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The search for a universal equation of state correct up to very high pressures

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Abstract. The universal equations of state of solids recently proposed by several authors have been examined by comparing them with the theoretical results calculated by the augmented-plane-wave method and the quantum-statistical model proposed by Kalitkin and Kuz'mina from low to ultra-high pressures. It has been shown that the Vinet equation is in good agreement with the theoretical results both for the P - V relation and for the pressure dependence of the isothermal bulk modulus up to 10 TPa ($V/V_0 = 0.20$) for monatomic solids and up to 1 TPa ($V/V_0 = 0.35$) for diatomic solids. The Kumari-Dass and the Dodson equations become less successful below $V/V_0 = 0.7$ if the zero-pressure values for B_0 , B'_0 and B''_0 are used. For monatomic solids the Holzapfel equation has a very similar structure to that of the Vinet equation at low and medium compressions and it is in good agreement with the theoretical values up to ultra-high pressures. For the application to polyatomic solids a remedy for the shortcomings of the Vinet equation at very high pressures is given on the basis of the quantum-statistical model. The resulting equation is in good agreement with the theoretical values from low to ultra-high pressures both for monatomic and for diatomic solids.

1. Introduction

The equation of state (EOS) is fundamentally important in studying the high-pressure properties of solids. Up to now a number of workers have endeavoured to search for a simple form of the EOS of solids which has a small number of parameters and predicts correct high-pressure behaviours irrespective of the material. The parameters are determined by using available low-pressure data such as the volume V_0 , the isothermal bulk modulus B_0 and its pressure derivatives B'_0 and B''_0 at zero pressure. Hitherto the Murnaghan [1] and the Birch [2] equations have been used widely in high-pressure physics and geophysics to analyse experimental data. These EOSs are, however, derived from the second-order Taylor series expansion of the bulk modulus or the elastic strain energy with respect to pressure or strain, so their validities are, in principle, restricted to a narrow range of compression unless the high-order terms are taken into account. This is why the values of B_0 , especially those of B'_0 and B''_0 obtained from experiments which cover different ranges of compression by using a fitting method, are usually different. Though present-day first-principles calculations may predict the EOSs of solid accurately, they are time-consuming because the calculations have to be done individually for a number of volumes. If we find a correct form of the EOS, we can predict the high-pressure properties of solids with a little effort by determining the parameters from theoretical calculations or experimental data. Furthermore pressure, bulk modulus and its pressure derivatives are estimated usually

by fitting calculated numerical data to an appropriate equation such as the Birch equation instead of by numerical differentiation. Therefore the search for a universal form of the EOS of solids is still an important problem in high-pressure physics and geophysics. In the following we write out the Murnaghan and the Birch equations for later convenience:

$$P_M = 2(B_0/B'_0)(1 - x^\eta)/[\xi - 1 + (\xi + 1)x^\eta] \quad (1)$$

with $x = (V/V_0)^{1/3}$, $\xi = (1 - 2B_0B''_0/B_0'^2)^{1/2}$ and $\eta = 3\xi B'_0$, and

$$P_B = (3B_0/2)(x^{-7} - x^{-5})[1 + (3\xi/4)(x^{-2} - 1) + (\eta/2)(x^{-2} - 1)^2] \quad (2)$$

with $\xi = B'_0 - 4$ and $\eta = (3/4)(B_0B''_0 + B_0'^2 - 7B'_0 + 143/9)$. The EOS recently proposed by Parsafar and Mason (PM) [3]

$$P_{PM} = (B_0/2) [(B'_0 - 7) - 2(B'_0 - 6)x^{-3} + (B_0 - 5)x^{-6}]x^{-6} \quad (3)$$

belongs to this category, where the internal energy is expressed via density expansion up to the cubic term.

An extension of the Murnaghan equation was given by Kumari and Dass (KD) [4, 5] who took the higher-order terms in the Taylor series expansion into account by using the assumption that $B_0^{(n+1)}/B_0^{(n)} = -B_0''/B_0'$ for $n > 1$ with $B_0^{(n)}$ as the n th-order pressure derivative of the isothermal bulk modulus at zero pressure. The resulting KD equation is written as

$$P_{KD} = -(B'_0/B''_0) \ln \{ [1 + (\xi - 1)x^\eta]/\xi \} \quad (4)$$

with $\xi = 1 - B_0B''_0/B_0'^2$ and $\eta = -3B'_0\xi$. On the other hand, assuming a relation $B = [a(V_0/V)^{1/3} - b]^2$ with a and b as material constants, Dodson [6] obtained

$$P_D = (3/2)^3 B_0 B_0'^2 (x^{-2} - 4\xi x^{-1} - 2\xi^2 \ln x + 4\xi - 1) \quad (5)$$

with $\xi = 1 - 2/(3B'_0)$. Both of these EOSs are, however, based on empirical relations, so their validities are limited to the ranges within which the empirical relations are approximately correct. A more fundamental derivation was given by Vinet and co-workers [7, 8] who assumed the interatomic interaction in solids related mainly to compression to be expressed by a form $A(1 + ar) \exp(-br)$ with A , a and b as material constants, and derived

$$P_V = 3B_0x^{-2}(1 - x) \exp[\eta(1 - x)] \quad \eta = (3/2)(B'_0 - 1). \quad (6)$$

Recently these EOSs have been shown to be in much better agreement with experimental data than the previous EOSs given by Murnaghan and by Birch for a number of materials—metals, dielectrics and ionic solids, etc—if no phase transition is observed, though non-negligible differences exist between the fitted values of B_0 , B'_0 and B''_0 for each of the EOSs [9]. However, their derivations are quite different from one another, so the high-pressure behaviours beyond the range of the compression used for fitting may be different. Moreover, all of these EOSs have a fatal shortcoming in that they do not approach the correct theoretical values at extreme compressions [10]. Thus there remain some doubts as to whether all of these EOSs can predict correct pressures beyond the range used for fitting and whether they predict the high-pressure properties correctly when the real zero-pressure values are used for B_0 , B'_0 and B''_0 .

In this paper we shall discuss the validity of the EOSs recently proposed on the basis of theoretical calculations and propose a new form correct up to ultra-high pressures. We shall also discuss the temperature effect on the EOS and compare several isobars of MgSiO_3 with experimental data.

