Five-parameter equation of state for solids correctly incorporating cohesive energy data*

Tian Rong-Gang(田荣刚) and Sun Jiu-Xun(孙久勋)†

Department of Applied Physics, University of Electronic Science and Technology, Chengdu 610054, *China*

(Received 25 November 2010; revised manuscript received 1 April 2011)

A five-parameter equation of state (EOS) is proposed to correctly incorporate the cohesive energy data in it without physically incorrect oscillations. The proposed EOS is applied to 10 selected metals. It is shown that the calculated compression curves are in good accordance with the experimental data. The values of the bulk modulus and its derivative with respect to pressure extracted from the proposed EOS remain almost unchanged while the data range used is varied.

Keywords: equation of state, cohesive energy, physically incorrect oscillations

PACS: 05.70.Ce, 64.30.Ef, 62.50.–p **DOI:** 10.1088/1674-1056/20/8/080508

1. Introduction

The equation of state (EOS) of a compressed solid plays an important role in many fields, such as condensed matter physics and geophysics.[1−5] Nowadays, the embedded atom model (EAM) has become the most successful potential model for metallic materials and the EOS plays an important role in the construction of the EAM.[1,2,6,7] Many EOSs have been proposed with different degrees of success, such as the mixed power-exponential-type (MPE),[1,2] and those presented by Qin *et al.*,[1,2] Rose *et al.*,[8] Vinet *et al.*[9] (in fact, it should be the effective Rydberg (ER) EOS as pointed out by Qin *et al.*[1,2,9] and Stacey *et al.*[10]), Boanza *et al.*,[11] and Kumar *et al.*[12] adapted a polynomial expansion of the order 3 (AP3) and Holzapfel[13] equations, etc. However, the pressure derivatives of the isothermal bulk modulus are different for different EOSs. Sun *et al.*[14] proposed a modified ER (MER) EOS and Li *et al.*[15,16] proposed a generalized Rose (GRS) EOS. We notice that the GRS potential was first introduced by Chantasiriwan and Milstein,[6] although the GRS EOS was extensively applied to many solids by Li *et al.*[15,16] The parameters for the MER and GRS equations, deduced from experimental data in high and low pressure ranges, are in good agreement with each other.[14−16]

Besides the shortcomings mentioned above, the recent work of Qin *et al.*[1,2] and our calculations show that most of these EOSs have some other disadvantages. The equations given by Boanza *et al.*,[11] Kuchhal *et al.*,[12] and Holzapfel[13] cannot give the physical reasonable cohesive energy.[13−16] We compare the theoretical values deduced from the ER, MER and Morse EOSs with experimental data[15,16] in Table 1. The table shows that the deviations of cohesive energy deduced by the three equations from the experimental data[16] are fairly large. The deviations of Birch and Rose EOSs are also fairly large.[1,2,16]

The GRS EOS proposed by Li *et al.*[15,16] seems to be a unique one that can incorporate the experimental cohesive energy. However, Qin *et al.*[1,2] pointed out the unphysical oscillations of the four-parameter Birch EOS in high-pressure regions for some solids, they did not mention the unphysical oscillations of the GRS EOS. Our calculations show that unphysical oscillations also exist in the GRS EOS[15,16] in both extremely high pressure and expansion regions, as shown in Fig. 1. The unphysical oscillations would bring about unreliable results in some problems, especially relating to the EAM.[1,2,6−9]

*Project supported by the Joint Fund of National Natural Science Foundation of China and China Academy of Engineering Physics (Grant No. 10876008), the New Century Excellent Researcher Award Program from the Educational Ministry of China (Grant No. NCET-05-0799), and the Academic Excellence of University of Electronic Science and Technology of China (Grant No. 23601008).

†Corresponding author. E-mail: sjx@uestc.edu.cn

© 2011 Chinese Physical Society and IOP Publishing Ltd

Table 1. Comparison among cohesive energy E_0 values (kJ/mol) from ER,[1,2,9] Morse,[1,2] MER,[14] and MPE[1,2] equations. The experimental data of V_0 (cm^3/mol) and average fitting error Δ_P% for pressure by using the ER,[1,2,9,10] Morse,[1,2] MER,[14] and the present GEF equations. Values of parameters α, β and n are for the GEF EOS.

