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Thermal Vinet Equation of State and Its Applications*

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Abstract: Based on the Einstein model, the universal equation of state for solids proposed by Vinet *et al*. is extended to include the thermal effect. Employing the nearest neighbor generalized Lennard-Jones potential to describe the effective interaction between the ions, the lattice part of potential energy per atom is expanded as quadratic function of displacement of ion to derive the Einstein temperature and Debye-Grüneisen parameter as a function of the volume. The theory contains four potential parameters except for the three parameters in the Vinet EOS, but only five of them are independent, and as the temperature being higher than the Debye temperature, the number of independent parameter can be further reduced to four. The theory is applied for 23 metallic solids, to predict Debye-Grüneisen parameters and compressibility coefficients at chamber temperature. The predicted results are in good agreement with the experimental data. The predicted variation of compressibility and thermal expansivity coefficients with temperature for gold, copper, xenon and sodium chloride also are in good agreement with the experimental data.

Key words: equation of state; Einstein model; thermodynamic properties

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1 Introduction

The equation of state (EOS) of a system describes the relationships among thermodynamic variables such as pressure, temperature, and volume. In 1986, Vinet *et al*. argued[1~4], based on theoretical calculations and experimental data, there is a universal EOS for all classes of solids in compression and in the absence of phase transitions. The Vinet EOS[4] is as follows

$$p = 3B_0 \frac{1-y}{y^2} e^{\eta_0(1-y)} \tag{1}$$

$$y = \left(\frac{V}{V_0}\right)^{1/3}, \eta_0 = \frac{3}{2}(B'_0 - 1) \tag{2}$$

Where p is the pressure, V is the volume of material containing N ions, V_0 is the volume at zero pressure, B_0 and B'_0 are, respectively, the isothermal bulk modulus and its first pressure derivative at zero pressure.

The Vinet EOS is a cold pressure EOS, soon after its proposition, Vinet *et al*. modified their EOS to include thermal effect at high temperature[5,6]. However, their derivation is based on an empirical

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assumption that the thermal pressure is independent of the volume and linear with temperature above the Debye temperature. So the modified EOS is not applicable to the low range of temperature, and even at high temperature, the prediction of thermal properties also is not too satisfactory.

In this paper, we proposed a simple method to establish a Grüneisen function and extend the Vinet EOS for metallic solids to include thermal effects. We employ the nearest neighbor generalized Lennard-Jones (GLJ) potential to describe the effective pair potential between ions and combining the Einstein model to consider the temperature effect of Vinet EOS. By expanding the lattice part of potential energy per ion as quadratic function of displacement of ion near its equilibrium position, we derived the Einstein characteristic temperature and the Debye-Grüneisen parameter as a function of volume. With the appropriately determined parameters the extended EOS can excellently predict the compressibility and thermal expansivity coefficients at whole range of temperature. Even the nonlinear effects in the thermal expansion, which have been difficult to obtain, are accurately predicted by this approach.

In Section 2, the Einstein temperature and the Grüneisen parameter for the generalized Lennard-Jones potential are derived, and the Vinet EOS is extended. The theory is applied to 23 metallic solids, and the theoretical results for gold are compared with the Vinet's modified EOS and the experimental data in Section 3. The conclusion is presented in Section 4.

2 Extension of Universal Equation of State

In Ref. [7], Xu and Zhang have given out the expression for the Einstein characteristic temperature

$$\Theta_{\mathrm{E}}=\frac{\hbar}{k}\left(\frac{1}{\mu}\nabla_r^2 u(r)\mid_0\right)^{1/2} \tag{3}$$

The expression is based on the Einstein model (or cell model)[8], and $u(r)$ is the potential energy of per ion contributed by the pair potential $\varepsilon(r)$. In order to derive the analytic expression of Θ_{E}, we adopt the nearest neighbor generalized Lennard-Jones potential to describe the interaction between ions

$$\varepsilon(r)=\frac{\varepsilon_0}{m-n}\left[n\left(\frac{r_0}{r}\right)^m-m\left(\frac{r_0}{r}\right)^n\right] \tag{4}$$

