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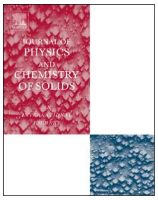

Interrelations between EOS parameters and cohesive energy of transition metals: Thermostatistical approach, ab initio calculations and analysis of "universality" features

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ABSTRACT

We present a theoretical analysis of the equation of state (EOS) of metals using a quasi-harmonic Einstein model with a dimensionless cohesive energy *versus* distance function ($F(z)$) involving the Wigner-Seitz radius and a material-dependent scaling length, as suggested in classical works by Rose, Ferrante, Smith and collaborators. Using this model, and "universal" values for the function and its first and second derivatives at the equilibrium distance (z=0), three general interrelations between EOS parameters and the cohesive energy are obtained. The first correlation involves the bulk modulus, and the second, the thermal expansion coefficient. In order to test these results an extensive database is developed, which involves available experimental data, and results of current ab initio density-functional-theory calculations using the VASP code. In particular, the 0 K values for volume, bulk modulus, its pressure derivative, and the cohesive energy of 27 elements belonging to the first (Sc, Ti, V, Cr, Fe, Co, Ni, Cu, Zn), second (Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag, Cd) and third (Hf, Ta, W, Re, Os, Ir, Pt, Au) transition row of the Periodic Table are calculated ab initio and used to test the present results. The third correlation obtained, allows an evaluation of the third derivative of $F(z)$ at z=0 for the current elements. With this new information, a discussion is presented of the possibility of finding a "universal" $F(z)$ versus z function able to account accurately for the pressure derivative of the bulk modulus of the transition elements.

1. Introduction

The knowledge of the cohesive properties and the equation-of-state (EOS) parameters of solids is a subject of permanent interest in solid-state science. In this field, empirical, semi-empirical as well as theoretical approaches have been applied to reveal rather general (often called "universal") features of the systematics and interrelations. In particular, Gschneidner [1] showed long ago that the experimental cohesive energy (E_{coh}), the bulk modulus (B_T), and the inverse atomic volume (v) of the elements exhibit the same general behavior when plotted *versus* the group number in the Periodic Table. In another pioneering work, Moruzzi et al. [2] demonstrated that these trends can be well accounted for by density-functional-theory (DFT) ab initio calculations, and that B_T for the elements can be described as a single function of the interstitial charge density [2]. In turn, Miedema and collaborators [3,4] showed empirically that a specific combination of EOS parameters for various types of metals, *viz*., the ratio B_T/v could be represented by a single function of a parameter representing the electron density at the boundary of the Wigner-Seitz cell. This "universal" feature was one of the bases of the Miedema powerful semi-empirical approach to cohesion in metals [3].

More recently, the ab initio approach to cohesive properties and EOS parameters of elements have become a standard tool in the development of thermodynamic databases of interest in, *i.a.*, the calculation of phase diagrams [5,6]. In addition, the accuracy of the ab initio predictions using DFT calculations has been the subject of a considerable attention. In particular, a detailed assessment of such predictions for the elemental crystals has been presented, which might be adopted as benchmark for new correlations (see below) [7]. Moreover, there has been a continuous interest in the application of models and approaches to the EOS parameters of solids able to account, in a simple way, for the main features of the microscopic picture of cohesion developed in the theoretical work. These methods might lead to reasonably accurate estimates of lacking data and often

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reveal physically relevant trends. As a key example of this kind of studies, it might be mentioned that Sigalas et al. [8] analyzed the results of augmented plane wave calculations to correlate E_{coh} and B_T in terms of a simple model involving a volume-dependent interstitial electron density and the bonding valence of the elements.

Very recently, the present authors performed an analysis of the systematics of cohesive properties and EOS parameters for a large number of Me_aX_b type intermetallic phases formed by Me=Cu, Ni with X=In, Sn [9]. To this aim, an ab initio database obtained by DFT calculations was adopted. Two findings of that study may be highlighted, which are part of the motivations of the present work. First, it was shown that E_{coh}, B_T, and v of these compounds are smoothly varying functions of the "average group number" (AGN), a variable calculated as the weighted average of the number of valence electrons involved in the VASP calculations. Second, it was found that a strikingly simple interrelation holds between these three properties, *viz.*, B_T is proportional to the ratio E_{coh}/v.

