Physica B 406 (2011) 1276–1282

Contents lists available at ScienceDirect

Physica B

journal homepage: www.elsevier.com/locate/physb

Five-parameter equation of solids considering thermal effect which correctly incorporates cohesive energy

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ARTICLE INFO

Article history:
Received 25 July 2010
Received in revised form
10 December 2010
Accepted 10 January 2011
Available online 19 January 2011

Keywords:
Equation of state
Cohesive energy
Einstein modal
Thermodynamic properties

ABSTRACT

A five-parameter equation of state (EOS) is proposed, which correctly incorporates the cohesive energy data without physically incorrect oscillations in both extreme high pressure and expansion regions. Based on a modified Einstein model, the thermal effect is included in the proposed EOS complying with the zero-pressure condition. With this thermal EOS applied to five solids (Ar, Al, Au, Cu and Li), some important thermodynamic properties as isotherm, isochore, thermal expansion coefficient, volume modulus, heat capacity and Hugoniot are calculated for each selected solid with good agreement with experimental data, which confirms the validity of the present work

1. Introduction

Characterized by describing relationships among thermodynamic variables of compressed solids, the equation of state (EOS) plays an important role in scientific research and engineering application. Nowadays, the embedded atom model (EAM) has become the most successful potential model for metallic solids, and the EOS takes significant part in the construction of EAM [1–4]. So far, a lot of forms of EOSs have been proposed with varying extent of success, such as the mixed power-exponential-type (MPE) [1,2], Murnaghan EOS, Birch EOS [1,2], Rose et al. [5], Vinet et al. [6] (in fact should be the effective Rydberg, or ER EOS as pointed out by Qin et al. [1,2]), Baonza et al.'s [7] equations, etc. However, a fundamental problem with these EOSs is that the pressure derivative of the isothermal bulk modulus deduced from them varies much and even deviates much from the experimental data [8,9]. Both of the modified ER (MER) EOS proposed by Sun et al. [10] and the generalized Rose (GRS) EOS proposed by Li et al. [8,9] solve this problem well. The GRS EOS is expressed as

$$E_c = E_0[-1+\eta(1-X)+\delta\eta^3(1-X)^3]\exp[\eta(1-X)] \tag{1}$$

$$P_c = 3B_0X^{-2}(1-X)(1-3\delta\eta X+\delta\eta^2X^2)\exp[\eta(1-X)] \tag{2}$$

here, $X=(V/V_0)^{1/3}$. η and δ are the dimensionless reduced parameters defined as

$$\eta = \sqrt{9B_0V_0/E_0}, \quad \delta = -1/3+(B'-1)/(2\eta) \tag{3}$$

where V_0 and E_0 are the molar volume and the cohesion energy (in positive value) at the ambient pressure, respectively. B_0 and B'_0 are the isothermal bulk modulus and its first pressure derivative at the ambient pressure, respectively. Eq. (2) will reduce to the Rose or ER EOS as long as δ takes the fixed value 0.05 or 0, respectively [8,9].

In addition, the recent works of Qin et al. [1,2] and our calculations exhibit that most of these EOSs have some other disadvantages concerning cohesive energy E_0. Firstly, the theoretical cohesive energy values deduced from some of these EOSs deviate from the experimental records a lot. For instance, the values of E_0 in kJ mol^{-1} for Au calculated by MPE, Morse [1,2], ER [1,2,6] and MER [10] equations are 436.32, 475.19, 821.69 and 427.43, respectively, all of which fairly deviate from the experimental data 367.6 [8,9]. Secondly, the others even cannot represent physically reasonable cohesive energy. Take Al for an example, the theoretical values of its cohesive energy derived from the AP3 and Holzapfel are −127.04 and 85.181, receptively, [10] which obviously are physically incorrect. Futhermore, the deviations between the experimental data and the computed results coming of Birch and Rose EOSs are also fairly large as shown in Ref. [10]. For the GRS EOS considering binding energy E_0 as one of its parameters, however, these disadvantages are conquered perfectly because E_0 itself is set as the experimental value.