2. Comparison of the EOSs with theoretical results

In this section we shall compare the EOSs mentioned in section 1 with the theoretical results calculated by the augmented-plane-wave (APW) method [11] and by the quantum-statistical model (QSM) [12]. The latter, in which both the gradient correction to the kinetic energy and the exchange energy are included, gives the correct values at extreme compressions. The APW result tends, of course, to the QSM result at extreme compressions where the difference between the P - V relations for the crystal structures is negligibly small. Though the temperature effect on the EOS may be taken into account approximately by using the Debye model, which will be discussed in section 5, we shall restrict ourselves to the EOS in the static lattice in this section for the sake of definiteness and simplicity in the comparison. The theoretical values of B_0 , B'_0 and B''_0 are determined from the calculated pressures at about $V/V_0 = 1.05 - 0.85$ with V_0 as the calculated zero-pressure volume. In the following we shall call the solids with one (two) atom(s) in the unit cell monatomic (diatomic) solids.

Table 1. The theoretical values of V_0 (au), B_0 (GPa), B'_0 and B''_0 (GPa^{-1}), and the values of ζ in equation (20) determined by the QSM and the values of B''_0 calculated from equation (20) which are expressed as $[B''_0]$.

Material	V_0	B_0	B'_0	B''_0	ζ	$[B''_0]$
Ne	102.128	6.36	7.61	-2.86	-1.385	-2.94
Ar	210.517	6.28	7.07	-2.53	-1.414	-2.62
Al	109.600	72.6	4.85	-0.104	0.253	-0.105
Cu	78.137	135	5.93	-0.083	0.191	-0.082
LiH	101.947	39.1	3.51	-0.106	1.417	-0.086
MgO	123.747	157	4.37	-0.040	1.101	-0.036

In figure 1 pressure is plotted as a function of V/V_0 for monatomic solids. We select here four kinds of solid: (a) a typical sp metal Al(fcc) [14, 15], (b) a rare-gas metal Cu(bcc) [15, 16], (c) a substance which is the most difficult to metallize Ne(fcc) [13, 17] and (d) a large-gap insulator with a small bulk modulus Ar(fcc) [13]. In the figure P_M , P_B , P_{PM} , P_{KD} , P_D and P_V are also plotted. The theoretical values of V_0 , B_0 , B'_0 and B''_0 are tabulated in table 1. The figure shows that the Vinet equation is accurate up to about $V/V_0 = 0.2-0.3$ or up to about 10 TPa in pressure. On the other hand the Dodson, the KD and the Murnaghan equations deviate substantially from the theoretical EOSs for about $V/V_0 > 0.7$. It is interesting to note that the Birch equation is unexpectedly accurate up to about $V/V_0 = 0.40$: the sudden breakdown of the Birch equation at large compressions for metals (Cu, Al) results from η in equation (2) being negative for these substances in contrast to the rare-gas solids. The PM equation is very similar to the Birch equation, but it becomes less successful for about $V/V_0 < 0.65$. Similar behaviours are found for B/B_0 and ΔE (see section 3). In figure 2 similar plots are given for diatomic solids with a small bulk moduli, (a), LiH (B1) [11, 18]; and those with a large bulk modulus, (b), MgO (B1) [15]. The theoretical values of V_0 , B_0 , B'_0 and B''_0 are listed in table 1. The figure shows that the Vinet equation departs from the theoretical pressures at a larger value of V/V_0 for diatomic solids than for monatomic solids, but it is still in good agreement with theoretical values among the others. The breakdown of the Birch and the PM equations below about $V/V_0 = 0.35$ and 0.65 respectively results from these being derived from the lower-order Taylor series expansion of the corresponding energies with the respective expansion variables $\frac{1}{2}[(V_0/V)^{2/3} - 1]$ and $(V_0/V) - 1$: the density expansion converges