Motivated by these recent findings, the general purpose of the current work is to study theoretically the interrelations between cohesive properties and EOS parameters of the 3d, 4d and 5d-transition metals using, for the sake of consistency, the same ab initio technique previously adopted to treat the intermetallic compounds [9]. Specifically, the work aims at establishing rather general correlations between E_{coh}, B_T, and v, and also explore the possibility of treating the thermal expansion coefficient α. To this end two theoretical methods are applied. In the first place, a simple thermostatistical model, *viz.*, a quasi-harmonic Einstein solid with a volume-dependent cohesive energy is used to derive various relations between B_T or α and E_{coh}. In the second place, in order to test the predictions of this model, ab initio calculations are performed for 27 elements, *viz.*, Sc, Ti, V, Cr, Fe, Co, Ni, Cu, Zn, Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag, Cd, Hf, Ta, W, Re, Os, Ir, Pt and Au.

The structure of the paper is as follows. In Section 2, we describe the thermostatistical model and in Section 3 we obtain the EOS of this idealized solid and the key parameters involved, *viz.*, B_T, $(\partial B/\partial P)_T$ and α. On these bases we establish theoretically three correlations involving the EOS parameters. In Section 4, we describe the experimental and theoretical database used to test the correlations. In particular, the results of systematic ab initio calculations are presented. Finally, in Section 5 the thermostatistical predictions are compared with experimental data and the ab initio results. In particular, the current results are compared with the database reported as Supplementary Material in the recent paper by Lejaeghere et al. [7]. Section 6 is devoted to a discussion of the "universal" implications of the present results. In Section 7 we summarize the work and present the conclusions.

2. Thermostatistical model

Consider a finite sample of volume of an infinite Einstein solid with a volume per atom v. This set of Einstein oscillators will be treated in the framework of the quasi-harmonic approximation (QHA), which assumes that the atomic vibrations are harmonic but the frequency ω is a function of the volume of the solid [10]. This implies that the Einstein characteristic temperature (θ_E), defined by the relation $\theta_E(v) = \hbar\omega(v)/k_B$ [11,12] depends upon v. By adopting the canonical formalism, we express the Helmholtz energy (A) per atom of the system as [13,14]:

$$A = u_0 + 3k_BT\left[\frac{x}{2} + \ln(1 - e^{-x})\right] \tag{1}$$

where $x = \theta_E(v)/T$. The quantity u_0 is related to the cohesive energy of the solid E_{coh} as follows:

$$u_0 = E_{coh}F(z) \tag{2}$$

where E_{coh} is evaluated at T=0 and at the volume v_0 corresponding to the equilibrium with a pressure P=0. F is a dimensionless function, whose properties are to be established. Following Rose et al. [15] F will be expressed as a function of the dimensionless variable z, defined as $z = (r - r_0)/l$, where $r = (3v/4\pi)^{1/3}$ is the Wigner-Seitz radius, r_0 is the Wigner-Seitz corresponding to v_0 and l is a material-dependent scaling length.

In order to obtain the EOS and the compression and expansion parameters from Eq. (1) it is necessary to evaluate, at $v = v_0$, the function u_0, and its first and second derivatives with respect to volume: u'_0 and u''_0. According to Eq. (2) this implies the evaluation at z=0 of the function $F(z)$ and its derivatives $F'(z)$ and $F''(z)$ with respect to z. The following material-independent (referred to in the following as "universal") values were adopted. By definition, $F(0) = -1$, whereas the equilibrium condition at P=0 requires $F'(0) = 0$. The value $F''(0) = 1$, early proposed by Rose et al. will be adopted in the present work because this is the value one would obtain if the $F(z)$ *vs.* z function was strictly parabolic [16]. This is compatible with the present adoption of a quasi-harmonic solid. We remark, however, that one of the correlations obtained in the present study allows a systematic evaluation of the third derivative of the function $F(z)$ from the current experimental and theoretical database. The implications of these results upon the possibility of designing a "universal" $F(z)$ for the transition metals are discussed in Section 6.

3. Thermophysical properties and interrelations

3.1. Equation of state (EOS)

The equilibrium pressure (P) of the solid will be obtained from Eq. (1) by applying the identity $P = -(\partial A/\partial v)_T$. This yields:

$$P = -\frac{u'_0}{2} + \frac{3k_B\theta_E}{v}f_1 \tag{3}$$

where,

$$f_1 = \left(\frac{1}{2} + \frac{1}{e^x - 1}\right)\gamma_E \tag{4}$$

and $\gamma_E = -d\ln\omega(v)/d\ln v = -d\ln\theta_E(v)/d\ln v$. The parameter γ_E, which is a kind of Grüneisen parameter, will be assumed, as a first approximation, to be constant, with values roughly comparable to the usual thermodynamic Grüneisen parameter γ_G. We remark, however, that the current γ_E and the γ_G parameter should in general be considered as different quantities [17].

