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Universal features of the equation of state of solids from a pseudospinodal hypothesis

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We provide evidence of a universal equation of state for solids using a pseudospinodal hypothesis. A simple model to estimate the pseudospinodal curve is presented. This model combined with a previously reported (isothermal) volumetric equation [Baonza *et al.*, Phys. Rev. B **51**, 28 (1995)] yields a complete equation of state applicable over the whole range of temperature. The resulting equation appears to be a well-behaved equation of state over the whole range of temperatures using a single reference thermodynamic state of the solid at atmospheric pressure as input data. Comparison with experimental results of molar volume, bulk modulus, and thermal- (volumetric) expansion coefficient are presented. Comparison with previous equations of state are also presented and discussed. Our results imply that the thermodynamics of any solid are governed by its pseudospinodal curve.

I. INTRODUCTION

The equation of state (EOS) of a system describes the relationships among thermodynamic variables such as pressure, temperature, and volume. The mutual dependence of these properties can be theoretically studied by quantum and statistical mechanics methods. Recent theoretical developments have resulted from rapid advances in computational capabilities and accurate high-pressure experimental techniques.[1,2] Significant progress has been achieved over the past years to describe the properties of condensed matter in terms of universal relationships involving a small number of parameters;[3,4] however, a simple and accurate EOS valid for all types of solids and reliable over the whole temperature range is not yet available. With independence of the model used in their derivation, those EOS which incorporate temperature effects are limited to temperatures above the Debye temperature, θ_D, this feature being introduced by supposing constancy or linearity on the thermal- (volumetric) expansion coefficient, α_p, or constancy on the product $(\alpha_p B)$, with B the isothermal bulk modulus.[3]

In this paper we show that there exists a simple universal EOS valid for all solids which can be derived from a pseudospinodal hypothesis. The EOS is accurate over the whole temperature range, i.e., from zero temperature to the melting point of the solid (in absence of other phase transitions). The only necessary inputs are zero-pressure quantities (the molar volume V_0, the bulk modulus B_0, and its pressure derivative B_0') evaluated at a single (reference) temperature, as well as an estimate of the Grüneisen parameter γ^G at the reference temperature and the Einstein characteristic temperature of the solid θ_E.

II. DERIVATION

We recently proved that there exists a simple universal isothermal EOS applicable to all condensed materials,[5] including solids,

$$V(P)=V_{\rm sp}\exp\{[-\kappa^*/(1-\beta)][P-P_{\rm sp}]^{(1-\beta)}\}, \qquad (1)$$

where $V_{\rm sp}$ and $P_{\rm sp}$ are the volume and the divergence pressure along a certain pseudospinodal curve (PSC), respectively, and κ^* and β are, respectively, an amplitude and the pseudocritical exponent that characterize the pressure behavior of the isothermal compressibility $\kappa_T(=B^{-1})$ through the universal relation[6]

$$\kappa_T(P)=\kappa^*[P-P_{\rm sp}]^{-\beta}, \qquad (2)$$

β being a universal constant close to 0.85, the value which will be used here.

The PSC represents the mechanical-stability limit for a given phase of a substance. Here it can be considered as the negative hydrostatic pressure at which the solid ruptures.

We recently stated[5] that the *shape* of the PSC in P-T variables determines the ratio (α_p/κ_T) in solids [i.e., the thermal pressure coefficient $\gamma_v=(dp/dT)_v$] over the whole range of pressures. This follows from the fact that both quantities follow the same power law in the pressure, i.e.,

$$\alpha_p(P)=\alpha^*[P-P_{\rm sp}]^{-\beta}, \qquad (3)$$

with a value of β about 0.85 also, unlike liquids, where α_p diverges following a mean-field exponent.[7]

The previous statement can be written as follows:[5]

$$(dP/dT)_v=(\alpha_p/\kappa_T)=(\alpha^*/\kappa^*)=(dP_{\rm sp}/dT). \qquad (4)$$

The coefficients in Eq. (1) are related to zero-pressure quantities through the following relations:

$$B_0=[1/\kappa^*](-P_{\rm sp})^{\beta}, \qquad (5)$$

$$B_0'=\beta B_0/(-P_{\rm sp}), \qquad (6)$$

$$(V_{\rm sp}/V_0)=\exp\{\beta/[(1-\beta)B_0']\}. \qquad (7)$$

We have observed that both κ^* and $V_{\rm sp}$ are usually almost temperature independent within their estimated uncertainties over a wide range of temperatures. Therefore, through the present work we shall assume constancy on both quantities.