	V_0	E_0					Δ_P%				α	β	n
		Exp	ER	Morse	MER	MPE	ER	Morse	MER	GEF			
Cu	7.115	336.7	226.4	268.8	427.7		1.05	0.76	0.50	0.49	9.4497	0.70647	2.8346
Mo	9.387	658.0	1235	1262	1137	1161	1.47	1.03	0.90	0.90	7.7576	0.58757	4.2998
W	9.550	858.7	1363	1542	2139	1206	0.24	0.20	0.22	0.20	7.2956	0.62246	3.9529
Ag	10.27	284.6	172.5	198.7	194.6	368.6	0.82	0.66	0.64	0.44	9.9613	1.3771	1.8528
Pt	9.098	563.5	588.3	638.3	1243	705.3	1.05	0.76	0.77	0.70	11.002	0.55360	4.3903
Ta	10.80	781.5	1186	1275	1234	1024	0.93	0.69	0.63	0.60	5.7618	0.84998	2.8708
Au	10.22	367.6	436.3	475.2	821.7	427.4	0.94	0.71	0.64	0.64	11.136	0.52942	4.9426
Pd	8.896	375.3	390.0	417.5	881.2	503.1	1.06	0.76	0.72	0.72	10.856	0.59147	4.2455
Ca	26.13	177.5	912.8	1064	925.3		0.48	0.50	0.47	0.42	5.0830	0.43890	5.1109
Mg	14.00	145.7	196.6	230.9	232.2		0.26	0.24	0.26	0.23	7.7301	0.58285	3.9497
	$\bar{\Delta}$						0.80	0.61	0.57	0.48			

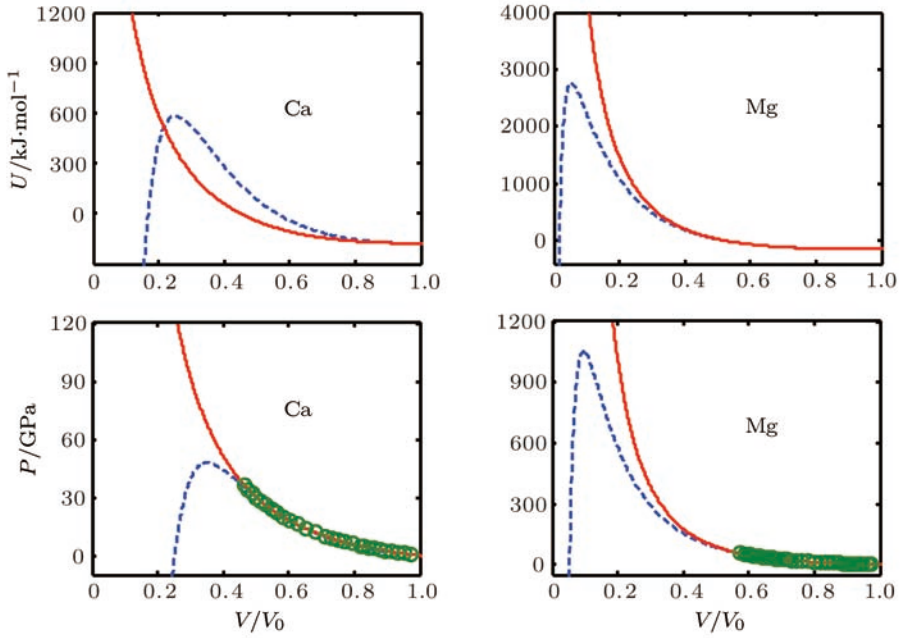


Fig. 1. Comparison of variations of pressure and energy with compression ratio between the GRS (with parameters in Refs. [15] and [16] by Li *et al.*) (dashed lines) and the present GEF equations (solid lines) for Ca and Mg. Please note that the oscillations of the GRS EOS in the region $V/V_0 < 0.4$ are physically incorrect.