3.2. Isothermal bulk modulus

The isothermal bulk modulus (B_T) is obtained from Eq. (3), *viz.*,

$$B_T = -v\left(\frac{\partial P}{\partial v}\right)_T = \frac{u''_0 v}{2} + \frac{3k_B\theta_E}{v}\left[f_1(1 + \gamma_E) + \frac{\partial f_1}{\partial x}x\right] \tag{5}$$

where $\partial f_1/\partial x = -e^x\gamma_E/(e^x - 1)^2$. By applying Eq. (5) at T=0 and $v = v_0$, and replacing u''_0 for the second derivative of Eq. (2) evaluated at z=0, we obtain:

$$B_0 = \frac{E_{coh}}{v_0}\left(\frac{1}{9\lambda^2}\right) + B^* \tag{6}$$

where $B^* = 3/2(k_B\theta_E/v_0)(\gamma_E + \gamma_E^2)$ and $\lambda = l/r_0 = l(4\pi/3v_0)^{1/3}$.

Considering in the first place Eq. (6) we note that the B^* term is two orders of magnitude smaller than the first term. As a consequence, by keeping only the leading term in the sum we obtain the approximate expression:

$$B_0 \simeq \frac{E_{coh}}{v_0}\left(\frac{1}{9\lambda^2}\right) \tag{7}$$

We remark that a correlation between B_T and the E_{coh}/v ratio was obtained empirically by Brahzkin and Lyapin [18] by analyzing experimental data and determining values of the proportionality constants appropriate for various groups of elements. In addition, their result was given some justification by relying on simple models of the energy *vs*. volume of the elements that had been discussed in ref. [19]. More recently, Wacke et al. [20] motivated the correlation by dimensional arguments, based on interpreting the bulk modulus as a volumetric energy density related to the thermodynamic compression work. The present work offers a theoretical justification of the empirical results, and a systematic test of the interrelation by using an extensive experimental and theoretical database.

3.3. Isobaric thermal expansion coefficient

The isobaric thermal expansion coefficient α is obtained from Eqs. (3) and (5) as

$$\alpha = \left(\frac{\partial P}{\partial T}\right)_v B_T^{-1} = \frac{-3k_B x^2 \dfrac{\partial f_1}{\partial x}}{\dfrac{u''_0 v^2}{2} + 3k_B\theta_E\left[f_1(1+\gamma_E) + \dfrac{\partial f_1}{\partial x}x\right]} \tag{8}$$

By applying Eq. (8) at a temperature equal to the characteristic Einstein temperature of the solid, *viz*., at $T/\theta_E = 1$ and neglecting, as a first approximation, the difference between the equilibrium volume at $T = \theta_E$ and the equilibrium volume v_0 corresponding at 0 K, we get:

$$\alpha_1 = \frac{2.76k_B\gamma_E}{\dfrac{E_{coh}}{9\lambda^2} + k_B\theta_E(0.48\gamma_E + 3.24\gamma_E^2)} \tag{9}$$

Then, by keeping only the leading term in the denominator of Eq. (9), which is approximately two orders of magnitude larger than the second term, we obtain the approximate expression

$$\alpha_1 \simeq \beta E_{coh}^{-1} \tag{10}$$

Gschneidner [1] and later on Van Uitert et al. [21] empirically correlated the thermal expansion coefficient with the inverse temperature of fusion (T_f). In view of the trends in the variation of T_f across the Periodic Table, it is reasonable to expect a similar correlation between α and E_{coh}^{-1}. This expectation has recently been tested in a phenomenological fashion by constructing α versus E_{coh} plots for metals and ceramics [22]. The present work shows that such correlation can, in fact, be derived from a very general thermostatistical account of the cohesive and vibrational properties of solids.

3.4. Pressure derivative of the bulk modulus

The pressure derivate of the bulk modulus is obtained from the identity

$$\left(\frac{\partial B}{\partial P}\right)_T + 1 = \frac{v^2}{B_T}\left(\frac{\partial^2 P}{\partial v^2}\right)_T \tag{11}$$

Starting from Eq. (3) and making $T = 0\,K$ and $v = v_0$, we obtain $(\partial^2 P/\partial v^2)_0 = -u'''_0/2 + (3k_B\theta_E/2v_0^2)(\gamma_E + \gamma_E^2)(1 + \gamma_E)$. By inserting this result in Eq. (11) together with the third derivative of u_0 evaluated at z=0, we obtain

$$\left(\frac{\partial B}{\partial P}\right)_0 + 1 = \frac{1}{B_0}\left[-\frac{E_{coh}}{v_0}\frac{1}{27\lambda^2}\left(\frac{F'''(0)}{\lambda} - 6\right)\right] + \frac{B^*}{B_0}(1 + \gamma_E) \tag{12}$$