Thus, it follows from Eqs. (3) and (4) that the thermal-expansion coefficient at $P=0$ can be calculated as

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$\alpha_{p0}=(dP_{\mathrm{sp}}/dT)/B_0$. Finally, according to Eqs. (3)–(7), the temperature dependences of α_{p0}, V_0, B_0, and B_0' should be only determined by the shape (on temperature) of the PSC.

Let us now consider the Mie-Grüneisen equation, widely used in the correlation shock-wave experiments as well as to generate the EOS from P-V-T measurements.[1] This equation expresses the pressure as a function of volume and temperature as

$$P(V,T)=-(\partial U_{\mathrm{coh}}/\partial V)_{T=0}+(\gamma^G/V)E_{\mathrm{vib}}(T), \qquad (8)$$

where U_{coh} is the cohesion or binding energy and E_{vib} is the vibrational energy, which is only temperature dependent. The second term of Eq. (8) is called the thermal pressure.

Assuming that the ratio (γ^G/V) is temperature independent, a widely used approximation which is in good agreement with experiment,[8] we can write, according to Eqs. (4) and (8),

$$(dP/dT)_v=(\gamma^G/V)C_v=(dP_{\mathrm{sp}}/dT), \qquad (9)$$

where C_v is the isochoric heat capacity.

Integration of the second equality in Eq. (9) between zero temperature and a generic temperature T yields the PSC as a function of temperature, so the generic form of the Mie-Grüneisen equation is recovered,

$$P_{\mathrm{sp}}(T)=P_{\mathrm{sp}}^0+(\gamma^G/V)E_{\mathrm{vib}}(T), \qquad (10)$$

where P_{sp}^0 plays the role of the rupture (negative) pressure of the solid at 0 K.

The important feature of the present model is that only E_{vib} is temperature dependent in Eq. (10), so it drives the temperature variation of the PSC. Thus, provided $E_{\mathrm{vib}}(T)$ is known, the EOS of any solid can be determined from four experimental quantities only: V_0, B_0, B_0', and $\gamma^G(V_0)$, evaluated at a single reference temperature, T_{ref}.

In order to obtain an analytic approximation to the EOS, let us account for $E_{\mathrm{vib}}(T)$ using the Einstein's expression (so the characteristic temperature θ_E is also required as an input parameter). The PSC can be therefore written as follows:

$$P_{\mathrm{sp}}(T)=P_{\mathrm{sp}}^0+(\gamma^G/V)3Nk_B\theta_E\{(1/2)+1/[\exp(\theta_E/T)-1]\}, \qquad (11)$$

where k_B and N are the Boltzmann constant and the number of particles, respectively.

III. RESULTS

In the preceding section we established the universal EOS model; as the universal EOS applies to all classes of solids, in this section we shall apply our model to Xe, NaCl, and Au, as examples of molecular, ionic, and metallic bonding, respectively. Comparison will also be made, where appropriate, with the EOS of Vinet *et al.*[3] This EOS has been selected among others existing in the literature[4] because it proved reliable above the Debye temperature taking the same input values we shall use here. It must be pointed out that their predictions at high temperature require the thermal-expansion coefficient at the reference temperature as an addition input. This is an important difference with our model which will be discussed below. In order to compare both EOS directly we have used the reference values taken by Vinet *et al.* Table I records the input data for these solids, along with selected references.

TABLE I. Summary of the input parameters as well as reference temperatures for the three solids studied in this work. Parameters taken from Vinet *et al.* (Ref. 3) except where stated.

	Xe	NaCl	Au
V_0 (cm^3 mol^{-1})	35.54[a]	27.0 [b]	10.21[c]
B_0 (GPa)	3.02	23.5	166
B_0'	7.8	5.35	6.5
γ^G (V_0)	2.8 [d]	1.59[e]	2.99[c]
θ_E (K) $(=0.75\theta_D)$	48	240	122
T_{ref} (K)	60	298	300

[a] Reference 15.
[b] Reference 16.
[c] Reference 11.
[d] Reference 17.
[e] Reference 18.