The six-parameter MPE EOS proposed by Qin *et al.* has the following form:[1,2]

$$U = Mx^{-m}\,\mathrm{e}^{\alpha(1-X)} - Nx^{n}\,\mathrm{e}^{\beta(1-X)}, \quad (1)$$

$$P = (3B_0X^{-2}/C)[(\alpha + mX^{-1})(\beta - n)X^{-m}\,\mathrm{e}^{\alpha(1-X)} - (\alpha + m)(\beta - nX^{-1})X^{n}\,\mathrm{e}^{\beta(1-X)}], \quad (2)$$

where M and N can be written explicitly in terms of the equilibrium volume V_0 and bulk modulus B_0 as

$$M = 9B_0V_0(\beta - n)/C, \quad N = 9B_0V_0(\alpha + m)/C \quad (3)$$

with

$$C = (\alpha + m)(\beta - n)[(\alpha + m) - (\beta - n)] + (an + \beta m),$$

in the above equations, U and P are the internal energy and pressure at 0 K, $X = (V/V_0)^{1/3}$, V the volume of material, V_0, B_0, m, n, α, and β are the six parameters of EOS. Equation (2) can include several typical EOSs in some special cases. As $m = 0$, $n = 1$, $\beta = \alpha$, equation (2) reduces to the ER EOS; as $\beta = \alpha = 0$, it reduces to the generalized Lennard–Jones (GLJ) EOS; as $m = n = 0$ and $\alpha = 2\beta$, it reduces to the Morse EOS.[1,2] However, the cohesive

energy deduced from the MPE EOS is equivalent to those from the ER and Morse EOSs. Thus a reliable EOS for solids that can correctly incorporate the experimental cohesive energy data without unphysical oscillations is unavailable at present. In this paper, we address these problems of the ER and GRS EOSs, and then suggest an improved analytic form to overcome the inherent difficulties appearing in the present EOSs.

2. Five-parameter equation of state

For convenience, we refer to the proposed equation as a generalized exponential function (GEF) EOS. The proposed potential and corresponding EOS are as follows:

$$U = (E_0/\alpha)[n\beta\,\mathrm{e}^{\alpha(1-X)} - n\beta - \alpha]\,\mathrm{e}^{\beta(1-X^n)}, \quad (4)$$

$$P = \frac{n\beta E_0}{3\alpha V_0 X^3}[(\alpha X + n\beta X^n)\,\mathrm{e}^{\alpha(1-X)} - (\alpha + n\beta)X^n]\,\mathrm{e}^{\beta(1-X^n)}, \quad (5)$$

where there are five parameters, V_0, E_0, α, β, and n. V_0 and E_0 are the molar volume and the cohesion energy (in positive value) at zero pressure. It is evident that equation (4) reduces to the Morse potential and equation (5) reduces to the Morse EOS, as $\beta = \alpha$ and $n = 1$. The repulsive part of Eq. (4), $n\beta\,\mathrm{e}^{\alpha(1-X)+\beta(1-X^n)}$, is a monotonically decreasing function of X. The attractive part, $(-n\beta - \alpha)\,\mathrm{e}^{\beta(1-X^n)}$, is a monotonically increasing function of X. Therefore, there exists only one minimum in potential function equation (4), as $X = 1$, and no physically incorrect oscillations exist in Eqs. (4) and (5).

The bulk modulus and its derivative with respect to pressure can be analytically derived by using the following formulas:[14]

$$B = -\frac{1}{3}\left(X\frac{\partial}{\partial X}\right)P, \quad (6)$$

$$B' = \frac{\partial B}{\partial P} = \frac{1}{9B}\left(X\frac{\partial}{\partial X}\right)^2 P. \quad (7)$$

The derivation is straightforward, but the expressions are cumbersome. We merely give the values of B and B' at zero pressure for clarity as follows:

$$B_0 = \frac{n\beta E_0}{9V_0}(\alpha + n\beta + n - 1), \quad (8)$$

$$B_0' = 1 + (Q/3)\cdot(\alpha + n\beta + n - 1)^{-1}, \quad (9)$$

$$Q = (\alpha + n\beta)(\alpha + 2n\beta) - (n-1)(n-2). \quad (10)$$

In Refs. [17]–[19], Stacey *et al.* argued that as pressure P tends to infinity ($P \to \infty$, or $X \to 0$), the bulk modulus should satisfy the following relationship:

$$(B/P)_\infty = B'_\infty, \quad (P \to \infty). \quad (11)$$

We can easily verify that the GEF EOS in Eq. (5) satisfies the relationship. As the values of n are all larger than 1, X^n is a higher order infinitesimal as $X \to 0$, equation (5) changes into the following form:

$$P \to \frac{n\beta E_0}{3V_0}\,\mathrm{e}^{\alpha+\beta}\frac{1}{X^2}, \quad (12)$$

$$B \to \frac{2n\beta E_0}{9V_0}\,\mathrm{e}^{\alpha+\beta}\frac{1}{X^2}, \quad (13)$$

$$(B/P)_\infty = 2/3 = B'_\infty, \quad (P \to \infty). \quad (14)$$

Otherwise, maybe the values of n are all larger than 1 for some other materials, X^n is a lower order infinitesimal as $X \to 0$, equation (5) changes into the following form:

$$P \to \frac{n\beta E_0}{3\alpha V_0}(n\beta\,\mathrm{e}^{\alpha} - n\beta - \alpha)\,\mathrm{e}^{\beta}\frac{1}{X^{3-n}}, \quad (15)$$

$$B \to \frac{(3-n)n\beta E_0}{9\alpha V_0}(n\beta\,\mathrm{e}^{\alpha} - n\beta - \alpha)\,\mathrm{e}^{\beta}\frac{1}{X^{3-n}}, \quad (16)$$

$$(B/P)_\infty = (3-n)/3 = B'_\infty, \quad (P \to \infty). \quad (17)$$

Thus the GEF EOS in Eq. (5) is shown to satisfy the relationship in Eq. (11).

3. Numerical results and discussion

In order to verify the applicability of the GEF EOS, we apply it to 10 typical metals. The experimental data of cohesive energy E_0 and volume at zero-pressure V_0 are cited from Refs. [15] and [16] and listed in Table 1. The experimental compression data for W are cited from Ref. [20] and the other metals are taken from Ref. [21]. The average fitting error $\Delta_\mathrm{p}\%$ for pressure ($P = P(V)$) is defined as

$$\Delta_\mathrm{p}\% = [(P_\mathrm{cal} - P_\mathrm{exp})/P_\mathrm{exp}] \times 100\%.$$

In Table 1, we also list the values of parameters α, β, and n, determined through fitting experimental compression data, and the average fitting errors as well.

Table 1 shows that the values of average error $\bar{\Delta}$ of the 10 selected metals for the ER, Morse, MER and GEF EOSs are 0.80%, 0.61%, 0.57%, and 0.48%, respectively. The new GEF EOS is the best one in the sense of the average error. The table also shows

that the values of parameter n are all larger than 1 for the metals studied here (most of them are transition metals). This implies that the interaction ranges in these metals are all very short. In Fig. 1, we plot the variations of binding energy U and pressure versus reduced volume V/V_0 for solid Ca and Mg. We also plot experimental compression data for comparison. The figure shows that the GRS EOS[15,16] gives reasonable binding energy and compression curves merely in low pressure regions, at slightly high pressures. The binding energy is about 40 GPa for Ca and 200 GPa for Mg, they both deviate from the correct curves; at higher pressures they diverge and incorrectly tend toward negative infinity. Whereas, the present GEF EOS gives reasonable binding energy and compression curves under all pressure conditions.

In Fig. 2, we plot the curves for variation of binding energy for Mo and Ca, deduced from ER[1,2,8−10] and the present GEF equations. The figure shows that the difference between the two curves is fairly prominent, especially in the expansion region ($V/V_0 > 1$). In Fig. 3, we plot the curves for variations of pressure and relative error with reduced volume V/V_0 for Cu and Mo, deduced from ER,[1,2,8−10] MER[14], and the present GEF equations, respectively. The figure shows that the MER[14] and the present GEF equations give equivalently good results. The ER equation gives slightly worse results as compared with experimental data.

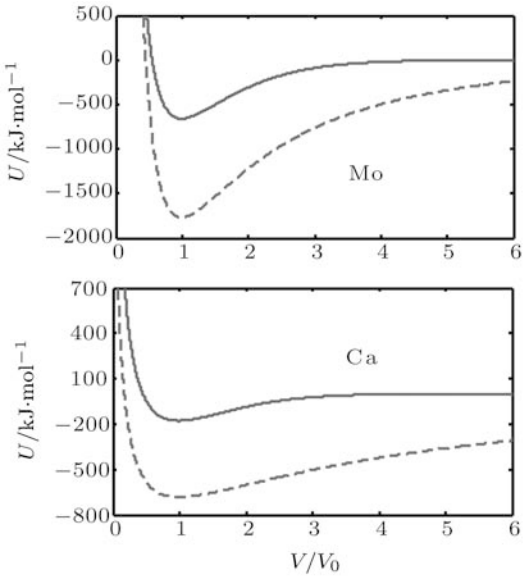


Fig. 2. Variations of binding energy with reduced volume V/V_0 for Mo and Ca, deduced from ER[1,2,9,10] (dashed lines) and the present GEF (solid lines) equations, separately.