Eq. (12) yields the most general relation between the pressure derivative of the bulk modulus and the cohesive properties of the solid. Two approximate expressions will be derived in the following. The first expression is obtained by combining Eq. (12) with Eq. (7), *viz*.,

$$\left(\frac{\partial B}{\partial P}\right)_0 \simeq 1 - \frac{F'''(0)}{3\lambda} + \frac{B^*}{B_0}(1 + \gamma_E) \tag{13}$$

The second expression is obtained by neglecting the third term in Eq. (13), which yields:

$$\left(\frac{\partial B}{\partial P}\right)_0 \simeq 1 - \frac{F'''(0)}{3\lambda} \tag{14}$$

We remark that Eq. (14) has previously been reported in [15,16]. The current work shows that this expression involves the approximation $B^* \ll B_0$.

3.5. Account of the electronic contribution to thermophysical properties

Before the present results are compared with experimental or theoretical values, it is emphasized that the description of the Helmholtz energy (Eq. (1)) does not include the electronic contribution to the entropy of the solid, which is usually present in the metallic elements. It order to obtain a rough estimate of the effect of such contribution upon the EOS parameters of interest here, suppose that the actual electronic contribution to entropy can be described at low temperatures as $\Phi(v)T$, where the electronic heat-capacity coefficient Φ is a function of volume. This would lead to a $-\Phi/2T^2$ term in the Helmholtz energy of the element, and a $(1/2)\Phi' T^2$ contribution to P. The corresponding contribution to B_T, described by a $(-v/2)\Phi'' T^2$ term, would tend to zero when approaching zero kelvin. This suggests that the existence of an electronic contribution to the bulk modulus of metals does not, in principle, preclude a meaningful comparison between experimental or ab initio B_T values at $T = 0$ K and the results of the present treatment.

In the same way, we can analyze the possible effects upon α_1 of an electronic contribution to entropy. Assuming that the electronic contribution to pressure would yield a $(1/2)\Phi' T^2$ term we evaluate a contribution to $(\partial P/\partial T)_V$ equal to $\Phi' T$. This is equivalent to say that the expression for α_1 for metals (Eq. (9)) would have a material-dependent additional $\Phi'\theta_E$ term in the numerator. We conclude that this term would simply contribute to the proportionality coefficient of a correlation between α_1 and E_{coh} without affecting the existence of the correlation itself.

Finally, the already considered electronic entropy of the metallic elements would yield an additional contribution, described by a $(-1/2)(v^2/B_T)\Phi'' T^2$ term in the expression for $(dB/dP) + 1$ (Eq. (11)). This term would vanish at T=0 K. Hence, the existence of an electronic entropy contribution would not preclude a meaningful comparison between experimental or ab initio $(\partial B/\partial P)_T$ for metals at $T = 0$ K and the results of the present treatment.

4. Thermophysical database

4.1. Experimental information

The experimental cohesive energy values listed in Ref. [23] were corrected to include the zero-point energy. To this end the standard correction term $9/8k_B\theta_D$ [10], where θ_D is the Debye temperature, was added to the experimental values. The necessary θ_D information was taken from Ref. [23].

Since an appropriate database with thermal expansion data at $T = \theta_E$ was not available, only a preliminary test of the correlation will be made, by approximating α_1 for the elements with their respective room-temperature (RT) values. A similar limitation is found concerning the information on the bulk modulus. Accordingly, when comparing with experimental data we will assume, as a reasonable approximation, that $B_0 \simeq B_{RT}$ and $B'_0 = B'_{RT}$. The experimental values of v_0, B_{RT} and α_{RT} are taken from Ref. [23] and B'_{RT} from Ref. [24].