A. Pseudospinodal curve

Let us first analyze the values of P_{sp}^0 obtained from Eq. (8) since it can be also estimated from the condition $(\partial^2 U_{\mathrm{coh}}/\partial V^2)_{T=0}=0$ [notice that the divergence of κ_T at the PSC can be also expressed as $(\partial P/\partial V)_T=0$]. Three potential models have been used to represent U_{coh}, namely, Lennard-Jones (12,6) for Xe, Madelung for NaCl, and the universal function for metals of Rose *et al.*[9] for Au (it can be proved that the final expression for P_{sp}^0 can be always written as CB_0, where C is a constant different for each potential model). The comparison with results obtained from Eq. (11) using parameters from Table I is shown in Table II; considerable agreement is found between both sets of data. These results confirm the physical significance of the parameters involved in Eq. (11).

Figure 1 compares the PSC obtained from fittings of experimental isotherms of Xe to Eq. (1) with that calculated from Eq. (6) using experimental data of B_0 and B_0',[10] and that predicted by Eq. (11) using parameters from Table I. Similar results are represented in Fig. 2 for NaCl, where the PSC estimated from $\alpha_p(P)$ experimental results correlated in terms of Eq. (3) is also included. The agreement is very satisfactory in both cases over the whole range of temperatures.

An indirect comparison of the adequacy of our model in calculating the PSC of metals can be made through the thermal pressure. Thus, we have checked our model with the calculated EOS for gold metal given by Anderson, Isaak, and Yamamoto.[11] The slope of the PSC for Au from Eq. (11) is 7.29 MPa K^{-1} for temperatures above θ_D, in excellent

TABLE II. Divergence (rupture) pressures at 0 K, P_{sp}^0 (GPa).

	Xe	NaCl	Au
Eq. (11)	-0.45	-4.66	-23.93
$(\partial^2 U_{\mathrm{coh}}/\partial V^2)_{T=0}=0$	-0.34	-4.25	-21.64

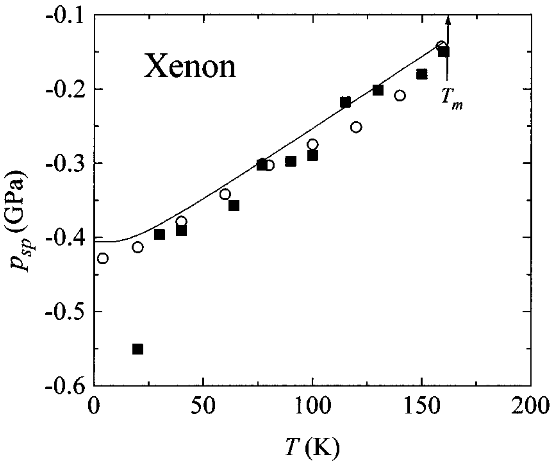

FIG. 1. PSC for Xe. Continuous line, Eq. (11) using the parameters recorded in Table I; (■), Baonza, Cáceres, and Núñez (Ref. 5), these results were obtained by fitting to Eq. (1) the experimental P-V-T results of Packard and Swenson (Ref. 8); (○), calculated from Eq. (6) using data of Anderson and Swenson (Ref. 10). T_m is the melting point temperature. Outlier at 20 K probably due to inaccuracies in experimental data.

agreement with the value 7.14 MPa K^{-1} reported by these authors for the temperature variation of the thermal pressure of this metal.

B. Prediction of thermodynamic properties

We shall now study the temperature dependence of several thermodynamic properties of the three model solids according to Eqs. (3)–(7). Comparisons will be shown for both experimental data and the EOS of Vinet *et al.*[3]

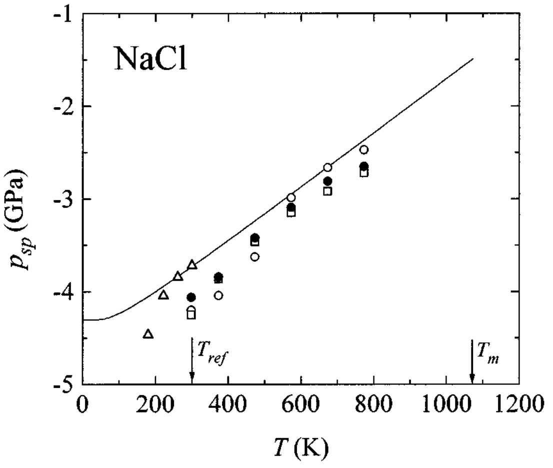

FIG. 2. PSC for NaCl. Continuous line represents the estimation given by Eq. (11) using the parameters recorded in Table I. Symbols: (○), Eq. (1) (Ref. 5); (□), Eq. (3) (Ref. 5); (●), Eq. (6) (Ref. 5); and (Δ), Eq. (6) using experimental data of Ghafelehbashi and Koliwad (Ref. 19). T_m is the melting point temperature.