Of the EOSs mentioned above, the GRS EOS proposed by Li et al. seems to be unique one, which not only deduces accurate

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0921-4526/$ - see front matter © 2011 Published by Elsevier B.V.
doi:10.1016/j.physb.2011.01.016

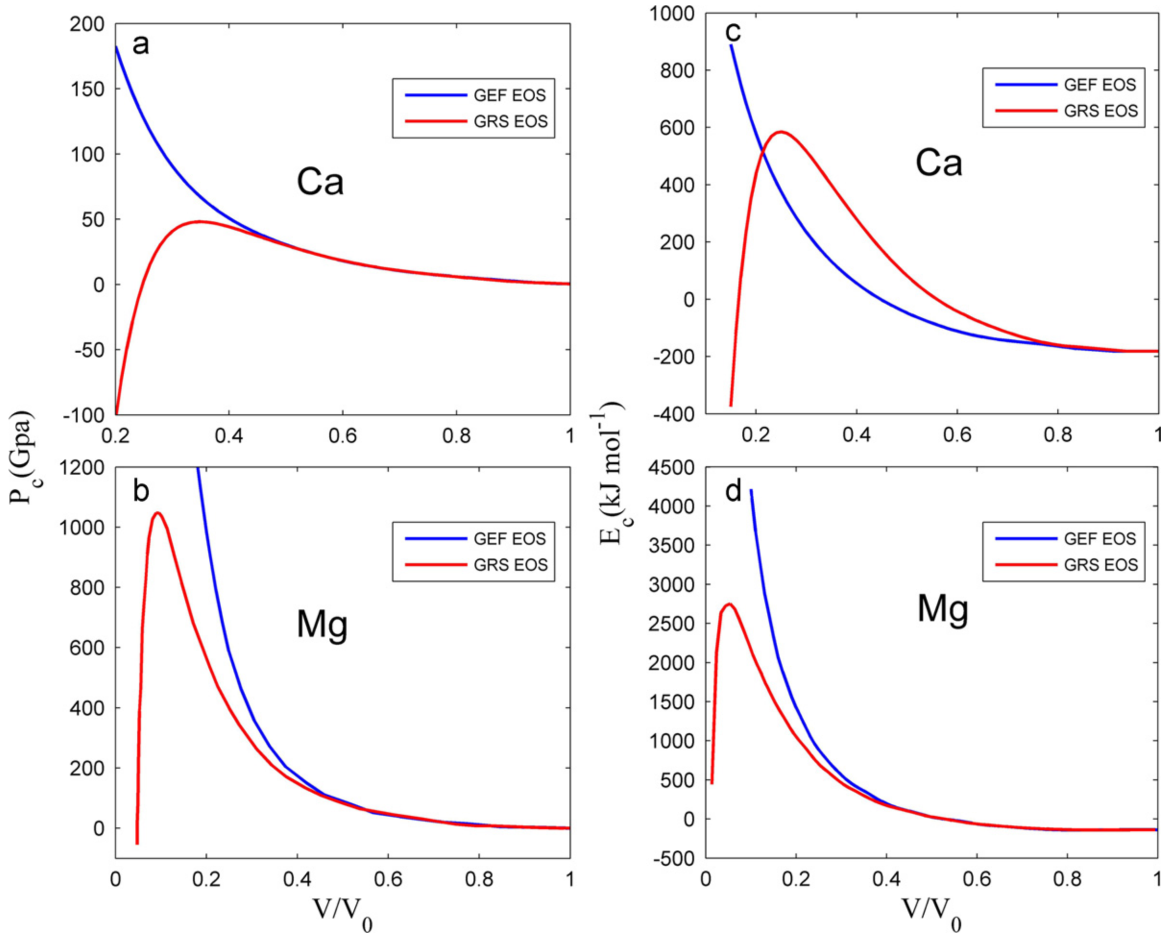

Fig. 1. Comparison of variation of the cold pressure and energy versus the compression ratio for Ca and Mg between the GRS (using the parameters cited in Refs. [8,9]) and the present GEF equations. Please note that the oscillations of the GRS EOS in the region $V/V_0<0.4$ are physically incorrect.