Where m, n, ε_0, r_0 are four potential parameters. In terms of Ref. [7~9], we have

$$\nabla_r^2 u(r)\mid_0=\frac{mn\Lambda^*}{(m-n)a^2}\left[(m-1)y^{-m}-(n-1)y^{-n}\right] \tag{5}$$

Here a is the distance between the nearest neighbors, z is the coordination number, γ_0 is the structure constant, and

$$\Lambda^*=z\varepsilon_0,\ y=a/r_0=(V/V_0)^{1/3} \tag{6}$$

$$V=Na^3/\gamma_0,\ V_0=Nr_0^3/\gamma_0 \tag{7}$$

The meanings of V and V_0 are the same as Eq. (2). Substituting Eq. (5) into Eq. (3), the Einstein temperature is given by following equation

$$\Theta_{\mathrm{E}}=\frac{\hbar}{kr_0 y}\left\{\frac{mn\Lambda^*}{3(m-n)\mu}\left[(m-1)y^{-m}-(n-1)y^{-n}\right]\right\}^{1/2} \tag{8}$$

If we have the experimental value of Θ_{E}^0 and γ_{G}^0 at V_0 ($y=1$), from Eq. (6) we have

$$\Theta_{\mathrm{E}}^0=\frac{\hbar}{kr_0}\left(\frac{mn\Lambda^*}{3\mu}\right)^{1/2} \tag{9}$$

Substituting Eq. (9) into Eq. (8), we obtain

$$\Theta_{\mathrm{E}}=\frac{\Theta_{\mathrm{E}}^0}{y}\left\{\frac{1}{m-n}\left[(m-1)y^{-m}-(n-1)y^{-n}\right]\right\}^{1/2} \tag{10}$$

The experimental value of Θ_{E}^0 can be estimated by the relationship, $\Theta_{\mathrm{E}}=(3/4)\Theta_{\mathrm{D}}$. In terms of the defi-

nition of Debye-Grüneisen parameter, $\gamma_G = -(V/\Theta_E)(\partial\Theta_E/\partial V)$, we obtain

$$\gamma_G = \frac{(m-1)(m+2)y^{-m} - (n-1)(n+2)y^{-n}}{6[(m-1)y^{-m} - (n-1)y^{-n}]} \tag{11}$$

In terms of Eq. (7) and Eq. (8), the extended Vinet EOS is derived as

$$\xi = \frac{pV}{NkT} = \frac{3B_0V_0}{NkT}y(1-y)\exp[\eta_0(1-y)] + \frac{3\gamma_G(\Theta_E/T)}{\exp(\Theta_E/T)-1} \tag{12}$$

Eqs. (10, 11) show that both Einstein characteristic temperature Θ_E and Grüneison parameter γ_G are volume dependent, and consequently the thermal pressure in Eq. (12) also is volume dependent. The experimental value of γ_G^0 at V_0 ($y=1$) can be used as a condition to determine the parameters in the extended EOS, supposing $y=1$ in Eq. (11), we have

$$\gamma_G^0 = \frac{1}{6}(m+n+1) \tag{13}$$

It should be pointed out that there seemingly exist seven parameters in Eq. (12), they are not independent each other, only five of them are independent. Because we found the parameter n can be taken as universal constant in the fitting procedure, and the experimental data V_0 not only is directly a parameter and is related Θ_E and γ_G. Otherwise, if the temperature of material is higher than Θ_E, then parameter Θ_E can be eliminated from Eq. (12), and the equation can be changed as following simpler form

$$p = 3B_0\frac{1-y}{y^2}\exp[\eta_0(1-y)] + \frac{3\gamma_G NkT}{V} \tag{14}$$

Eq. (14) contains only four independent parameters, thus is more convenient for practical applications.