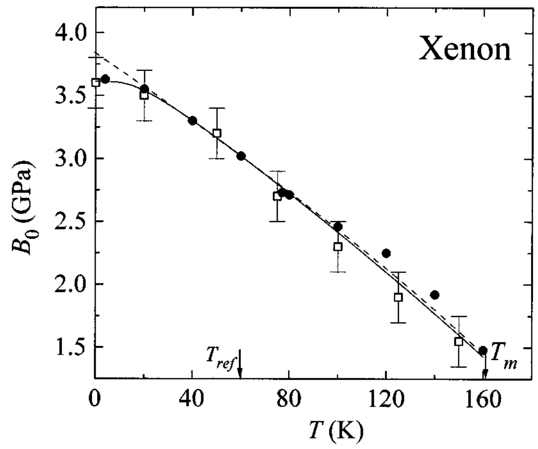

FIG. 3. Temperature dependence of zero-pressure bulk modulus, B_0, for solid Xe. Experimental results taken from (□), Packard and Swenson (Ref. 8) and (●) Anderson and Swenson (Ref. 10). Dashed line calculated using the EOS of Vinet *et al.* (Ref. 3). Continuous line calculated from Eq. (5) as described in the text using the parameters recorded in Table I.

The results for Xe are summarized in Figs. 3, 6, 8, and 9. Some results for NaCl are compared in Figs. 4, 7, and 10. Selected results are shown in Figs. 5 and 11 for Au. As can be seen, the overall agreement with experiment is very good. However, let us now analyze the general behavior of each property separately.

Due to the relative inaccuracy on B_0' as calculated from experimental results, comparisons of this quantity are not included in this section. The general behavior with temperature of this property is, however, well reproduced by our model through Eq. (6) (see Sec. IV for details).

1. Bulk modulus

As shown in Figs. 3, 4, and 5 our model reproduces adequately the experimental results of B_0. Besides the good

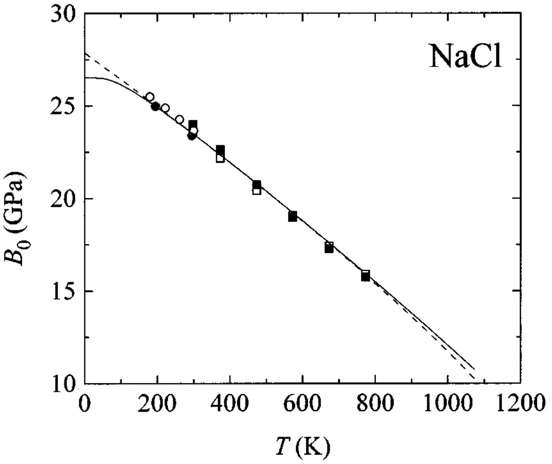

FIG. 4. Temperature dependence of zero-pressure bulk modulus, B_0, for solid NaCl. Experimental sources: (□) Boehler and Kennedy (Ref. 20) (calculated from Murnaghan equation); (■) Boehler and Kennedy (Ref. 20) (calculated from Birch equation); (●) Bartels and Schuele (Ref. 16) and (○) Ghafelehbashi and Koliwad (Ref. 19). Dashed line calculated from the EOS of Vinet *et al.* (Ref. 3). Continuous line calculated from Eq. (5) as described in the text using the parameters recorded in Table I.