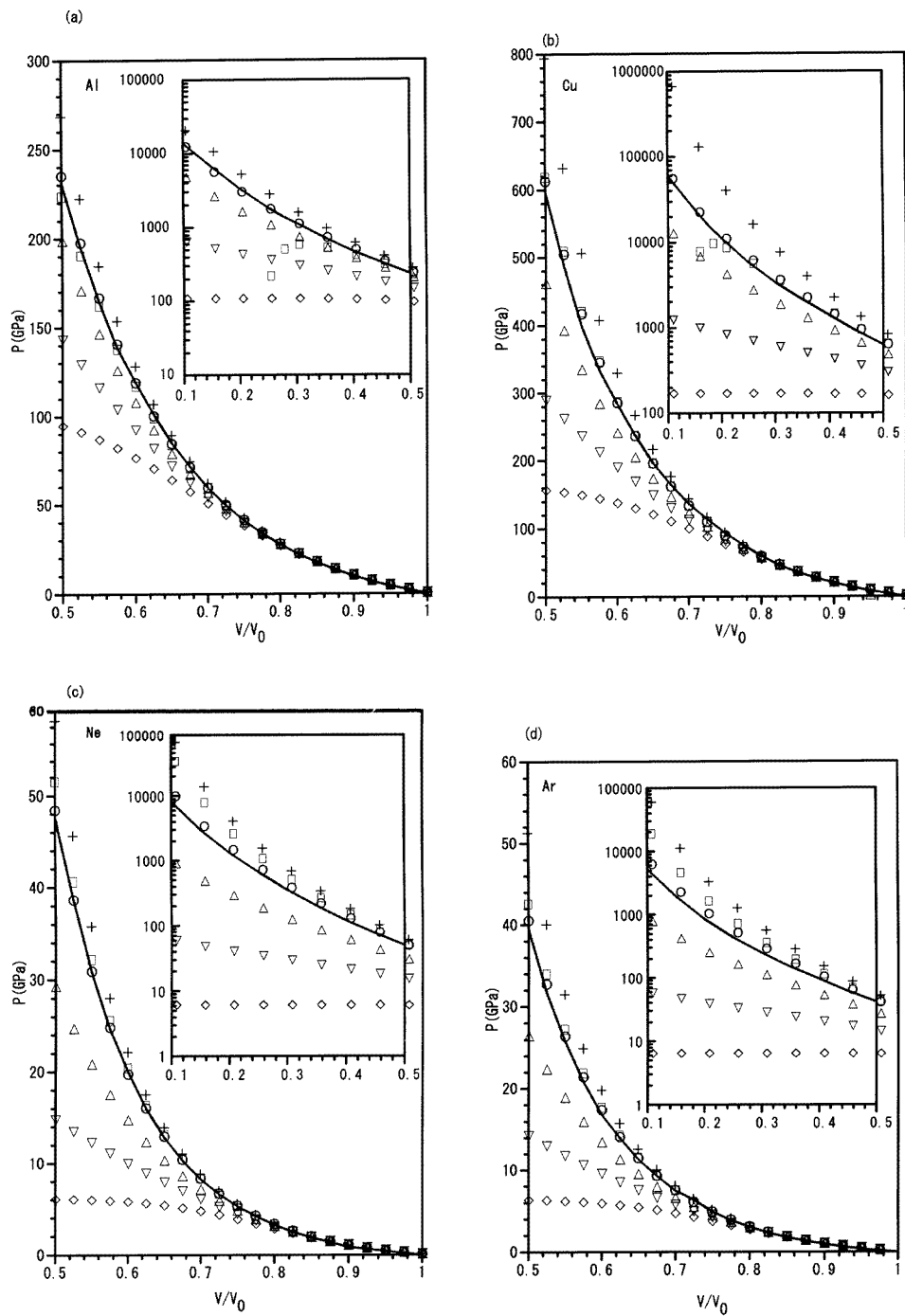


Figure 1. A comparison of the P - V curves of several EOSs with the theoretical results for monatomic solids. (a) Al, (b) Cu, (c) Ne and (d) Ar: solid line: theory; \circ : Vinet; \square : Birch; $+$: Parsafar-Mason; \triangle : Dodson; ∇ : Kumari-Dass; \diamond : Murnaghan. The parameters of the EOSs are determined by the theoretical values of V_0 , B_0 , B'_0 and B''_0 .

more slowly than the strain expansion. Judging from the present results the excellent agreement of the KD equation with the experimental data reported in [4], [5] and [9] seems fortuitous, though it may achieve good fitting if the parameters B_0 , B'_0 and B''_0 are adjusted by a fitting method. However, it is difficult to get a fitting beyond about $V/V_0 = 0.5$. The shortcoming of the KD equation at high pressures is easily understood from the fact that the bulk modulus of the KD equation approaches a constant, $B_0 - B_0^2/B'_0$, in the limit of extreme compressions contrary to the theoretical prediction (see figure 2). The Dodson equation is in moderate agreement with the theoretical results for monatomic metals, but large deviations are found for easily compressible solids at low pressures. As for diatomic solids, however, the agreement is moderate both for LiH and MgO. According to the spirit of a universal EOS it is desirable that B_0 , B'_0 and B''_0 are not adjustable parameters but the real values at zero pressure. Therefore the KD and the Dodson equations do not have the desired characteristics of a universal EOS.

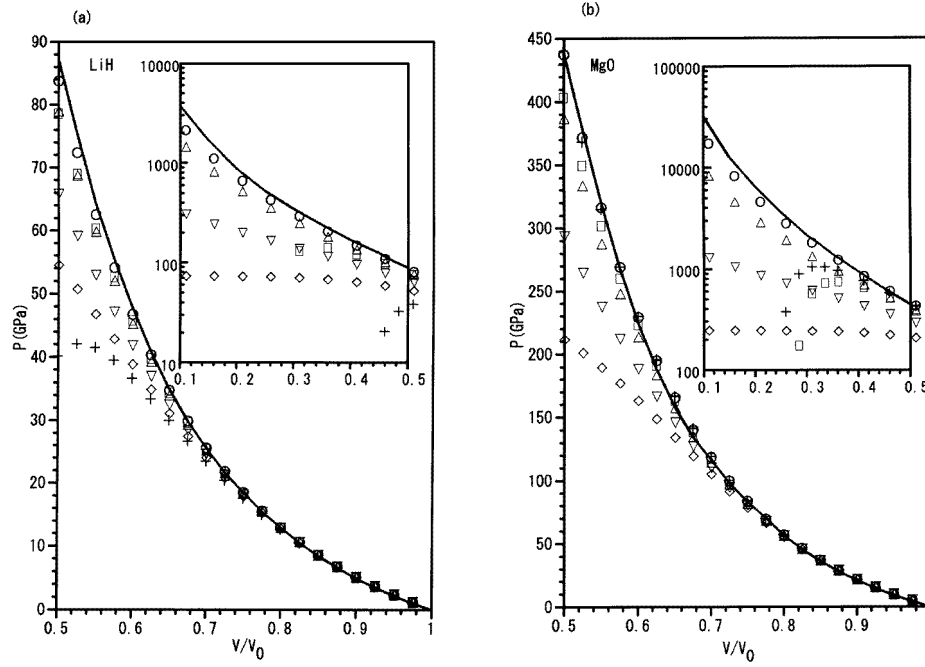


Figure 2. A comparison of the P - V curves of several EOSs with the theoretical results for diatomic solids. (a) LiH and (b) MgO: solid line: theory; \circ : Vinet; \square : Birch; $+$: Parsafar-Mason; \triangle : Dodson; ∇ : Kumari-Dass; \diamond : Murnaghan. The parameters of the EOSs are determined by the theoretical values of V_0 , B_0 , B'_0 and B''_0 .

The EOSs mentioned in section 1 can be classified into three categories:

(a) the derivative form (Birch, PM and Vinet equations):

$$P = -\partial E / \partial V$$

(b) the volume-integral form (the Dodson equation):

$$P = - \int_{V_0}^V \frac{B(V)}{V} dV$$

(c) the pressure-integral form (Murnaghan and KD equations):

$$\frac{V}{V_0} = \exp \left[- \int_0^P \frac{dP}{B(P)} \right]$$

with E as the total energy of a solid.

