PHYSICAL REVIEW B VOLUME 62, NUMBER 1 1 JULY 2000-I

Mean-field potential approach to thermodynamic properties of metal: Al as a prototype

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(Received 21 December 1999; revised manuscript received 10 March 2000)

We propose a classical mean-field potential (MFP) model for evaluating the vibrational contribution of the lattice ion to the total free-energy, where the mean-field potential $g(r,V)$ seen by the lattice ion is entirely and yet simply derived from the 0-K total-energy volume curve. The physical basis of the MFP is supported by the fact that, as a second-order approximation of the MFP, the three commonly used expressions for the Grüneisen parameter, i.e., that due to Slater, that due to Dugdale and MacDonald, and that for the free-volume theory, can be explicitly deduced. Furthermore, a first-principles scheme for calculating thermodynamic properties of a metal is developed. The present scheme permits efficient computation and allows us to investigate almost all kinds of thermodynamic parameters, since it only needs the 0-K total-energy curve and electronic density of states as the inputs. Taking aluminum (Al) as a prototype, we demonstrate that our scheme correctly describes most of the thermodynamic properties, such as static compression, shockwave compression, thermal expansion, bulk modulus, and anharmonic effect.

I. INTRODUCTION

The thermodynamic property study of materials is of importance to extend our knowledge on their specific behaviors when undergoing severe constraints such as high-pressure and high-temperature environment. This is particularly true since the coming of modern technologies (geophysics, astrophysics, particles accelerator, fission and fusion reactor, etc.), from which we always expect new advances and innovations in materials science to reach higher performances. From a fundamental point of view, there are needs for refinements of theoretical models for the computation of a more accurate equation of state (EOS) of the material.[1,2]

The study of the temperature dependence of the properties of materials requires a proper account of nuclear motions and thermal excitation of electrons. While a high accuracy can be obtained in the 0-K *ab initio* calculation,[3,4] the *ab initio* thermodynamic calculation still remains a great challenge to us. The basic difficulty in the systematic theoretical calculation of the thermodynamic properties of a substance by means of statistical physics is how to incorporate correctly the structurally complicated interparticle interaction of the many-body problem. In this regard, some theoretical methods have been developed, such as the Debye-Grüneisen theory by Moruzzi, Janak, and Schwarz,[5] the elaborate generalized pseudopotential theory (GPT) by Moriarty,[6] the delicate tight-binding total-energy classical cell model by Wasserman, Stixrude, and Cohen,[7] and the well-known free-volume theory by Kirkwood[8] and by Vashchenko and Zubarev.[9]

In previous work,[10] we briefly reported a classical mean-field potential [in this paper, we change mean-field potential (MFP) for CMF used in Ref. 10] approach for evaluating the vibrational contribution of the lattice ion to the total free energy. An *ab initio* scheme for calculating thermodynamic properties of a substance was furthermore developed in conjunction with (i) the accurate calculations of 0-K total-energy curve with the full-potential linearized augmented plane-wave (LAPW) method[11] within the generalized gradient approximation (GGA),[12] and (ii) the accurate calculation of the thermal excitation of electrons with one-dimensional numerical integration. Coupled further with the treatment of the contribution from the magnetic disorder to the free energy by generalizing the Hund's rule, the well-known γ-α isostructural transition, the experimental Hugoniot state (shock-wave compressed state), and the 300-K static equation of state (EOS) for metal Ce had been well described. The MFP model had been also applied for the five reference metals Al, Cu, Ta, Mo, and W, indicating that both the calculated Hugoniot states and 293-K isotherms fell well in the experimental uncertainties.[13]

In this paper, the MFP model is expanded to more general cases where as a second-order approximation of the mean-field potential (MFP), the three commonly used expressions for the Grüneisen parameter, i.e., that due to Slater,[14] that due to Dugdale and MacDonald,[15] and that for the free-volume theory,[9] can all be explicitly deduced on the common physical basis while the MFP $g(r,V)$, seen by the lattice ion, is still constructed in terms of the 0-K total energy. Taking aluminum (Al) as a prototype, we demonstrate that our scheme correctly describes most of the thermodynamic properties.

The rest of this work is organized as follows. In Sec. II we present the construction of the MFP. The details of the 0-K LAPW-GGA total-energy calculations for aluminum are given in Sec. III. In Sec. IV we present our calculated thermodynamic properties. Finally, Sec. V contains our summary.