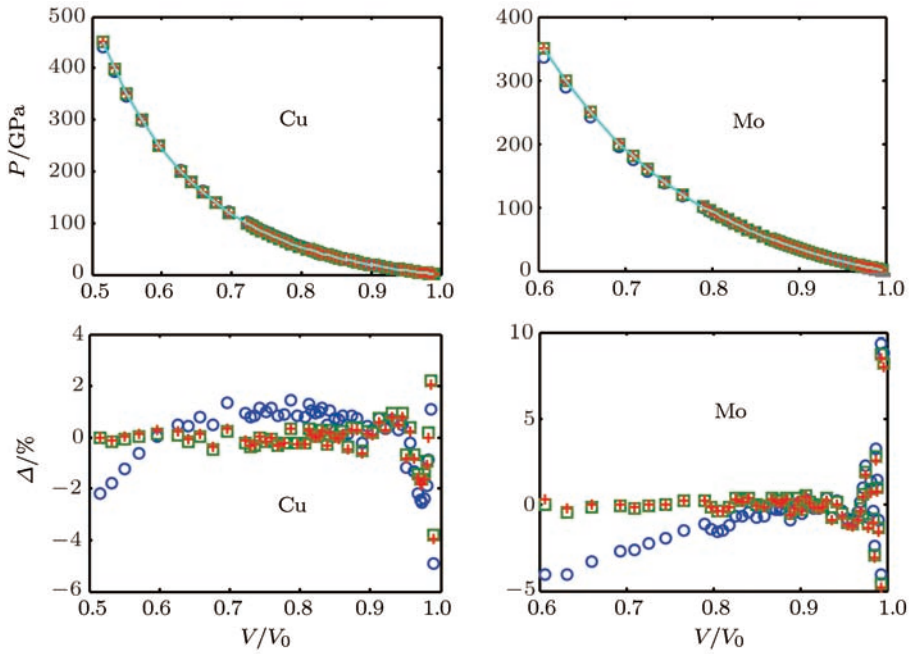


Fig. 3. Variations of pressure and relative errors with reduced volume V/V_0 for Cu and Mo, deduced from ER[1,2,9,10] (circles), MER[14] (squares) and the present GEF (pluses) equations, separately.

It is evident that the parameters of an ideal EOS should be insensitive to variations of the data number and data range used in fitting procedure. We compare the values of parameters B_0 and B_0' extracted from the ER,[1,2,9,10] MER, and GEF equations in Fig. 4 separately. The figure shows that the values of B_0 and B_0' extracted from the GEF EOS remain almost unchanged while the used data range is changed. Whereas the

variations of the values of B_0 and B_0' are slightly evident for the MER EOS and are prominent for the ER EOS. Thus the GEF EOS exhibits the merits of an ideal EOS.