4.2. Theoretical values from ab initio calculations

Theoretical values of the 0 K cohesive energy and EOS parameters for the elements Sc, Ti, V, Cr, Fe, Co, Ni, Cu, Zn, Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag, Cd, Hf, Ta, W, Re, Os, Ir, Pt and Au in their stable structure at 0 K, were obtained in the present work by spin polarized total energy DFT calculations, performed applying the projector augmented wave method (PAW) [25,26] and using the VASP code [27]. For the exchange-correlation energy we adopted the generalized gradient approximation (GGA) due to Perdew and Wang (GGA-PW91) [28]. The choice of the cutoff energy was tested until the changes in the total energies and in the cohesive energies were less than 2 meV/atom. For the solids the Brillouin zone integration was mapped on well-converged (within 1 meV/atom) Monkhorst–Pack k-point meshes [29] and the Methfessel–Paxton technique [30] with a smearing factor of 0.1 to define the occupation of the electronic levels. We used the Rose–Vinet formula to evaluate B_0 and B'_0 from the ab initio total energy *vs.* volume values. To evaluate the cohesive energy per atom the calculation of the total energies of the isolated atoms is required. For this purpose we consider an isolated atom in a sufficiently large cubic supercell (a lattice parameter of up to 20 A was considered). The cutoff energy was carefully checked independently from the bulk calculations to guaranty the required convergence criteria. The Brillouin zone was mapped only at the Γ point, and the Gaussian method with a very small smearing factor (0.001 eV) was used to occupy the electronic levels as recommended. Since in some cases the magnetic atomic groundstates might differ from the configurations for which the potential was generated, the correct atomic magnetic moment was set by fixing the difference between spins up and down along the run.

The calculated properties of the transition elements are listed in Table 1.

5. Results

5.1. Bulk modulus

In Fig. 1 we plot using symbols the experimental and theoretical values of B_0 for several elements as a function of their ratio E_{coh}/v_0. Each dashed line corresponds to a single value of the λ parameter entering into Eq. (7). Various aspects of the results in Fig. 1 are discussed in the following. In the first place, the experimental and theoretical data in this graphic lend support to the idea that linear relations between B_0 and the E_{coh}/v_0 ratio, with different proportionality constants, can be established, as previously reported on purely empirical grounds in Refs. [18,20]. Moreover, Fig. 1 suggests that the metallic elements with similar λ values belong to the same group in the Periodic Table and have the same structure. The latter observation provides a new, phenomenological interpretation of the correlation between B_0 and the E_{coh}/v_0 ratio, in the framework of the approach by Rose et al. According to the present work, the observation that several elements can be described by the same proportionality constant between B_0 and the E_{coh}/v_0 ratio, is a manifestation of the fact that their cohesive energy *vs.* volume function can be scaled by adopting similar values of the λ parameter.

It is interesting to note that in the work by Wacke et al. [20] the correlation between B_0 and E_{coh}/v_0, for various metals was described by using two proportionality relations, *viz.*, $B = (4.068 \pm 0.193)E_{coh}/v_0$ and $B = (2.01 \pm 0.116)E_{coh}/v_0$. The values given by their suggested formulas (solid lines) with their reported uncertainty (dotted lines) are compared in Fig. 2 with the individual experimental and theoretical values included in the current database. It is evident that there is a group of the elements (in particular with the bcc structure) which are not described by the lines. In fact, Fig. 2 suggests that the equations given by Wacke et al. [20] should rather be interpreted as manifestations of the maximum and minimum values of the λ parameter appropriate for these transitions metals. Finally, in Fig. 2 we also plot using symbols the ab initio results presented in the most recent study of the elemental solids by Lejaeghere et al. [7]. There is a general agreement with the predictions of their PAW-VASP calculations based on the PBE exchange-correlation potentials, which adds to the confidence on the current methodology.

5.2. Thermal expansion coefficient

In Fig. 3, experimental values of the logarithm of α_{RT} for various elements according to ref. [1] are plotted *vs.* the logarithm of the E_{coh} from Ref. [23]. The experimental trends in this graphic suggest that the present dataset can be described using Eq. (10) with a reasonably well defined average value for the β parameter. Specifically, a linear least-squares fit to the data, represented by the dashed line in Fig. 3, yields a slope -1.09 ± 0.06, which agrees very well with the theoretical slope of -1, and $\beta \approx 0.2$. Since the approximation $\alpha_1 \approx \alpha_{RT}$ surely contributes to the scatter of the datapoints in Fig. 3, we suggest that a new database with assessed α_1 values is necessary for a rigorous test of the present correlation, and to refine the evaluation of the β coefficient for the elements.

6. Discussion of “universal” features

So far, the predictions of the thermostatistical model for B_0, E_{coh}/v_0 and α_{RT} were based on the “universal” values $F(0) = -1$, $F'(0) = 0$ and $F''(0) = 1$, without assumptions about $F'''(0)$. The values of $F'''(0)$ will be discussed in the following by using the results in Section 3. Since the

Table 1
Ab initio equilibrium volume per atom (in $\AA^3$/atom), bulk modulus (in GPa), its pressure derivative and cohesive energy (in eV/atom) for the current set of transition metals. The fifth value is the λ parameter.