By using Eq. (12), other thermodynamic quantities can be evaluated. For example, the equation for the thermal expansivity coefficient is

$$\alpha_T = \frac{1}{V}\frac{\partial V}{\partial T} = \frac{1}{y}\frac{\partial y}{\partial T} \approx \frac{1}{y(T,p)} \cdot \frac{y(T+\Delta T,p) - y(T,p)}{\Delta T} \tag{15}$$

and the equation for the compressibility coefficient is

$$\beta_p = \frac{1}{V}\frac{\partial V}{\partial p} = \frac{1}{y}\frac{\partial y}{\partial p} \approx \frac{1}{y(T,p)} \cdot \frac{y(T,p+\Delta p) - y(T,p)}{\Delta p} \tag{16}$$

In this work, we only calculate the thermal expansivity coefficient and the compressibility coefficient at normal conditions with pressure $p \approx 0$, Eqs. (15, 16) can be simplified as

$$\alpha_T \approx \frac{1}{y(T,0)} \cdot \frac{y(T+\Delta T,0) - y(T,0)}{\Delta T} \tag{17}$$

$$\beta_p \approx \frac{1}{y(T,0)} \cdot \frac{y(T,\Delta p) - y(T,0)}{\Delta p} \tag{18}$$

Where $y(T,0)$, $y(T+\Delta T,0)$ and $y(T,\Delta p)$ should be solved from Eq. (12).

3 Results and Discussion

For determining the parameters in the extended EOS, we need five experimental data, B_0, B'_0, V_0, Θ_E^0, γ_G^0 (or thermal expansivity at some temperature α_T^0). As in the original Vinet EOS, the former three experimental data can be directly used in EOS, and strictly speaking, all of them should be at zero temperature. However, because their temperature dependence is not evident except B'_0, we use their experimental values at a reference temperature, and B_0 is taken as the value at zero temperature. We determine m by fitting α_T^0, and solve n from Eq. (13), then all parameters in Eq. (12) can be determined. The experimental data used are taken from Ref. [7, 10～13].

We have applied the extended EOS to 23 metallic solids and find that the parameter n can be taken as a universal constant with value 2 or 3, the two different values have little influence to the the-

oretical results. However, the value 3 may result two metallic solids Li and Ca have a physically meaningless value of $m(m<n)$, so we recommend the value 2 of n. Thus by using Eq. (12), we only need the experimental values of compressibility coefficient at zero temperature and thermal expansivity coefficient at any one temperature point, but we can predict the compressibility coefficient and the thermal expansivity coefficient at any temperature, even other thermodynamic properties also can be predicted, including the Debye-Grüneisen γ_G. The predicted γ_G and the compressibility coefficients at chamber temperature are compared with the experimental data in Table 1. The values of m are also listed in the table. The table shows that the theoretical results are in good agreement with the experimental data.

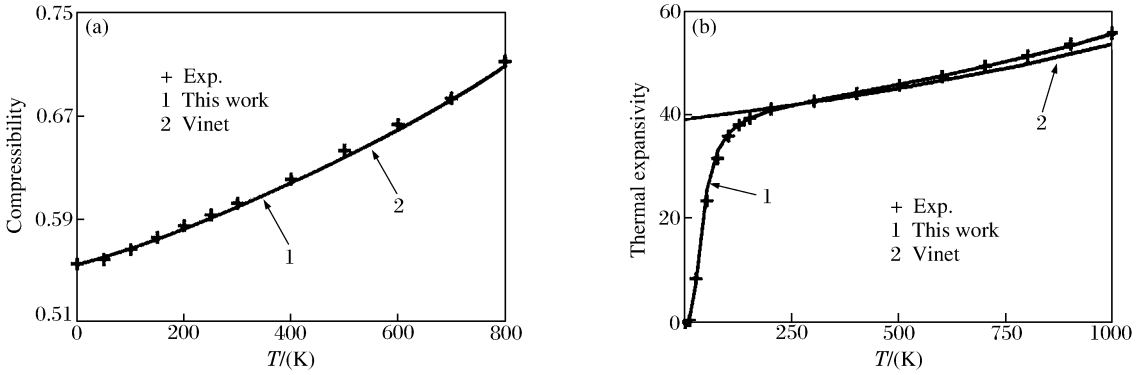
Table 1 The potential parameters m determined in this paper with $n=2$, and the experimental and calculated Grüneisen parameters and the compressibility coefficients for 23 metallic solids at 293 K (The experimental data used are taken from Ref. [10～13])