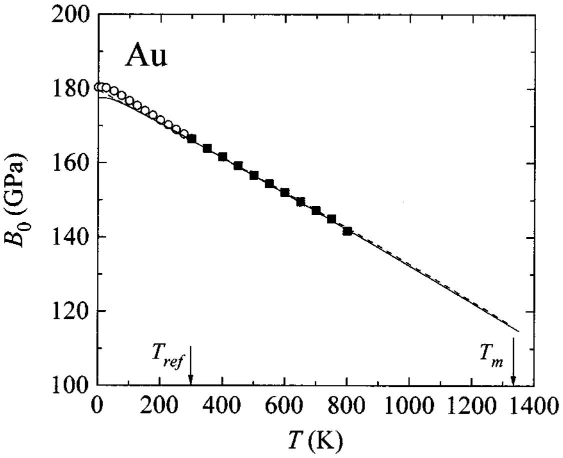

FIG. 5. Temperature dependence of B_0 for solid Au. Experimental results taken from (○) Neighbours and Alers (Ref. 21) and (■) Chang and Himmel (Ref. 22). Dashed line calculated from the EOS of Vinet *et al.* (Ref. 3). Continuous line calculated from Eq. (5) using the parameters recorded in Table I.

agreement found for this property at high temperatures the most striking results are those at the lowest temperatures. The slope of $B_0(T)$ must be zero at zero temperature on general thermodynamic grounds. This feature is confirmed by the experimental data, but commonly not well reproduced by other EOS available in the literature. It can be easily confirmed that Eq. (5) obeys this condition through P_{sp}.

2. Molar volume

Figures 6 and 7 show the comparison between the experimental values of the molar volume of Xe and NaCl, respectively, with predictions from Eq. (7). The agreement is quite satisfactory even at very low temperatures, although small discrepancies may appear as the difference between the temperature considered and T_{ref} increases (see, however, the comment on α_p of NaCl at the end of the following section). The ability of our model to account for volume changes with temperature can be better analyzed in terms of the thermal-expansion coefficient, as discussed in the following paragraphs.

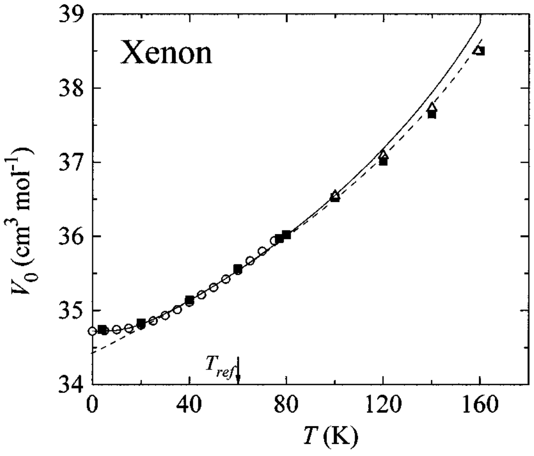

FIG. 6. Molar volume of solid Xe at zero pressure as a function of temperature. Experimental results taken from (○) Sears and Klug (Ref. 15); (■) Anderson and Swenson (Ref. 10); and (Δ) Gavrilko and Manzhelii (Ref. 23). Dashed line calculated using the EOS of Vinet *et al.* (Ref. 3). Continuous line calculated from Eq. (7) using the parameters recorded in Table I.

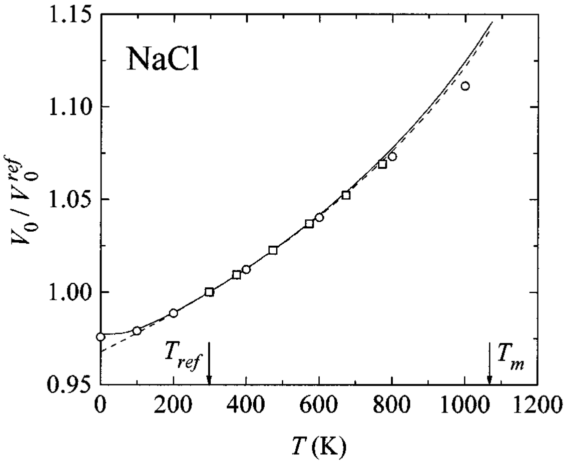

FIG. 7. Molar volume of solid NaCl at zero pressure as a function of temperature. Experimental results taken from: (○) Tallon (Ref. 12) and (□) Boehler and Kennedy (Ref. 20). Dashed line calculated using the EOS of Vinet *et al.* (Ref. 3). Continuous line calculated from Eq. (7) using the parameters recorded in Table I.