Sc	**Ti**	**V**	**Cr**		**Fe**	**Co**	**Ni**	**Cu**	**Zn**
24.01	17.28	13.17	11.69		11.33	10.82	10.87	12.05	15.38
58.2	111.5	189.5	198.7		187.6	216.5	195.4	136.9	53.6
3.9	3.9	3.8	3.9		5.8	4.7	4.9	4.9	6.5
4.36	5.5	5.5	4.02		5.28	5.54	4.84	3.49	1.11
0.235	0.225	0.198	0.175		0.210	0.205	0.201	0.194	0.155
Y	**Zr**	**Nb**	**Mo**	**Tc**	**Ru**	**Rh**	**Pd**	**Ag**	**Cd**
32.63	23.36	18.1	15.97	14.53	13.89	14.27	15.52	17.94	23.03
41.8	97.4	172.3	263.5	297.5	310.6	252.6	168.0	91.8	36.7
2.8	3.1	3.7	3.1	4.4	3.6	4.9	5.2	5.3	5
4.33	6.44	7.12	6.38	7.18	7.22	6.03	3.71	2.55	0.765
0.238	0.225	0.201	0.164	0.172	0.172	0.172	0.159	0.166	0.127
	Hf	**Ta**	**W**	**Re**	**Os**	**Ir**	**Pt**	**Au**	
	22.34	18.29	16.23	15	14.38	14.62	15.82	18.15	
	112	196.6	302.4	369.6	397.7	345.3	244.8	140.8	
	3.4	3.6	4.1	4.3	4.5	4.8	5.4	6.2	
	6.76	8.39	8.45	8	8.6	7.68	5.55	3.03	
	0.219	0.203	0.175	0.160	0.163	0.164	0.159	0.145	

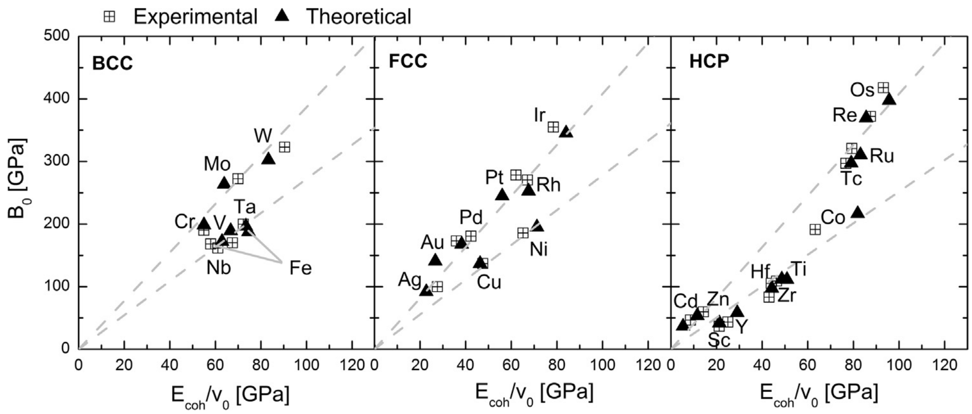

Fig. 1. Bulk modulus *vs.* the ratio of the cohesive energy and the volume per atom for the transition elements. The square symbols represent experimental values (here we took $B_0 \simeq B_{RT}$) and the triangles represent theoretical values calculated in the present work. The dashed lines were drawn by adopting average values of the λ parameter.

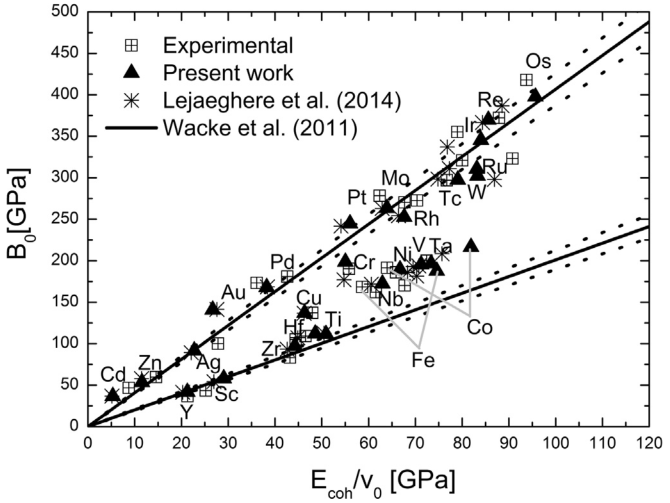

Fig. 2. The B_0 *vs.* E_{coh}/v_0 relation according to experimental (squares) and the present theoretical (triangles) values. The solid lines represent the values given by the equations suggested by Wacke et al. [20] and the dotted lines represent the uncertainty of their correlations. The values obtained by using the ab initio results of Lejaeghere et al. [7] are also plotted (asterisks).