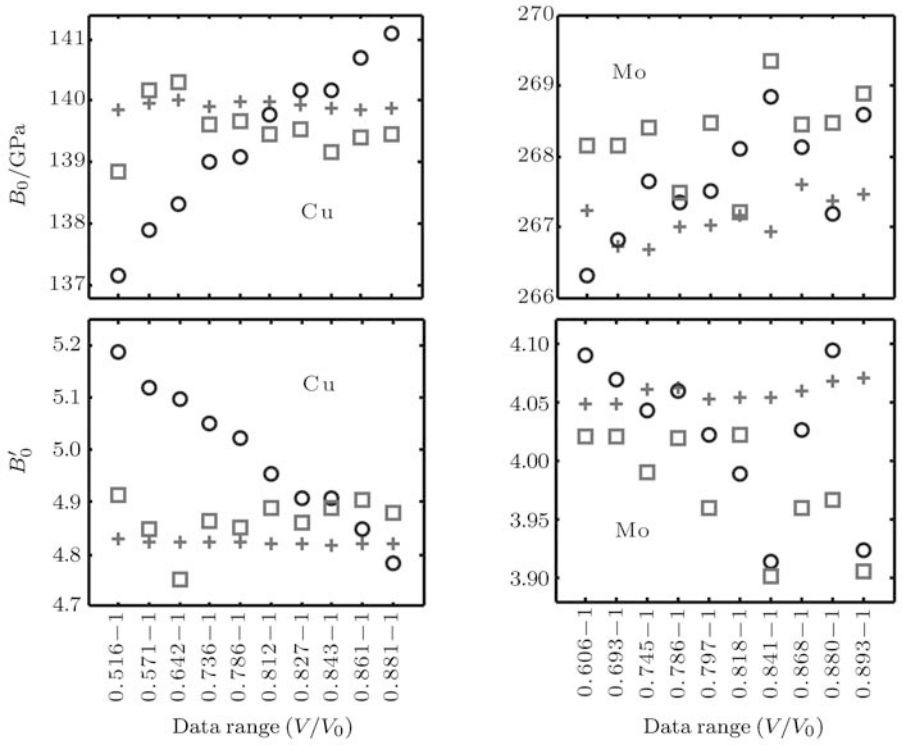


Fig. 4. Values of B_0 (GPa) and B_0' for Cu and Mo, deduced from ER[1,2,9,10] (circles), MER[14] (squares), and the present GEF (pluses) equations using a series of data in various ranges.

4. Conclusion

We proposed a five-parameter EOS that can correctly incorporate cohesive energy data without physically incorrect oscillations. The values of the bulk modulus and its derivative with respect to pressure extracted from the proposed EOS remain almost unchanged while the used data range is varied. This exhibits the universality of an ideal EOS. The proposed EOS is applied to 10 selected metals. The calculated compression curves are in good accordance with the experimental data.

References

[1] Qin T, Drautz R and Pettifor D G 2008 *Phys. Rev.* B **77** 220103 (R)

[2] Qin T, Drautz R and Pettifor D G 2008 *Phys. Rev.* B **78** 214108

[3] Wang L G, Sun J X and Yang W 2008 *Chin. Phys.* B **17** 2867

[4] Huang Z F, Ou C J and Chen J C 2009 *Chin. Phys.* B **18** 1380

[5] Sun X W, Liu Z J, Chen Q F, Song T and Wang C W 2009 *Chin. Phys.* B **18** 5001

[6] Chantasiriwan S and Milstein F 1998 *Phys. Rev.* B **58** 5996

[7] Baskes M I 2000 *Phys. Rev.* B **62** 15532

[8] Rose J H, Smith J R and Guinea F 1984 *Phys. Rev.* B **29** 2963

[9] Vinet P, Smith J R, Ferrante J and Rose J H 1987 *Phys. Rev.* B **35** 1945

[10] Stacey F D, Brennan B J and Irvine R D 1981 *Geophys. Surveys* **4** 189

[11] Baonza V G, Taravillo M, Caceres M and Nunez J 1996 *Phys. Rev.* B **53** 5252

[12] Kuchhal P, Kumar R and Dass N 1997 *Phys. Rev.* B **55** 8042

[13] Holzapfel W B 2003 *Phys. Rev.* B **67** 026102

[14] Sun J X, Wu Q, Cai L C and Jing F Q 2006 *Physica* B **371** 257

[15] Li J H, Dai X D, Liang S H, Tai K P, Kong Y and Liu B X 2008 *Phys. Rep.* **455** 1

[16] Li J H, Liang S H, Guo H B and Liu B X 2005 *Appl. Phys. Lett.* **87** 194111

[17] Stacey F D 1995 *Phys. Earth Planet. Inter.* **89** 219

[18] Stacey F D and Davis P M 2004 *Phys. Earth Planet. Inter.* **142** 137

[19] Stacey F D 2005 *Rep. Prog. Phys.* **68** 341

[20] Hixon R and Fritz J N 1992 *J. Appl. Phys.* **71** 1721

[21] Kennedy G C and Keeler R N 1972 *American Institute of Physics Handbook* 3rd edn. (New York: McGraw-Hill) p. 438