3. Thermal- (volumetric) expansion coefficient

The temperature dependence of α_{p0} of solid Xe is shown in Figs. 8 and 9. Comparison with experimental data reveals

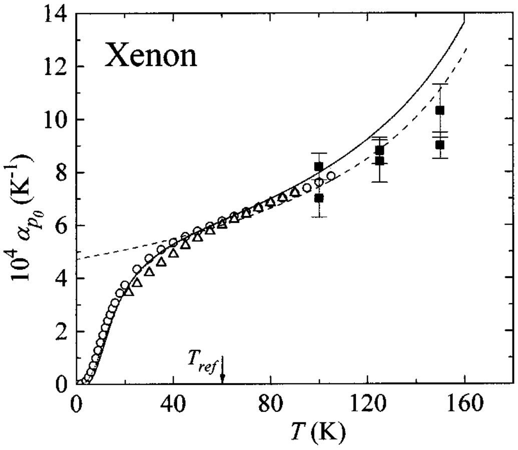

FIG. 8. Temperature dependence of thermal (volumetric) expansion coefficient of solid Xe. Experimental sources: (○) Tilford and Swenson (Ref. 17); (Δ) Manzhelii, Gavrilko, and Voitovich (Ref. 24); and (■) Packard and Swenson (Ref. 8). Dashed line calculated using the EOS of Vinet *et al.* (Ref. 3). Continuous line calculated from Eqs. (3) and (4) as described in the text. Dotted line represents the prediction of $\alpha_{p0}(T)$ using Debye's model instead of Einstein's model to calculate the pseudospinodal curve in Eq. (10).

quite good even at temperatures below θ_D. It can be also observed that the EOS of Vinet *et al.* is not adequate for low temperatures, as expected from its derivation. Recall that our model, unlike that of Vinet *et al.* through α_p at the reference temperature, does not incorporate any other temperature information different than that included in the PSC. The result is a *prediction* of the whole $\alpha_p(T)$ curve without any additional assumption. The goodness of the prediction is a direct consequence of Eq. (4), so the present results represent an additional confirmation to the approximations included in our model. In Fig. 10 similar results are plotted for NaCl; it can be observed as a good agreement with experimental data, although small deviations arise at high temperatures. Although our model tends to exhibit small positive deviations at high temperatures, we are not sure of attributing these discrepancies to our model only, since other sources reveal a greater thermal expansion for NaCl near the melting point, as already pointed out by Tallon.[12] Finally, the comparison with experimental data for Au is shown in Fig. 11.

At this point it is interesting to analyze the influence of the model employed to account for E_{vib} in Eq. (10). This analysis was not shown for other properties since the predictions obtained using Debye's model instead of Einstein's model are strictly indistinguishable. The differences are appreciable only for $\alpha_p(T)$ in the low-temperature range. Figures 9 and 11 confirm the widely known fact that Debye's model must improve the predictions near $T=0$. However, both models are indistinguishable at high temperatures and for the sake of simplicity we recommend Einstein's model since it leads to an analytical EOS. This means that the PSC is rather insensitive to the model employed for E_{vib}.

IV. DISCUSSION

Regarding the PSC, three important findings of this work are the following: (a) the PSC can be obtained through the elementary Einstein's theory of solids, leading to a simple analytical EOS, (b) this PSC agrees with that obtained from fittings of experimental P-V isotherms to Eq. (1), and (c) P^0_{sp} preserves its physical meaning and agrees with that calculated from the binding energy of the solid.

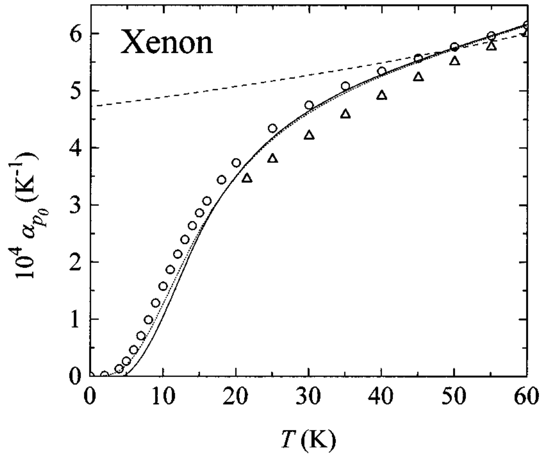

FIG. 9. Low-temperature range magnification of Fig. 8. Symbols as in Fig. 8.