B_0' but also incorporates the cohesive energy correctly for solids. Nevertheless, an obvious deficiency of the GRS EOS indicated by our calculation is that the unphysical oscillations exist in the potential function Eq. (1) and corresponding EOS Eq. (2) in both extreme high pressure and expansion regions, which would bring on amount of adverse effects in the researches, especially for those relied on the EAM [1–4]. Actually, Qin et al. [1,2] have pointed out that such physically incorrect oscillation exists in the four-parameter Birch EOS at high-pressure regions for some solids, but they neglected the same problem with the GRS EOS. The reason of these oscillations is that the polynomial factor of Eq. (1) $1-3\delta\eta X+\delta\eta^2X^2$ has multiple zero roots. E.g. for Au, $\delta=-0.004$ and $\eta=6.725$ [8,9], which result in two corresponding zero roots $X=3.5747$ and $X=-1.1386$ of which the former is physically incorrect in the expansion region, and the latter, though out of the deformation region, probably brings on deviations from the experimental observation of Au at an extremely high pressure. In Fig. 1, Ca and Mg are taken for other two examples to illustrate this physically incorrect oscillation induced from the GRS EOS.

The discussion above suggests us that further development of the EOS in a simple form which incorporates correct cohesive energy without unphysical oscillations is of great necessity, which is also a main task in the work.

2. Definition of the five-parameter equation of state

We write out the analytical form of the proposed EOS directly to illuminate its physical meaning. For convenience, we nominate our potential equation as generalized exponential function (GEF) EOS. The proposed potential and corresponding EOS are expressed as

$$E_c(V)=\frac{E_0}{\alpha}\{n\beta\exp[\alpha(1-X)]-n\beta-\alpha\}\exp\left[\beta(1-X^n)\right] \tag{4}$$

$$P_c(V)=\frac{n\beta E_0}{3\alpha V_0X^3}\{(\alpha X+n\beta X^n)\exp[\alpha(1-X)]-(\alpha+n\beta)X^n\}\exp\left[\beta(1-X^n)\right] \tag{5}$$

which are parameterized by five parameters V_0, E_0, α, β and n. Of these parameters the meanings of V_0 and E_0 are the same as in Eq. (1), α mainly controls the property of repulsion part of cohesive energy and behavior of solids at high pressure region, and the other two coefficients, β and n, mainly control the property of attractive part and the behavior at low pressure and expansion regions. It can be seen that Eq. (4) reduces to the Morse potential, and Eq. (5) reduces to the Morse EOS as long as $\alpha=\beta$ and $n=1$. It should be emphasized, as in the GRS EOS, that the parameter E_0 in Eq. (4) quoted from experimental data guarantees that the GEF EOS can yields correct cohesive energy. Based on the relationships $B=-(1/3)X(\partial P/\partial X)$ and $B=(1/9B)X^2(\partial^2P/\partial X^2)$, the bulk modulus and its derivative with respect to zero pressure can be analytically expressed as follows:

$$B_0=\frac{n\beta E_0}{9V_0}(\alpha+n\beta+n-1) \tag{6}$$

$$B'_0=1+(Q/3)(\alpha+n\beta+n-1)^{-1} \tag{7}$$

in which $Q=(\alpha+n\beta)(\alpha+2n\beta)-(n-1)(n-2)$.

In Eq. (4), it is apparent that the repulsive part $n\beta\exp[\alpha(1-X)+\beta(1-X^n)]$ is a monotonously decreasing function of X and that the