II. MEAN-FIELD POTENTIAL APPROACH

Our analysis will be confined to the classical regime. For a system with a given averaged atomic volume V and a given temperature T, the Helmholtz free energy $F(V,T)$ per ion can be written as[16]

$$F(V,T)=E_c(V)+F_{ion}(V,T)+F_{el}(V,T), \qquad (1)$$

where E_c represents the static 0-K total energy, F_{ion} the vibrational free energy of the lattice ion, and F_{el} the free energy due to the thermal excitation of electrons.

Generally, the static 0-K total energy E_c in Eq. (1) can be evaluated very accurately by the modern first-principles technique, such as the LAPW method. Therefore the major issue is how to treat the thermal vibration of the lattice ion. In this paper, we take the mean-field approximation as the starting point.

A. Construction of the mean-field potential

It is known that the vibrational contribution to the partition function takes the form $Z_{ion}=\exp(-NF_{ion}/k_BT)$, where N is the total number of lattice ions. Under the mean-field approximation, the classical form of Z_{ion} can be expressed as[7–9]

$$Z_{ion}=\left(\frac{mk_BT}{2\pi\hbar^2}\right)^{3N/2}\left\{\int\exp[-g(\mathbf{r},V)/k_BT]d\mathbf{r}\right\}^N, \qquad (2)$$

where m is the weight of the lattice ion. Notice that $g(\mathbf{r},V)$ in Eq. (2) is referred as the mean-field potential (MFP).

The central issue of the mean-field theory is how to calculate the MFP $g(\mathbf{r},V)$. In this regard, the free-volume theory[9] was chosen to calculate the MFP $g(\mathbf{r},V)$ by the average of the empirically derived pairwise potentials, while the tight-binding total-energy classical cell model[7] was chosen to calculate the MFP $g(\mathbf{r},V)$ by the tight-binding total-energy method for which the parameters were determined by the first-principles LAPW calculation.

Inspired by the three commonly used expressions for the Grüneisen parameter,[9,14,15] we find a rather different way. For a crystal with the inversion symmetry, one can imagine that the vibration of the lattice ion is symmetrical with respect to its equilibrium position, i.e., the MFP seen by the lattice ion should be invariant under the inversion operation. Based on these physical consideration, we have simply constructed the MFP in terms of the *ab initio* 0-K total energy E_c as follows

$$\begin{aligned} g(r,V)=&\frac{1}{2}[E_c(R+r)+E_c(R-r)-2E_c(R)]\\ &+\frac{\lambda}{2}\frac{r}{R}[E_c(R+r)-E_c(R-r)], \end{aligned} \qquad (3)$$

where r is the distance that the lattice ion deviates from its equilibrium position, R is the lattice constant with respect to V, and λ is an integer and its physical significance is demonstrated below.

Let us make a Taylor expansion of Eq. (3); we have

$$g(r,V)=k(V)r^2+O(r^4), \qquad (4)$$

where

$$k(V)=\frac{1}{R^{2\lambda}}\frac{\partial}{\partial R}\left(R^{2\lambda}\frac{\partial E_c(R)}{\partial R}\right), \qquad (5)$$

and $O(r^4)$, which represents the term higher than the third order, may in part account for the so-called softening of phonon. We note that Eq. (4) does not contain the third-(or the odd-) order term. Furthermore, the Grüneisen parameter $\gamma_{ion}(V)$ from Debye-Grüneisen theory[5] can be estimated by $\gamma_{ion}(V)=-\partial\ln\nu/\partial\ln V$, where ν stands for the phonon frequency. Since $\nu\simeq[k(V)/m]^{1/2}$, we obtain

$$\gamma_{ion}(V)=\frac{1}{3}(\lambda-1)-\frac{V}{2}\frac{\partial^2(P_cV^{(2/3)(\lambda+1)})/\partial V^2}{\partial(P_cV^{(2/3)(\lambda+1)})/\partial V}, \qquad (6)$$

where $P_c(V)=-\partial E_c(V)/\partial V$ is the so-called cold pressure.