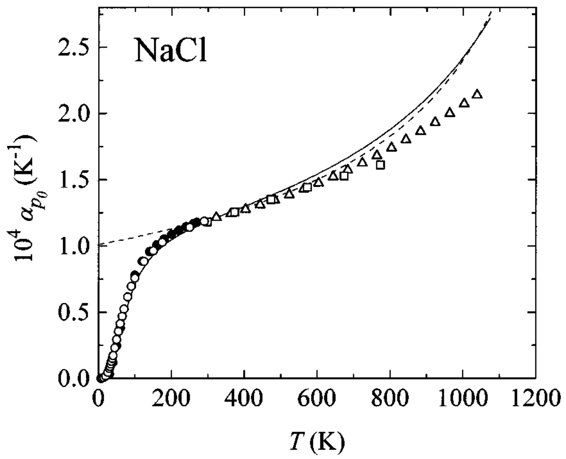

FIG. 10. Temperature dependence of thermal- (volumetric) expansion coefficient of solid NaCl. Experimental sources: (●) Yates and Panter (Ref. 25); (Δ) Enk and Dommel (Ref. 26); (○) Meincke and Graham (Ref. 27); (□) Boehler and Kennedy (Ref. 20). Dashed line calculated using the EOS of Vinet *et al.* (Ref. 3). Continuous line calculated from Eqs. (3) and (4) as described in the text.

A substantial difference between previous studies and ours is that the Mie-Grüneisen equation has been used to obtain the PSC, instead of using it to generate the thermal EOS of the solid. This procedure avoids some serious problems arising from the determination of the volume dependence of the ratio (γ^G/V).[13,14]

Regarding the improvements of our EOS over others recently proposed in the literature, the discussion can be focused on three aspects, namely, the number of initial parameters (i.e., experimental data) required to predict the EOS of a given solid, the quality of the estimation, and the goodness

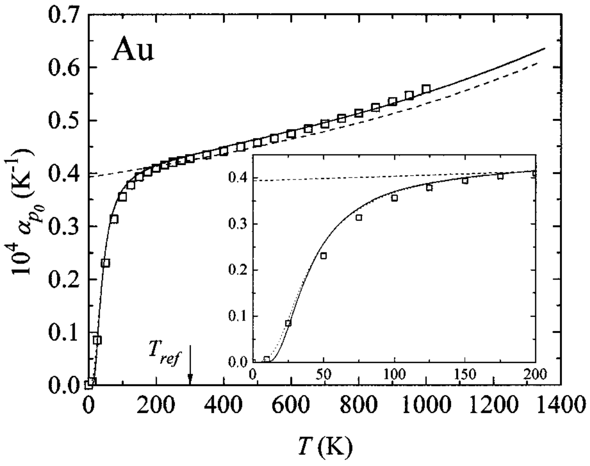

FIG. 11. Temperature dependence of thermal- (volumetric) expansion coefficient of solid Au. Experimental source: (□), Anderson, Isaak, and Yamamoto (Ref. 11). Dashed line calculated using the EOS of Vinet *et al.* (Ref. 3). Continuous line calculated from Eqs. (3) and (4) as described in the text. Low-temperature magnification (inset) compares the estimation obtained by using the Debye's model (dotted line) with that using Einstein's model.

of the method over the whole temperature range, including temperatures below the Debye temperature.

While most EOS needs three parameters (usually V_0, B_0, and B_0') for each isotherm, our model works equal or better using these three parameters of a *single* isotherm plus γ^G at this temperature and θ_E (strictly speaking, this quantity can be better referred to as a characteristic of the material more than a parameter).[3,4] For instance, the EOS of Parsafal and Mason[4] needs evaluation of three P-V isotherms (nine parameters) to predict the entire P-V-T surface. The only model which reduces drastically the number of parameters to account for the temperature effect in the EOS is that of Vinet *et al.* where, as already mentioned, is included by means of an additional parameter, namely, the thermal-expansion coefficient at a given temperature. As has been proved above, our model is of a quality comparable to that of Vinet *et al.*, with the advantage that is valid at any temperature between zero and melting temperatures and, in addition, *predicts* the thermal-expansion coefficient without including any additional assumption or experimental information.