Metals	V_0 /(cm³/mol)	B_0 /(GPa)	B'_0	m	γ_G		$\beta_p/(10^{-11}\,\mathrm{cm^2\cdot N^{-1}})$	
					Exp.	Cal.	Exp.	Cal.
Ag	10.32	108.72	5.55	11.9	2.40	2.48	1.01	0.996
Al	9.985	79.381	4.61	10.6	2.19	2.27	1.36	1.351
Au	10.21	180.32	6.18	9.0	3.03	3.00	0.59	0.591
Ca	26.13	15.2	4.48	3.18	1.07	1.03	—	6.975
Co	6.774	194.8	5.05	10.6	2.22	2.26	0.53	0.536
Cu	7.071	142.03	5.65	9.12	1.99	2.14	0.75	0.748
Fe	7.071	169	4.96	8.52	1.81	1.92	0.60	0.616
Ir	8.513	366.67	6.00	13.1	2.50	2.69	0.28	0.281
K	42.97	3.66	4.05	5.28	1.34	1.38	33.7	34.3
Li	13.02	12.65	3.51	4.14	0.878	1.19	8.65	8.42
Mo	9.393	265.29	5.49	7.86	1.57	1.81	0.38	0.383
Na	22.70	7.24	3.84	4.38	1.25	1.24	16.5	16.3
Nb	10.92	173.03	4.72	6.90	1.74	1.65	0.59	0.589
Ni	6.629	187.6	4.92	9.90	2.00	2.15	0.55	0.555
Pb	18.13	48.79	5.88	13.8	2.84	2.80	2.30	2.307
Pd	8.858	195.43	5.91	11.0	2.38	2.33	0.54	0.535
Pt	9.034	288.4	5.96	13.9	2.87	2.81	0.36	0.361
Re	8.858	371.5	5.70	13.9	2.66	2.82	0.27	0.276
Ta	10.72	194.21	4.76	7.20	1.74	1.70	0.52	0.526
Th	19.88	58.1	4.17	7.26	1.67	1.71	1.74	1.783
Ti	10.72	109.7	4.66	4.62	1.23	1.27	0.93	0.932
V	8.344	157.04	4.70	5.46	1.40	1.40	0.65	0.652
Zn	9.213	59.8	6.53	8.22	1.75(1)	1.87	—	1.877

Note: (1) Calculated from the experimental data in Ref. [9].

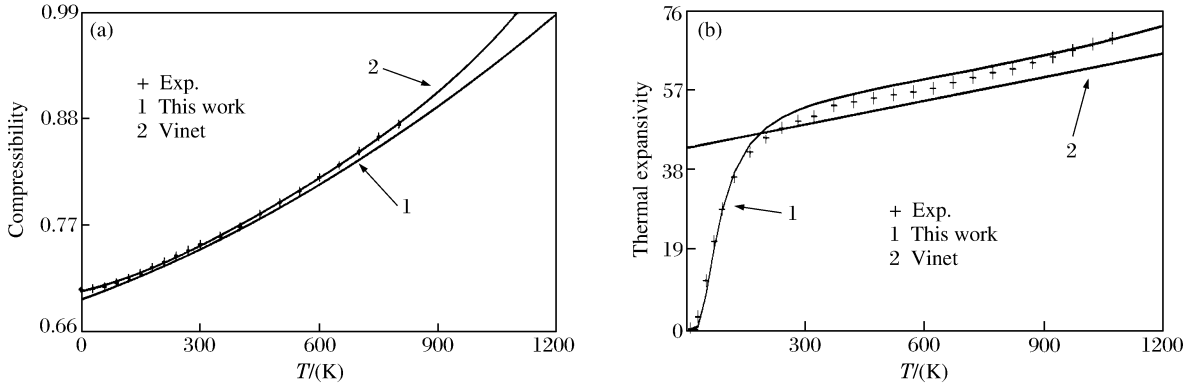
In Fig. 1 and Fig. 2, the predicted variations of compressibility and thermal expansivity coefficients with temperature for gold and copper are compared with experiments and the modified EOS of Vinet *et al*.[5] In order to compare both EOS directly, we use the same experimental data for both equations. It should be noted that the difference for the compressibility is invisible for gold. However, the improvement of our EOS as compared with the Vinet's one for the thermal expansivity is obvious. It can be observed that the modified EOS of Vinet *et al*. is not adequate for low temperatures, as expected

from its derivation. Our EOS is applicable over whole range of temperature, and at high temperatures, our results even are better than the EOS of Vinet *et al.*