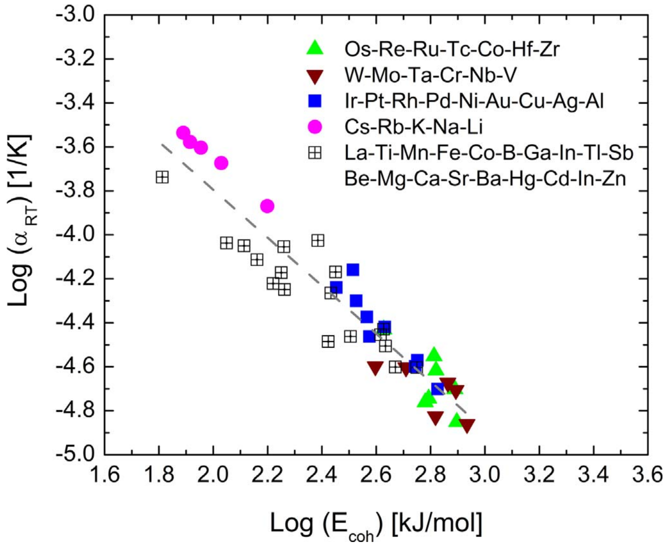

Fig. 3. Logarithm of the room-temperature thermal expansion coefficient *vs.* the logarithm of E_{coh}. The dashed line represents a linear least-squares fit with slope -1.09 ± 0.06.

aim of the current section is to bracket the possible values for $F'''(0)$, the simplest result given by Eq. (14) will be used. This choice also allows us to compare the present findings with those in Refs. [15,16]. Eq. (14) shows, in the first place, that a “strictly parabolic” $F(z)$ function, described by the condition $F'''(0) = 0$, would yield $(\partial B/\partial P)_0 = 1$. However, this value is not supported by the measured $(\partial B/\partial P)_T$ for elements, which are typically 3–6 times larger [10]. This indicates that an accurate account of the relation between the pressure derivative of the bulk modulus and other EOS parameters requires that $F'''(0)$ is given values different from zero, i.e., the dimensionless function F should describe a non-parabolic, truly anharmonic scaled-energy/scaled-distance relation.

In order to gain insight on the magnitude of the anharmonicity effect upon the description of $F(z)$, the $F'''(0)$ for each transition metal was evaluated by analyzing the experimental and the ab initio results in terms of Eqs. (14) and (7). The resulting values are plotted in Fig. 4 using symbols. The spread of the data-points is large, reflecting the uncertainties involved in the measurements, as well as in the procedure of extracting $(\partial B/\partial P)_T$ from the energy *vs.* volume relations obtained ab initio.

In spite of these uncertainties, it is possible to determine a probable range of values for $F'''(0)$, by considering those cases in which the use of experimental and theoretical values yielded similar results. By applying this criterion, a probable range of $F'''(0)$ for the transition metals is determined, and indicated by the horizontal dashed lines in Fig. 4.

The present results indicate that in order to account for the relation between $(\partial B/\partial P)_T$ and the other EOS parameters it is necessary to adopt negative values of the third derivative of the $F(z)$ *vs.* function at z=0. Such general result agrees with that of a previous analysis of specific

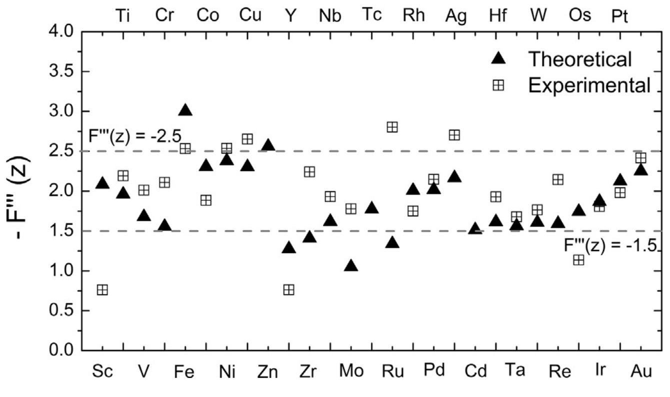

Fig. 4. The negative third derivative of $F(z)$ evaluated at z=0 evaluated from Eqs. (7) and (14) by using experimental (squares) and the present ab initio values (triangles) of the thermophysical properties. The dashed lines indicate the approximate limits of the currently determined range of $F'''(0)$ values.