One can now read the physical significance of λ. In particular, if $\lambda=-1$, Eq. (6) is reduced to the expression of Grüneisen parameter by Slater,[14] if $\lambda=0$, Eq. (6) is reduced to the expression of Grüneisen parameter due to Dugdale and MacDonald,[15] and if $\lambda=1$, Eq. (6) is reduced to the expression of Grüneisen parameter for the free-volume theory.[9]

Up to now we have derived the three commonly used expressions of Grüneisen parameter on the common base of MFP in Eq. (3). However, it should be mentioned that Eqs. (4)–(6) are just used to demonstrate the physical basis of the MFP. In the realistic calculations, Eq. (6) is never used since F_{ion} in Eq. (1) can be easily evaluated employing the MFP, which is more general, via one-dimensional numerical integration (see the next subsection).

B. Free-energy due to the lattice ion

Back to Eq. (2), F_{ion} can be formulated as

$$F_{ion}(V,T)=-k_BT\left(\frac{3}{2}\ln\frac{mk_BT}{2\pi\hbar^2}+\ln v_f(V,T)\right), \qquad (7)$$

where

$$v_f(V,T)=4\pi\int\exp\left(-\frac{g(r,V)}{k_BT}\right)r^2dr. \qquad (8)$$

Now, we can check the asymptotic behavior of $g(r,V)$ in Eq. (3). If $E_c(R)$ is a type of hard-sphere potential as

$$E_c(R)=0,\quad \text{if } R>b;\quad \infty,\quad \text{if } R\leqslant b, \qquad (9)$$

thus

$$g(r,V)=0,\quad \text{if } r<R-b;\quad \infty,\quad \text{if } r\geqslant R-b, \qquad (10)$$

then, v_f in Eq. (8) equals $(R-b)^3 4\pi/3$. Straightforwardly, by $P=-(\partial F/\partial V)_T$, we have the EOS for the hard-sphere model[8]

$$P=\frac{R}{R-b}\frac{k_BT}{V}. \qquad (11)$$

We note that Eq. (11) will be exactly reduced to that of ideal gas when b equals zero.

C. Free-energy due to thermal electrons

When the magnetic contribution and the electron-phonon interactions are neglected, the electronic contribution to the free energy $F_{el}=E_{el}-TS_{el}$, where the bare electronic entropy S_{el} takes the form[7,17]

$$S_{el}(V,T)=-k_B\int n(\epsilon,V)[f\ln f+(1-f)\ln(1-f)]d\epsilon, \qquad (12)$$

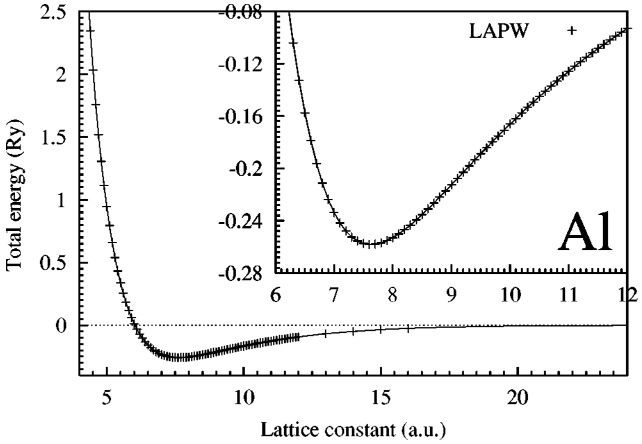

FIG. 1. The calculated 0-K total energies as a function of lattice constant for fcc Al. The crosses indicate the numerical points by the LAPW calculation. The solid line between 4.5 and 16.0 a.u. is derived by cubic spline interpolation, and that smaller than 4.5 a.u. and that greater than 16.0 a.u. are extrapolations by Morse function. The inset shows the region near the equilibrium.

where $n(\epsilon,V)$ is the electronic density of states (DOS) and f is the Fermi distribution. With respect to Eq. (12), the energy E_{el} due to the electron excitations can be expressed as

$$E_{el}(V,T)=\int n(\epsilon,V)f\epsilon d\epsilon-\int^{\epsilon_F}n(\epsilon,V)\epsilon d\epsilon, \quad (13)$$

where ϵ_F is the Fermi energy.

By now we have presented a classical mean-field potential (MFP) technique to evaluate the various kinds of contributions to the total free energy of a metal. In the following sections, we take aluminum as a prototype to demonstrate the accuracy and applicability of the present MFP approach.

III. CALCULATIONAL DETAILS

To calculate the 0-K total energy $E_c(V)$ in Eq. (1), we employ the full-potential LAPW method[11] within the GGA.[12] Constant muffin-tin radii (R_{mt}) of 1.6 a.u. is used. The plane-wave cutoff K_{cut} is determined by $R_{mt}\times K_{cut}=9.0$. 4096 k points in the full zone are used for reciprocal-space integrations.