(a) Isothermal compressibility coefficient (10^{-11} cm^2 · N^{-1})　　(b) Volume thermal expansivity coefficient (10^{-6} K^{-1})

Fig. 1　Temperature dependence of thermodynamic properties for the solid Au
(The experimental data used are taken from Ref. [10～13])



(a) Isothermal compressibility coefficient (10^{-11} cm^2 · N^{-1})　　(b) Volume thermal expansivity coefficient (10^{-6} K^{-1})

Fig. 2　Temperature dependence of thermodynamic properties for the solid Cu
(The experimental data used are taken from Ref. [10～13])

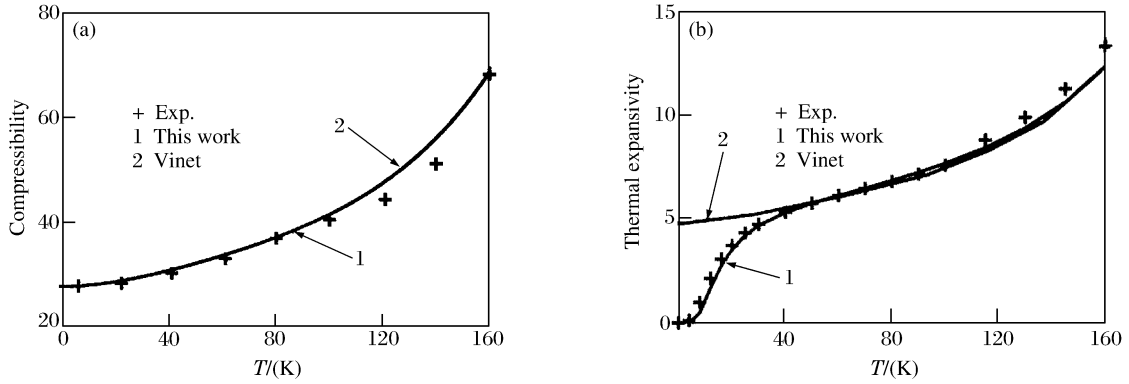
This may has two reasons. The first is because our extension of Vinet EOS has some theoretical foundation of molecular thermodynamics, yet the thermal modification of Vinet *et al.* only is a semi-empirical one. The second reason can been seen from Eq. (14) that the thermal pressure p^* at high temperature can be expressed as

$$p^* \approx 3\gamma_G NkT/V$$

It indeed is a linear function of temperature, this is in agreement with the assumption of Vinet *et al.*; however, it also is a inverse linear function of volume, this is in contradict with the assumption of Vinet *et al.* that the thermal pressure is independent with the volume. The third reason is that both Einstein characteristic temperature Θ_E and Grüneison parameter γ_G are volume dependent in our theory, it is more reasonable than the Vinet's assumption that γ_G is a constant independent of volume.