It is interesting to note that the derivative form is much better than the integral forms: the error at large compressions is much more exaggerated in the integral forms than in the derivative forms. The inadequacy of the Murnaghan and the KD equations at high pressures results from the error in $B(P)$ being enhanced greatly due to the exponential form. Therefore a more accurate estimate for B is required in the pressure-integral form: the pressure expansion of B becomes much less successful at large compressions than the $(V_0/V)^{1/3}$ -expansion of B because pressure is not an adequate expansion variable except for at low pressures. The bulk moduli, $B(P)$, approximated by the Murnaghan and the KD equations become less good at lower pressures than the other EOSs for every material investigated in the present paper if the real values are used for B_0 , B'_0 and B''_0 (see figure 3).

3. The bulk modulus and total energy

From the EOSs mentioned in section 1 we can derive the expressions for the bulk modulus and the total energy. It is interesting to investigate how accurately these EOSs predict these quantities at high pressures. Their expressions for the bulk modulus are given as follows:

$$B_M/B_0 = \{2\xi/[\xi - 1 + (\xi + 1)x^\eta]\}^2 x^\eta \quad (7)$$

$$B_B/B_0 = (1/2)(7x^{-7} - 5x^{-5})[1 + (3/4)\xi(x^{-2} - 1) + (\eta/2)(x^{-2} - 1)^2 + (x^{-9} - x^{-7})[(3/2)\xi + 2\eta(x^{-2} - 1)] \quad (8)$$

$$B_{KD}/B_0 = \xi/(\xi - 1 + x^\eta) \quad (9)$$

$$B_D/B_0 = [1 + 3B'_0(1 - x)/(2x)]^2 \quad (10)$$

$$B_V/B_0 = x^{-2}[1 + (\eta x + 1)(1 - x)] \exp[\eta(1 - x)] \quad (11)$$

where ξ and η are the same as those given in the corresponding equations, (1)–(6). In figure 3 the ratio B/B_0 is plotted as a function of pressure for (a) Cu, (b) Ar and (c) MgO. The figure shows that the Vinet equation is supreme among the others and predicts both the pressure and the bulk modulus correctly up to 10 TPa for monatomic solids and up to 1 TPa for diatomic solids. The superiority of the Vinet equation is shown by Schlosser and Ferrante [19] by comparing various EOSs for B/B_0 with experimental data. The present result confirms that this characteristic persists up to very high pressures. The estimate of the values of B'_0 and B''_0 may be not so accurate in comparison with that of B_0 , so there is a possibility that the agreement of the Dodson equation may be improved with a slight change of the value of B'_0 . Therefore we tried to fit the theoretical values of B/B_0 to equation (10) by changing the ranges for the fitting: (a) $V/V_0 \geq 0.50$ and (b) $V/V_0 \geq 0.10$. The resulting values of $B'_0(\text{fit.})/B'_0(\text{theoret.})$ are as follows for Ne, Ar, Al, Cu, LiH and MgO, respectively: (a) 1.41, 1.33, 1.19, 1.29, 1.17, 1.20, (b) 3.08, 2.58, 1.93, 2.49, 1.83, 2.03. The values seem to be large even for $V/V_0 \geq 0.50$. For the Dodson equation to achieve good fitting both for the P - V relation and the pressure dependence of the bulk modulus is difficult even for $V/V_0 \geq 0.50$. The inadequacy of the Dodson equation at high pressures is attributed to the convergence of the $(V_0/V)^{1/3}$ -expansion being slower than that of the strain or the density expansions. The Dodson equation is still less successful than the Birch and the PM equations even if the correct quadratic term is included in the expansion.

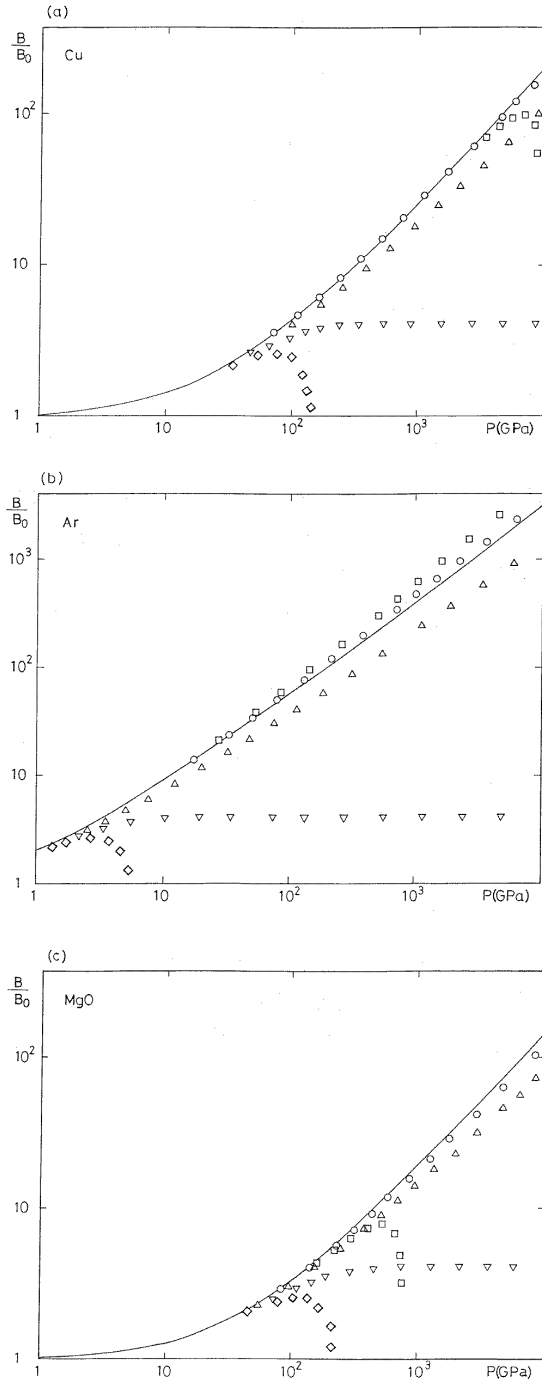


Figure 3. A comparison of the isothermal bulk modulus versus pressure curves of several EOSs with the theoretical result. (a) Cu, (b) Ar and (c) MgO: solid line: theory; ○: Vinet; □: Birch; △: Dodson; ▽: Kumari-Dass; ◇: Murnaghan. The parameters of the EOSs are determined by the theoretical values of V_0 , B_0 , B'_0 and B''_0 .