The MFP in our previous work[10,13] corresponded to the special case of $\lambda=0$ in Eq. (3). In this work, we use $\lambda=-1$. Choosing λ reminds us of the choices among the three expressions[9,14,15] of the Grüneisen parameter [seen from Eq. (6) and the associated discussions]. By comparing present calculation with our previous calculation[13] one can find that the different choices of λ do not have too much impact on the P-V curve. The similar results had also been derived by Moriarty (meaning different choices of the expression of Grüneisen parameter, see Ref. 18 and references therein). The reason why we use $\lambda=-1$ in this paper is that it can give better thermal expansion of ambient pressure for the specific case of Al.

IV. RESULTS AND DISCUSSIONS

A. Cold energy

Figure 1 shows a plot of the calculated curve of the cold energy E_c as a function of the fcc lattice constant by means of LAPW method. The calculated 0-K equilibrium lattice constant is 7.63 a.u., which is in 0.3% agreement with that of the experimental room-temperature value of 7.65 a.u.[19] Al is indeed a good prototype for theoretical modeling, as that if we fit the calculated 0-K total energies with Morse function, we obtain a cohesive energy of 3.53 eV, which only deviates from the experimental value[19] of 3.39 eV by 4%.

TABLE I. The calculated and experimental atomic volume V_0 (in Å^3), bulk modulus B (in GPa), and the volume thermal-expansion coefficient β (in 10^{-6} 1/K) under ambient conditions for fcc Al.

Method	V_0	B	β
Theory	16.81	70.2	74.9
Expt.	16.61[a]	72.2[a]	69.3[b]

[a] From Ref. 19.
[b] From Ref. 20.

B. Properties at ambient condition

To check an *ab initio* thermodynamic model, the calculations of the ground-state properties might be an important step. Knowing that we have calculated the Helmholtz free energy $F(V,T)$ as an explicit function of atomic volume V and temperature T, we can easily calculate the equilibrium $V(T)$ at a given T by solving $\partial F/\partial V=0$. With the equilibrium $V(T)$ in hand, the volume thermal-expansion coefficient β_P can be calculated by

$$\beta_P(V,T)=\frac{1}{V}\left(\frac{\partial V(T)}{\partial T}\right)_P. \quad (14)$$

The isothermal bulk modulus can be calculated by

$$B_T(V,T)=\frac{1}{V}\left(\frac{\partial^2 F(V,T)}{\partial V^2}\right)_T. \quad (15)$$

Collected in Table I are our calculated equilibrium atomic volume (V_0), isothermal bulk modulus (B_T), and the volume thermal-expansion coefficient (β) under ambient conditions for fcc Al together with the data[19,20] measured at room temperature. Inspecting of Table I, one can note that the calculated results are very good as compared with the experimental values.

C. Thermal expansion and isothermal bulk moduli

Figure 2 shows the calculated and measured[20] volume thermal expansions as functions of temperature at zero pressure. The agreement between the theory and the experiment is also good.

As a further test of the present approach to the zero-pressure properties, the calculated curve of isothermal bulk modulus versus temperature is compared with the experimental values[21,22] in Fig. 3. Note that the agreement between the theory and the experiment falls to 10% for this second-derivative quantity of energy to volume.

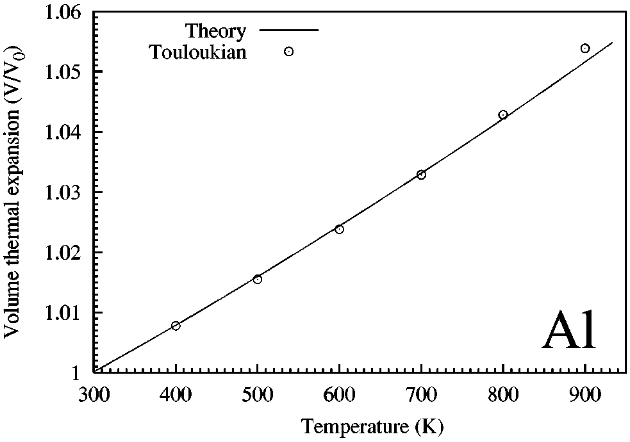

FIG. 2. The calculated (solid line) and measured (open circles, from Ref. 20) relative atomic volume (V/V_0) as a function of temperature under ambient pressure.