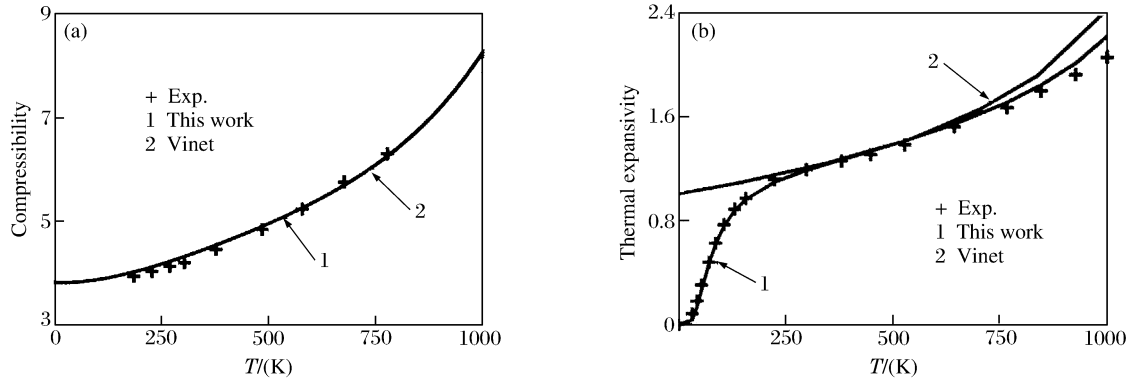
Otherwise, considering the Vinet EOS is claimed to be applicable to all solids, we also use our extended EOS to two nonmetallic materials Xe and NaCl. In Fig. 3 and Fig. 4, the predicted variations of compressibility and thermal expansivity coefficients with temperature are compared with experiments and the modified EOS of Vinet *et al.*[5] Although the difference for the compressibility is invisible in these figures, it also can be shown that the extended EOS are more appropriate to these materials.

In the extension to include the thermal effect, we have used the Einstein model. If supposing the average frequency for the Debye approximation equal to the Einstein frequency, one can easily obtain $\Theta_D=(4/3)\Theta_E$, and if replacing the Einstein function by the Debye function in Eq. (12), the Einstein model can be easily extended to the Debye model. The comparison between the two models was not shown since the predictions using Debye model instead of Einstein model are easily obtained. And as shown by Baonza *et al*.[9] in their EOS that the Debye model only improve the predictions near $T=0$. However, both models are indistinguishable at high temperatures and for the sake of simplicity we utilize Einstein model since it leads to an analytical EOS.



(a) Isothermal compressibility coefficient (10^{-11} cm^2 · N^{-1}) (b) Volume thermal expansivity coefficient (10^{-4} K^{-1})

Fig. 3 Temperature dependence of thermodynamic properties for the solid Xe
(The experimental data used are taken from Ref. [10～13])



(a) Isothermal compressibility coefficient (10^{-11} cm^2 · N^{-1}) (b) Volume thermal expansivity coefficient (10^{-4} K^{-1})

Fig. 4 Temperature dependence of thermodynamic properties for the solid NaCl
(The experimental data used are taken from Ref. [10～13])

4 Conclusion

Considering the screened effective interaction between the ions is short-range one, the nearest neighbor generalized Lennard-Jones potential is used to describe the effective interaction. The lattice part of potential energy of an ion is expanded as quadratic function of displacement of the ion to derive the harmonic frequency of an atom vibrating near its equilibrium position and the Debye-Grüneisen parameter as a function of volume. Combining the Einstein model, the universal EOS proposed by Vinet *et al*. is extended to include the thermal effect. Apart from the experimental value of Einstein characteristic temperature that usually can be found in literature, one only need the thermal expansivity coef-

ficient at a temperature to determine the parameters in the extended equation of state.

The variation of compressibility with temperature is not evident, so the theoretical prediction in this paper are in good agreement with the experiments and also are comparable to the EOS modified by Vinet *et al*. However, the results for thermal expansivity coefficients of four typical materials at low temperature are obviously improved, and are in fairly satisfactory agreement with the experiments when the EOS modified by Vinet *et al*. is inapplicable. Even at high temperature, the results for the thermal expansivity coefficients also are slightly improved as compared with the EOS modified by Vinet *et al*., this is because the assumption utilized by Vinet *et al*. is in fact not correct.

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考虑热效应的 Vinet 状态方程及其应用

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摘要: 基于爱因斯坦模型将 Vinet 等人提出的关于金属固体的通用物态方程推广到包括热效应。采用最近邻普遍化 Lennard-Jones 势描述金属离子之间的有效配对相互作用, 将每个离子的势能展开为离子位移的二阶泰勒级数, 从而推导出爱因斯坦温度和 Grüneisen 常数的解析表达式, 该表达式只与体积有关而与温度无关。推广方程包括的 7 个参数只有 5 个是独立的, 在高于德拜温度时, 只需要 4 个参数。对典型金属及两种非金属材料计算的结果与实验符合得很好。

关键词: 状态方程; 爱因斯坦模型; 热物理性质

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