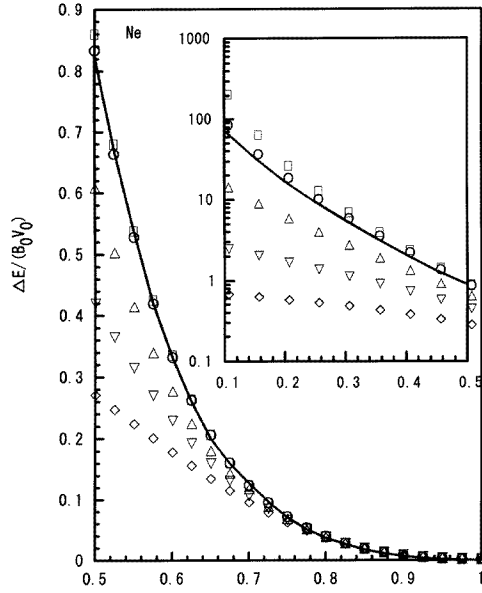


Figure 4. A comparison of the volume dependence of the total energy, $\Delta E/(B_0V_0)$, of several EOSs with the theoretical result for Ne: solid line: theory; ○: Vinet; □: Birch; △: Dodson; ▽: Kumari-Dass; ◇: Murnaghan. The parameters of the EOSs are determined by the theoretical values of V_0 , B_0 , B'_0 and B''_0 .

The total energy relative to the cohesive energy $\Delta E = E(V) - E(V_0)$ for these equations can be written as

$$\Delta E_M = \frac{6B_0V_0}{B'_0} \int_x^1 \frac{(1-t^\eta)t^2}{(\xi-1) + (\xi+1)t^\eta} dt \quad (12)$$

$$\Delta E_B = \frac{9}{8} B_0V_0(x^{-2}-1)^2 \left[1 + \frac{\xi}{2}(x^{-2}-1) + \frac{\eta}{4}(x^{-2}-1)^2 \right] \quad (13)$$

$$\Delta E_{KD} = \frac{B'_0V_0}{B''_0} \left\{ (1-x^3) \ln \xi - 3 \int_x^1 \ln [1 + (\xi-1)t^\eta] t^2 dt \right\} \quad (14)$$

$$\Delta E_D = \frac{9}{4} B_0V_0B_0'' \left[(\xi^2 - 3\xi + 3) - \frac{9}{2}x + 9\xi x^2 - \frac{3}{2}(4\xi - 1)x^3 + \xi^2(3 \ln x - 1)x^3 \right] \quad (15)$$

$$\Delta E_V = \frac{9B_0V_0}{\eta^2} \{ 1 - [1 - \eta(1-x)] \exp[\eta(1-x)] \}. \quad (16)$$

In figure 4 we compare these results with the theoretical values for Ne(fcc). The figure shows that the agreement is excellent for the Vinet equation. This manifests the fact that the Vinet form for the total energy is very accurate other than for very small compressions for a solid constituted by closed-shell atoms as is expected.

4. Behaviours at very high pressures

As was shown in sections 2 and 3, overall agreement of the P - V relation and $B(P)$ of the Vinet equation with theoretical results is excellent below about 1 TPa which seems to exceed the pressure range usually used. However, the Vinet equation and all of the other EOSs previously proposed do not describe the high-pressure behaviours predicted by the QSM. The inadequacy of the Vinet equation can be understood easily from equation (16) in which the total energy tends to a constant, $9B_0V_0/\eta^2[1 - (1 - \eta) \exp(\eta)]$, in the limit of extreme compression, instead of infinity, contrary to theoretical prediction. Recently

Holzapfel [10] analysed the experimental data on monatomic solids and proposed several EOSs applicable to monatomic solids which tend to the Thomas–Fermi values at strong compressions. Among these the EOSs called H11 and H12 are written as [20]

$$P_{\text{H11}} = P_{\text{FG0}}x^{-5}(1-x)\exp(-c_0x) \quad (17)$$

$$P_{\text{H12}} = 3B_0x^{-5}(1-x)\exp[(c_0 + c_2)(1-x) - c_2(1-x)^2]. \quad (18)$$

Here $c_0 = \ln(P_{\text{TF0}}/(3B_0))$, $c_2 = (3B'_0 - 2c_0 - 9)/2$ and P_{TF0} denotes the Thomas–Fermi pressure at $V = V_0$ given by $(1/5)(3\pi^2)^{2/3}(\hbar/m_e)(Z/V_0)^{5/3}$ with Z as the atomic number of the constituent atom. Recently the H11 equation was compared with DAC data and the room-temperature isotherm deduced from Hugoniot data up to 1 TPa for Al [21] where good agreement was shown with the use of the experimental B_0 . Though the H11 equation is certainly in good agreement with the theoretical result for Al, large deviations are found for rare-gas solids. On the other hand the H12 equation can be written approximately as $P_{\text{H12}}/P_V \sim \exp[(-c_2 + 3/2)(1-x)^2]$ for $(1-x)^3 \ll 1$. For Ne, Ar, Al and Cu the values of $-c_2 + 3/2$ are estimated, respectively, to be -1.30 , -0.70 , 0.73 and 0.39 . Therefore the H12 equation is very similar to the Vinet equation at low and medium compressions. Since the H12 equation is very similar to the simple form given by Thomas and Fermi in which only the kinetic energy contribution to pressure is included, its validity at less strong compressions, where the exchange contribution is not negligible, needs to be investigated. The present calculation shows that the agreement is excellent even in this range of compression because the reduction factor, $(1-x)\exp[(c_2 - c_0)x - c_2x^2]$, simulates the negative pressure due to the exchange energy very well in this equation. The Thomas–Fermi EOS becomes poor rapidly at smaller compressions for a material which has a small number of conduction electrons. We compare in figure 5 the H11 and H12 equations with the theoretical result for the case of Ne.