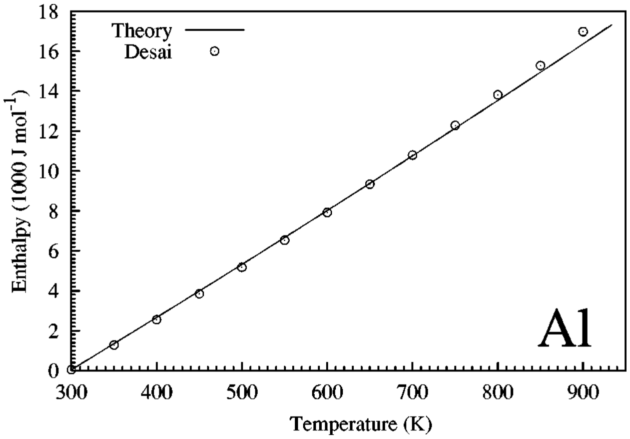

FIG. 4. Enthalpy as a function of temperature. The filled circles indicate the recommended experimental data by Desai (Ref. 23) and the solid curve represents the calculated value of the present work.

D. Temperature dependence of enthalpy and anharmonic effect

By dint of Eqs. (7) and (13), the internal energy (enthalpy at zero pressure) can be written as

$$E(V,T)=E_c(V)+\xi(V,T)k_BT+E_{el}(V,T), \tag{16}$$

where

$$\xi(V,T)=\frac{3}{2}+\left(\frac{\partial \ln v_f(V,T)}{\partial \ln T}\right)_V. \tag{17}$$

The calculated enthalpy from the room temperature up to melting point is compared with experiment[23] in Fig. 4. The agreement between the calculation and the experiment is very good.

By $\xi(V,T)$, the specific heat (heat capacity) due to the lattice ion at constant volume is then given by

$$C_V^{ion}(V,T)=k_B\left[\xi(V,T)+T\left(\frac{\partial \xi(V,T)}{\partial T}\right)_V\right]. \tag{18}$$

Since the classical harmonic value of constant-volume heat capacity due to lattice ion (C_V^{ion}) is just $3k_B$, it follows that the so-called anharmonic term $C_V^{ion,anh}$ may be extracted from the present calculation as simply $C_V^{ion,anh}=C_V^{ion}-3k_B$. The calculated $C_V^{ion,anh}$ as a function of temperature for aluminum is displayed in Fig. 5, which is also compared with the experimental values of Schmidt, Vollmer, and Kohlhaas.[24] It is very interesting to note from Fig. 5 that the present MFP approach can, on the whole, describe the so-called anharmonic effects.

E. Hugoniot state

Hugoniot states, which are derived by the conventional shock-wave technique,[25] are characterized using measurements of shock velocity (D) and particle velocity (u) with $V_H/V_0=(D-u)/D$ and $P_H=\rho_0 Du$ where P_H is the pressure and ρ_0 is the initial density. Through the Rankine-Hugoniot relations, these data define a compression curve [volume (V_H) versus pressure (P_H)] as a function of known Hugoniot energy (E_H).

$$\frac{1}{2}P_H(V_0-V_H)=E_H-E_0, \tag{19}$$

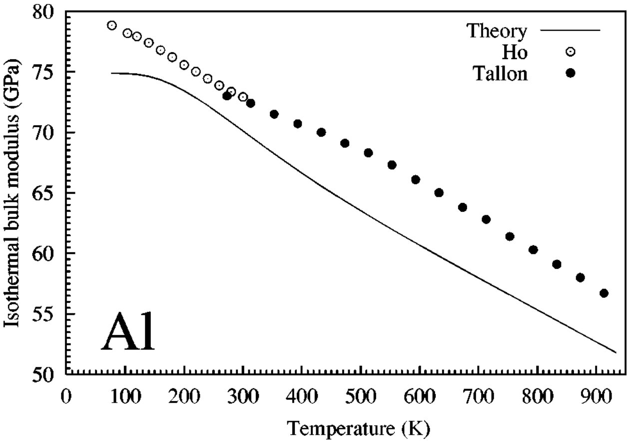

FIG. 3. The the calculated isothermal bulk modulus (solid line) as a function of temperature under ambient pressure. The open circles indicate the experimental values of Ho and Ruoff, (Ref. 21) and filled circles those of Tallon and Wolfenden (Ref. 22).