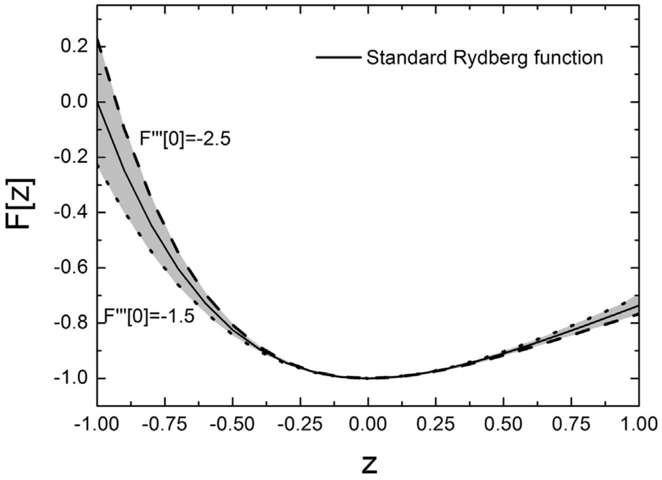

Fig. 5. The standard Rydberg function compared with the "extended" functions obtained by adopting the values $F'''(0) = -1.5$ and $F'''(0) = -2.5$. The shadowed region represents the range of values of the extended Rydberg function corresponding to the currently assessed range of $F'''(0)$ values.

$F(z)$ *vs.* z values obtained ab initio for the elements of the 4d-transition series [16]. Moreover, the current work indicates that the $F'''(0)$ values for the transition elements are material-dependent, and fall in the range $-2.5 < F'''(0) < -1.5$. This result may be compared with two previous assumptions about the $F(z)$ function. In the first place, Rose et al. described the $F(z)$ *vs.* z function for elements by using the standard Rydberg function ($-(1+z)\exp(-z)$), which yields $F'''(0) = -2.0$. In the second place, they also tested an extended form of Rydberg function of the type $-(1+z+az^3)\exp(-z)$, and chose the a parameter so that $F'''(0) = -2.3$. Indeed, these choices are well accounted for by the currently determined range.

Finally, we remark that even if the present work does not support the possibility of a strictly "universal" binding energy function for the transition elements, the standard Rydberg function is found to be a reasonably good approximation to $F(z)$. This is demonstrated in Fig. 5 where the standard Rydberg function (with $F'''(0) = -2.0$) is compared with the extended functions corresponding to $F'''(0) = -1.5$ and $F'''(0) = -2.5$. It is evident that the effects of the assumptions about $F'''(0)$ are particularly significant for values of z outside the range $-0.25 < z < 0.25$.

7. Concluding remarks

The main goal of the present work is the theoretical study of various correlations between the EOS parameters of solids using a quasi-harmonic Einstein model with a volume-dependent cohesive energy. By adopting the dimensionless $F(z)$ function of the scaled distance z introduced by Rose et al. [15], and the "universal" values $F(0) = -1$, $F'(0) = 0$, and $F''(0) = 1$, we obtain the EOS of the solid, the parameters B_0, B'_0 and α_T, and various very general correlations. One correlation, expresses the proportionality between two cohesive properties (B_0 and E_{coh}/v_0) and the other one, the fact that the thermal expansion coefficient at $T = \theta_E$ is proportional to the inverse of the cohesive energy.

In order to test the first of these material-independent predictions of the thermostatistical model we perform 0 K ab initio calculations for the elements of the 3d, 4d and 5d-transition rows of the Periodic Table in their stable structure. It is found that the thermostatistical predictions are supported by the current ab initio results, and agree very well with the most recent benchmarking study of the elemental solids [7], as well as the available experimental data. Moreover, the present results suggest that the existence of the proportionality relation between B_0 and E_{coh}/v_0 is a consequence of the fact that their characteristic λ parameters, related to the atomic volume (v_0) and the scaling length l (*viz.* $\lambda = l(4\pi/3v_0)^{1/3}$) are remarkably similar.

A preliminary comparison with thermal expansion data shows that the second correlation derived from the thermostatistical model accounts for the experimental trends at room-temperature.

Finally, the current work also yields a correlation between the cohesive properties and the $(\partial B/\partial P)$ parameter. By analyzing both experimental and ab initio results it is concluded that negative, material-dependent values should be given to $F'''(0)$. This contradicts the possibility of finding a single, i.e., "universal" $F(z)$ *vs.* z function able to describe accurately the pressure derivative of the bulk modulus of the elements of the transition series. On this basis the use of various forms of the extended Rydberg formula, *viz.* $-(1+z+a\,z^3)\exp(-z)$, to represent the $F(z)$ *vs.* z function is discussed.

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