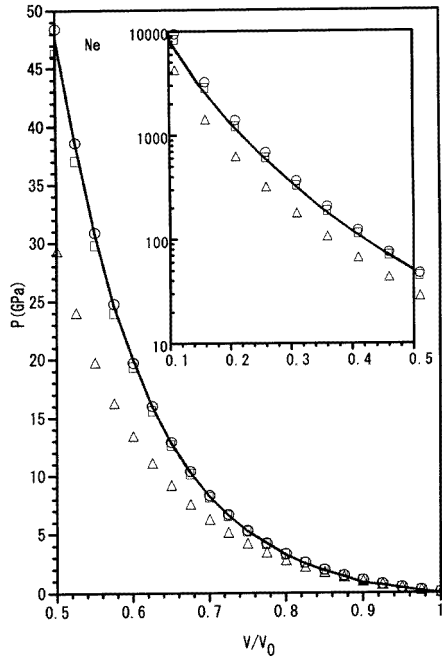


Figure 5. A comparison of the P – V curves for the H11, H12 and Vinet equations with the theoretical result for Ne: solid line: theory; \triangle : H11; \square : H12; and \circ : Vinet.

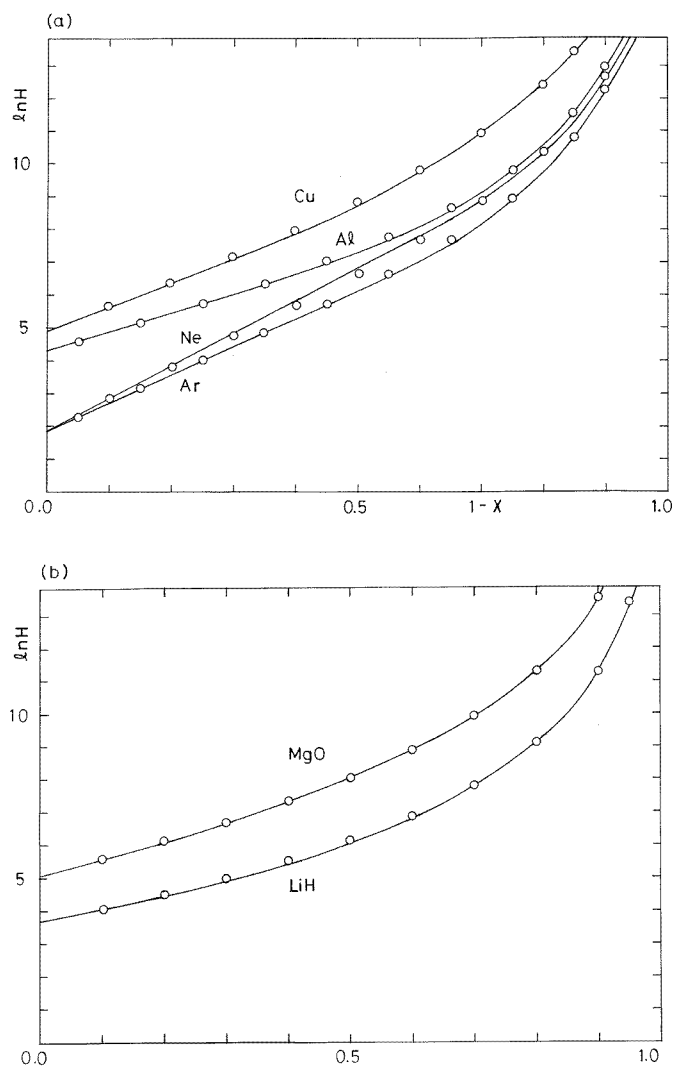


Figure 6. $\ln H(x)$ versus $(1-x)$ relations for (a) monatomic solids and (b) diatomic solids. The solid line and the circles denote, respectively, the theoretical values and those obtained from equation (20).

Since the H12 equation is applicable only to monatomic solids, we shall improve the Vinet equation on the basis of the QSM in the following. Following Vinet *et al.*, let us introduce a quantity $H(x) = x^2 P/[3(1-x)]$. For the Vinet equation $\ln H$ is expressed in terms of a linear function of $(1-x)$, as $\ln H = \ln B_0 + \eta(1-x)$. In figure 6 $\ln H$ versus $(1-x)$ is plotted. The figure shows that the linear relation holds up to $x = 0.6$ ($V/V_0 = 0.22$) for monatomic solids and up to $x = 0.8$ ($V/V_0 = 0.51$) for diatomic solids. As for Ne the linearity holds well up to $x = 0.4$ ($V/V_0 = 0.064$). Figure 6 demonstrates the usefulness and the limit of applicability of the Vinet equation. For about $x < 0.3$ ($V/V_0 < 0.027$) the QSM result becomes correct irrespective of the crystal structures and depends only upon the material. The solution of the QSM equation for monatomic solids is expressed in a very

convenient form by Kalitkin and Kuz'mina [12]; this is reproduced in the appendix. For polyatomic solids the QSM pressure and volume are calculated by using the relation of the addition of volumes at equal pressure. From the QSM solution given in the appendix we can express $\ln H$ approximately as $-3 \ln x + a_0 + a_1 x + a_2 x^2$ for $(1-x)^3 \ll 1$. Combining this form with the Vinet equation, we adopt the following simple form for $\ln H$:

$$\ln H = \ln B_0 + \eta(1-x) + \zeta(1-x)^2 - 3[\ln x + 1 - x + (1-x)^2/2] \quad (19)$$

where B_0 and η are the same as those of the Vinet equation and ζ is determined by the QSM results. The corresponding EOS is given by

$$P = 3B_0 x^{-5} (1-x) \exp[(\eta-3)(1-x) + (\zeta-3/2)(1-x)^2]. \quad (20)$$

In figure 6 the values of $\ln H$ obtained from equation (19) are compared with the theoretical results where ζ is determined by the QSM result at $x = 0.20$. The figure shows that the value obtained from equation (19) is in good agreement with the theoretical one for both monatomic and diatomic solids from small to extreme compressions. In table 1 the values of ζ are tabulated. It should be noted that the parameters, ζ , newly introduced in equation (20) can be determined theoretically independently of the crystal structure considered. For equation (20) B_0'' is expressed as $-(\eta^2 + 6\eta - 6\zeta + 2)/(9B_0)$. The calculated values are in good agreement with the theoretical ones (see table 1). However, it is not a good idea to estimate the value of ζ from the above relation because that requires a precise estimate of B_0'' . For $(1-x)^3 \ll 1$ equation (20) reduces to the equation proposed by Sikka [22, 23].

