by this. While in cases of phases II and V, the relative volume compression V/V_r obtained from equation (3) has been transferred into the normal volume compression V/V_0 using the values of V_r listed in table 1.

3. Discussion

The above tests have shown that equation (3) describes the isothermal compression behaviour of barium in different phases very well. From figures 1 and 2 we can see that the calculated results given by equation (3) are in good agreement with the corresponding experimental data of barium in all phases (I, II, and V), and the fitting accuracy of equation (3) is even better than that of equations (1) and (2) in cases of phases II and V. The root mean square deviations (RMSD)
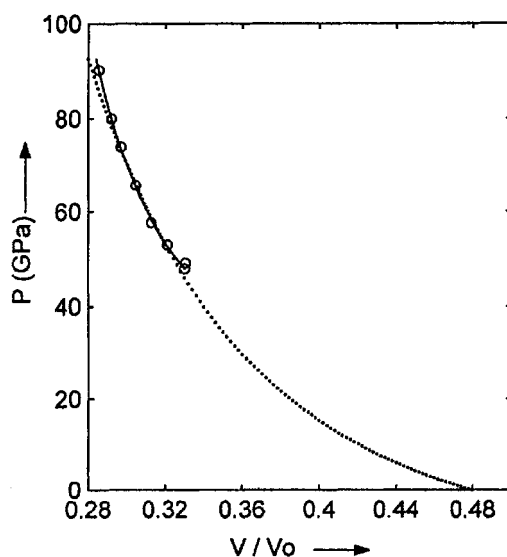
Figure 2. The pressure–volume ratio for barium in phase V. ——: equation (3) ······: equation (1); o: exp [1].

between the calculated values of V/V_0 and its experimental values given by equation (3) are 0.0019 of phase II and 0.0013 for phase V, but 0.0065 given by (2) for phase II and 0.0026 by (1) for phase V.

When applying equation (3) to the analysis of the experimental compression data of a solid in the low-pressure phase, i.e. phase I, we may simply set $P_r = 0$ and $V_r = V_0$, thus equation (3) is reduced to the UEOS of Vinet *et al* [9]. While the isothermal bulk modulus B_0 and its first pressure derivative B_0' both at zero pressure are obtained by fitting with equation (3), as is the same as with equations (1) or (2). For phase I the values of B_0 and B_0' determined by equation (3) are in close agreement with the reported values [1] determined by equation (1), as seen from table 1, and the fitting accuracies of equations (3) and (1) are also about the same for the curve given by (1) coinciding with that given by (3) very well.

However, the applicability of equation (3) for barium in phases II and V is quite different from that of equations (1) or (2). The advantage of equation (3) in the analysis of isothermal compression behaviour of solids in high-pressure phases is that we may choose one of the measured states (P_r, V_r) as the reference point, then the adjustable parameters B_r and B_r' correspond respectively to the isothermal bulk modulus and its first pressure derivative at the reference point. As for equations (1) or (2), the restriction of the zero-pressure boundary condition leads [9] to the adjustable parameters in the equation being increased and the fitting for barium in phases II and V has to be extrapolated to a non-existent state.

Besides the above defects I would like to point out that another serious fault is that the imaginary state cannot be uniquely determined. In [1], Takemura fixed artificially B_0' to 4.0 for phases II and V in order to get good convergence in the first, which is physically non-natural. As a matter of fact, there are numerous values suitable for B_0 if only the fitting accuracy is considered in the fits with equation (1) or (2). In order to demonstrate this point, we fit the experimental data of barium in phase V with equation (1) using different values for B_0'. The zero-pressure volume V_{h0}, (here we write V_{h0} for the zero-pressure volume so as to distinguish it from the normal volume V_0) and the corresponding bulk modulus B_0 thus determined, as

Table 2. Values of V_{h0}, B_0, and RMSD obtained by equation (1) using different values of B_0' for phase V.

B_0' (fixed)	V_{h0}/V_0	B_0 (GPa)	RMSD
2	0.3968	210.4	0.0030
4 [1]	0.48	58	0.0026
6	0.6253	11.4	0.0018
8	0.7186	4.17	0.0018
10	0.7666	2.34	0.0018

well as the RMSD obtained by equation (1) using these parameters (B_0, B_0', and V_{h0}), are all reported in table 2. From table 2 we can see that, as pointed out above, the fictitious zero-pressure volume or the imaginary state is uncertain because it depends on the values chosen for B_0', moreover, the same fitting accuracy may be obtained with equation (1) using these different values of parameters so that we cannot tell which of the imaginary states is superior. In fact, if B_0' is not fixed then the imaginary state is, in the same way, uncertain, for it depends on the input initial values of the free parameters that are necessary in the fitting.

In view of the above facts, we think that the extrapolation of the equation of state from the high-pressure phase to zero pressure is physically meaningless. Considering that equation (3) can eliminate successfully all the defects mentioned above, it is reasonable to think that the validity of equation (3) for the isothermal behaviour of solids in high-pressure phases is better. It is of much interest to note that the reference point may be fixed at the low-pressure end of a high pressure phase displays superiority of equation (3) used for solids in the high pressure phases, and equation (3) is obtained from the UEOS by scaling the pressure and volume for a high-pressure phase such as $P_s = P - P_r$ and $V_s = V/V_r$ [9]. Therefore, if one hopes to use the Birch–Murnaghan equation of state or other equations with the same zero-pressure boundary condition as for solids in high-pressure phases, the scale of the pressure and volume for a fitting reference point should be recommended strongly.

4. Conclusions

Equation (3) suits for barium in different structural phases very well. In the case of phase I, equation (3) is reduced to the UEOS [7] and the applicability of it is the same as that of equation (1). In cases of phases II and V, the applicability of equation (3) is clearly better than equations (1) and (2) as well as those equations with the fixed zero-pressure reference point. This is because when applying the equations with the fixed zero-pressure reference points to a solid in high-pressure phase, not only do the free parameters correspond to the zero-pressure thermodynamic quantities for the state that is actually not in existence, but also the imaginary state cannot be uniquely determined. However, these defects have nothing to do with the use of equation (3).

In view of this work as well as that done in [9], we think that equation (3) should be recommended for solids in high-pressure phases.

Acknowledgment

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