As already pointed out by Parsafal and Mason,[4] the method used by Vinet *et al.* to include temperature effects is equivalent to taking $(\partial P/\partial T)_v$ as independent of temperature, a feature which is not obeyed by many solids. This problem was solved by Parsafal and Mason by supposing that the internal energy of the solid is linear in temperature, but the price they paid was the appearance of nine undetermined constants in their EOS. In our treatment this variation is included in a natural way into the temperature dependence of the PSC. Moreover, the approximate linearity or constancy on $(\partial P/\partial T)_v$ depends exclusively on the value of the ratio (T/θ_D) at the temperature considered and so, on the characteristics of the solid under consideration.

Another issue which merits attention is the election of the reference thermodynamic state used to generate the EOS of a given solid. Thus, while most EOS require experimental information at temperatures above or near θ_D [otherwise $\alpha_p(T_{\mathrm{ref}})$ decreases too much, affecting the temperature dependency of all the properties], any temperature can be selected in our treatment. This feature is particularly useful for the study of solids with large values of θ_D, since most experimental data are available at room temperature, which eventually can be considered lower than θ_D.

In any case, the important conclusion which can be drawn is that the shape of the PSC determines the temperature dependence of the thermodynamic properties of solids. Notice that even nonlinear effects found in B_0 and α_{p0} at low temperatures are accurately predicted in our approach (this point was discussed by Vinet *et al.*[3]). This feature of our EOS represents a definitive improvement over others available in the literature. It must be emphasized that it is the simplicity of our model which leads to an analytical EOS; notice that, except at very low temperatures, no significant improvement is gained in our approach by using Debye's theory which, in addition, leads to a nonanalytic EOS.

Regarding the temperature behavior of other properties such as B_0', our model yields a fairly good agreement with values of this property as calculated from high-pressure experimental data. It must be emphasized that this kind of data are commonly rather inaccurate since they depend on the extrapolation method used to obtain B_0'. This question was discussed by Baonza, Cáceres, and Núñez.[5] They recommended Eq. (1), among others in the literature, to obtain B_0 and B_0' from high-pressure data, since their parameters are not influenced too much by the range of pressure considered in the correlation.

In order to illustrate this feature, we have calculated values of B_0' for gold at several temperatures. To our knowledge, experimental data of B_0' as a function of temperature is not available for Au. In addition, it is difficult to estimate this quantity using data from literature due to the very limited experimental high-pressure data. However, we can check our model with the calculated EOS for this metal given by Anderson, Isaak, and Yamamoto.[11] If one uses their recommended value for $B_0'(300\ \mathrm{K})=5.5$, one obtains from Eq. (6) the following results: $B_0'(1000\ \mathrm{K})=5.68$, $B_0'(2000\ \mathrm{K})=6.07$, $B_0'(3000\ \mathrm{K})=6.83$, in satisfactory agreement with their observations.

Finally, notice that, since the correct temperature dependences of the thermodynamic properties depend on the universal value given to the pseudocritical exponent β, the overall results corroborate the approximate value of $\beta=0.85$ used here.[5,6] A detailed numerical analysis of this parameter shows that it changes slightly for different substances, although it usually remains around 0.80. In addition, as occurs with V_{sp} and κ^* also, the pseudocritical exponent β depends on temperature (increases with temperature), although, to a first approximation, the constant value used here is good enough for our purposes. However, if one computes the values of the ratio (V_{sp}/V_0) obtained from our model, the values are considerably higher than physically expected, especially at low values of B_0'. This is a direct consequence of the strong variation of V near the PSC as the value of β increases.

It is interesting to point out that from the model developed by Rose *et al.*[9] for metals (which the EOS of Vinet *et al.* is based on), and using Eq. (6), one can calculate β at $T=0$. The resulting values of β (about 0.70, in average, for about 40 metals) are slightly smaller than ours. From the EOS of Vinet *et al.*[3] it is also possible to calculate β using Eq. (7). The values obtained are smaller once again, about 0.65. Lower values of β yield more reasonable ratios for (V_{sp}/V_0), but, within the frame of our model, these are inadequate to represent the temperature dependence of the EOS of solids. This feature needs therefore further study in order to obtain consistent values for β and (V_{sp}/V_0).

In this paper we have dealt with the temperature dependence of the characteristic parameters of Eq. (1). Since it proved reliable over the whole range of pressures,[5] in a forthcoming publication we shall show the validity of our approach to predict the whole P-V-T surface and other thermodynamic properties of several solids at high pressures.

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