5. The temperature effect on the EOS

For a weakly bounded solid such as a rare-gas solid the temperature effect is important at low pressures [13], and even for ionic solids its inclusion improves the agreement of the theoretical results with experimental ones [24]. In this section we shall show briefly that the Vinet equation is in good agreement with the theoretical result up to very high pressure even if the temperature effect is taken into account by using the Debye model for lattice vibration. For the sake of simplicity we restrict ourselves to monatomic solids in the following. We express the pressure as

$$P_T = P_s + \frac{9}{8} n k_B \frac{\gamma \Theta_D}{V} + 3 n k_B T \frac{\gamma}{V} D\left(\frac{\Theta_D}{T}\right) \quad (21)$$

where P_s , Θ_D , n and γ denote, respectively, the pressure in the static lattice, the Debye temperature, the number of atoms in the unit cell and the thermodynamic Grüneisen parameter which is expressed in the Debye model as $-(\partial \ln \Theta_D / \partial \ln V)_T$. Also $D(x)$ is the well-known Debye function. The pressure due to the thermal excitation of electrons is added to P_s if necessary [25]. The volume dependence of Θ_D can be estimated as follows:

$$\Theta_D = \frac{\hbar}{k_B} \left[\frac{5}{3} \langle \omega^2 \rangle \right]^{1/2} \quad (22)$$

$$\langle \omega^2 \rangle = \frac{1}{3N} \sum_{\mathbf{k}, \alpha} D_{\alpha\alpha}(\mathbf{k}) = \frac{1}{3M} \sum_R' [\nabla^2 \phi(r)]_{r=R} \quad (23)$$

where $\langle \omega^2 \rangle$ is the mean square vibration frequency, $D_{\alpha\alpha}(\mathbf{k})$ is a component of the dynamical matrix with $\alpha = x, y, z$, $\phi(r)$ is the interatomic pair potential, M is the mass of the

constituent atom and \mathbf{R} is a lattice vector. When we estimate the force constant at the nearest-neighbour distance d , we get [11, 13]

$$\Theta_D(V) = \frac{\hbar}{k_B d} \left(\frac{5V}{M} \right)^{1/2} \left(B_s - \frac{4}{3} P_s \right)^{1/2} \quad (24)$$

from equations (22) and (23) where B_s is the bulk modulus in the static lattice. Thus the Grüneisen parameter is expressed as

$$\gamma(V) = -\frac{4P_s + 24VP'_s + 9V^2P''_s}{6(4P_s + 3VP'_s)} \quad (25)$$

with the primes on P'_s and P''_s denoting the volume derivatives (equation (31) in [11] is misprinted). Equation (25) is equivalent to γ given by Zubarev and Vaschchenko. For the Vinet equation equations (24) and (25) are written as

$$\Theta_D = \Theta_0 \exp[\eta(1-x)/2][-\eta x + (\eta + 3) - 2/x]^{1/2} \quad (26)$$

$$\gamma = [\eta^2 x^3 - (\eta^2 + 4\eta)x^2 + 2\eta x + 2]/(6[\eta x^2 - (\eta + 3)x + 2]) \quad (27)$$

where $\Theta_0 = \Theta_D(V_0)$. In figure 7 we plot $\ln H$ as a function of $(1-x)$ for neon at room temperature together with the result in the static lattice and compare these results with the experimental data [26, 27] where the experimental value at ambient pressure at room temperature is used for V_0 . The figure shows that the linearity holds well at least up to $x = 0.40$ ($V/V_0 = 0.064$) even if the temperature effect is taken into account. The deviation of the experimental data from linearity at the smaller end of $(1-x)$ results from the solid–liquid transition. Therefore the Vinet form is effectively satisfied at finite temperatures when the finite-temperature values of V_0 , B_0 and B'_0 are used. This is used in the finite-temperature extension of the Vinet equation [28]

$$P(V, T) = P_V(V, T_R) + \alpha_0(T_R)B_0(T_R)(T - T_R) \quad (28)$$

where the thermal expansion coefficient α and the bulk modulus B are estimated at zero pressure and T_R ($> \Theta_D$) is a reference temperature. Equation (21) reduces to the above equation when $T > \Theta_D$, but equation (21) includes the volume dependences of α and B .

For an application to polyatomic solids Θ_0 is given approximately by equation (24) with the replacement of d and $1/M$ by the atomic radius and the averaged value respectively. However, the theoretical value of Θ_0 may be different from the experimental value. In practice, we adopt

$$\Theta_D(V) = \Theta_0(V/V_0)^{1/6} B_s(V_0)^{-1/2} [B_s(V) - (4/3)P_s(V)]^{1/2} \quad (29)$$

for polyatomic solids with the use of an experimental value for Θ_0 . Equation (29) can be derived also from the Zubarev and Vaschchenko model using $\gamma = -(\partial \ln \Theta_D / \partial \ln V)_T$. In figure 8 we plot several isobars of MgSiO_3 (perovskite) whose high-temperature and high-pressure properties have important implications as regards the composition of the lower mantle of the Earth. The theoretical values (static lattice) of V_0 , B_0 and B'_0 are taken from [29]: $V_0 = 40.25 \text{ \AA}^3$, $B_0 = 272 \text{ GPa}$, $B'_0 = 3.80$ and for Θ_0 the experimental value of 1030 K is used. The figure shows that the present result is in good agreement with experimental data [30, 32, 33] except for when $P = 36 \text{ GPa}$ [34]. The disagreement at $P = 36 \text{ GPa}$ may be attributed to a large uncertainty in temperature which amounts to 250 K at $T = 1900 \text{ K}$. For an application of the present model and the Hugoniot one with the use of the APW result to the total energy and pressure in the static lattice, a good agreement with experimental Hugoniot results is reported [11, 24]. Therefore it is reasonable to assume that the present model with the use of the Vinet equation can predict the high-pressure and high-temperature properties of solid quantitatively.

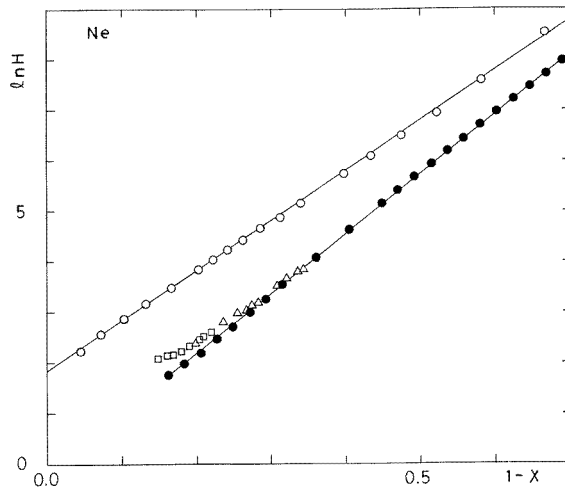


Figure 7. The effect of temperature on $\ln H(x)$ versus $(1-x)$ for Ne. The open and closed circles denote, respectively, the theoretical result in the static lattice and that at room temperature. Experimental data are taken from (\square) [26] and (\triangle) [27], both for room temperature. The lines are guides to the eye.

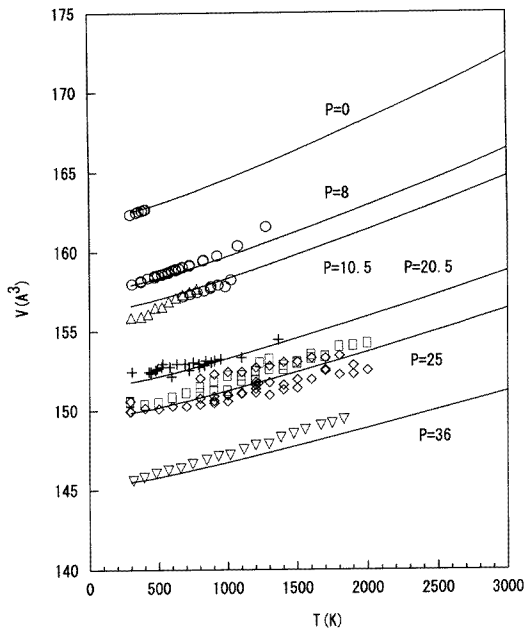


Figure 8. Several isobars of perovskite MgSiO_3 . V denotes the volume of the unit cell and pressure P is measured in units of GPa. The experimental data are taken from (\circ) [30], (\triangle) [31], (∇) [34], $(+)$ [32], and for $P = 25$ GPa [33] \square and \diamond denote the data which were determined by using the Au and MgO pressure markers respectively.

6. Discussion and conclusion

In the present paper we compared the universal EOSs of solid with theoretical values from low to ultra-high pressures. The present result shows that the Vinet equation is in better

agreement with the theoretical results than the KD and the Dodson equations for both the P - V relation and the pressure dependence of the isothermal bulk modulus, but it deviates from the theoretical values above 10 TPa for monatomic solids and from 1 TPa for diatomic solids. This indicates that at low and medium compressions the repulsive interaction, $A(1 + ar) \exp(-br)$, plays an important role for the P - V relation even for metals, and that at strong compressions a large number of conduction electrons due to metallization provide a main source for pressure. This observation conforms to the fact that neon, which is considered to be the most difficult substance to metallize (the estimated pressure of metallization amounts to 158 TPa [17]), obeys the Vinet equation well up to an ultra-high pressure. As for monatomic solids, the H12 equation is one of the simplest interpolation formulae from low to ultra-high pressures because it reduces to the Vinet equation when $(1 - x)$ is small and approaches the Thomas–Fermi values at strong compressions. The good agreement of the H11 equation for Al results from the fact that values of c_2 in equation (18) are small for this substance. The estimated values of c_2 are 2.798, 2.201, 0.773 and 1.112, respectively, for Ne, Ar, Al and Cu. The Birch and the PM equations may be accurate in a limited range of compression because they involve no approximation except the truncation of the expansion series, but their validities are limited approximately to $(1/2)[(V_0/V)^{2/3} - 1] < 1/2$ and $(V_0/V) - 1 < 1/2$, respectively; for the PM equation a further improvement is not expected so much even if the quartic term is included in the expansion. The present result show also that the use of a fitting method is indispensable for the KD and the Dodson equations in order to get a good agreement with experimental data, but their application ranges may not exceed $V/V_0 = 0.5$.

In order to search for the EOS of polyatomic solids correct at very high pressures, we have improved the Vinet equation at very high pressures on the basis of a quantum-statistical model where the parameters newly introduced can be determined theoretically irrespective of the crystal structure considered. The resulting equation is in good agreement with the theoretical result from low to ultra-high pressures for monatomic and diatomic solids. For monatomic solids equation (20) is equivalent to H12 if $\zeta - 3/2 = -c_2$ is assumed: the values of $\zeta - 3/2(-c_2)$ are estimated to be -2.885 (-2.798), -2.914 (-2.201), -1.247 (-0.773) and -1.309 (-1.112) for Ne, Ar, Al and Cu, respectively. Thus equation (20) is an extension of H12 for polyatomic solids. Since the Vinet equation is accurate for P and ΔE , the present model applicable to the calculation of the the Hugoniot values for solids on using the Rankine–Hugoniot conservation relation which reduces the computational effort greatly. The input parameters are V_0 , B_0 , B'_0 and Θ_0 .

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Appendix

Here we reproduce the analytically fitted electronic density $\rho(r)$ of the QSM solutions for a monatomic solid given by Kalitkin and Kuz'mina [12], where r denotes the atomic radius. All the quantities given below are measured in atomic units.

$$\rho(r) = (Z/V) \exp(-\alpha r - \beta r^2)$$

$$\alpha = 0.1935Z^{0.495-0.039 \log(Z)}$$

$$\beta = 0.068 + [0.078 - 0.086 \log(Z)] \log(Z)$$

where Z is the atomic number of the constituent atom, \log means \log_{10} and $V = (4\pi/3)r^3$. The pressure is calculated from

$$P = \frac{1}{5} [3\pi^2]^{2/3} \rho^{5/3} - \frac{13}{36} \left[\frac{3}{\pi} \right]^{1/3} \rho^{4/3}.$$

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