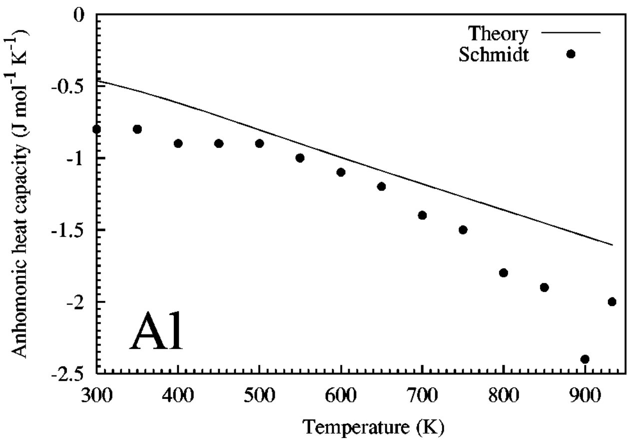

FIG. 5. The calculated anharmonic heat capacity $C_V^{ion,anh}$ compared with experiment. The filled circles indicate the experimental values of Schmidt, Vollmer, and Kohlhaas. (Ref. 24). The solid curve represents the calculated values.

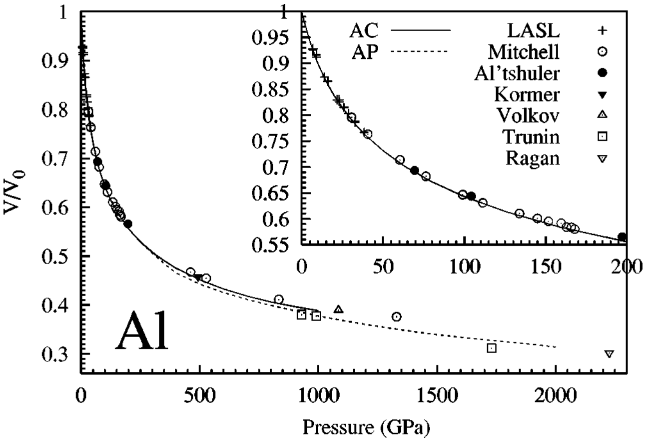

FIG. 6. Hugoniot pressure versus relative volume for Al. The solid and the dashed lines represent the cases that evaluate the thermal electronic energy through Eqs. (13) and (20), respectively, and the points are from the absolute measurements (Refs. 25–30) and relative measurements (Refs. 31 and 32). The inset shows the lower pressure region (up to 200 GPa).

where V_0 and E_0 refer to the atomic volume and energy under ambient condition, respectively. With that E_H is calculated through Eq. (16) and P_H is defined through $P_H = -(\partial F/\partial V)_T$, solving Eq. (19) one can easily derive the Hugoniot volume V_H and Hugoniot temperature T_H.

Since we only calculate the electronic density of state (DOS) by a width of 4.0 Ry, two cases have been considered in the following calculations: (i) the energy due to the thermal electron is accurately calculated with Eq. (13) (hereafter referred as AC), and (ii) the energy due to the thermal electron is approximated by the low-temperature expansion (hereafter referred as AP)

$$E_{el}(V,T)=\frac{\pi^2}{6}k_B^2 n(\epsilon_F,V)T^2. \tag{20}$$

Illustrated in Fig. 6 are the calculated curves of shock-wave pressure versus the reduced atomic volume V_H/V_0, where in the case of AC the calculation is proceeded to 1000 GPa and where in the case of AP the calculation is proceeded to 2000 GPa. Also depicted in Fig. 6 are the shock-wave data of absolute measurements[25–30] which are independent of any theoretical model, and of relative measurements[31,32] which depend on the EOS of a reference material. Inspection of Fig. 6, one can observe: (i) for $P \leqslant 300$ GPa, the two calculated curves are almost coincidental, (ii) for $300 \leqslant P \leqslant 1000$ GPa, the curve of AP is lower than that of AC by about 0.01 in V_H/V_0, and (iii) however, the two sets of calculated results all fall well in the experimental uncertainties. The agreement between the calculation and the experiment strongly supports the validity of Rankine-Hugoniot equation and the assertion that the shock process can generate nearly hydrostatic high-pressure state.

At this stage we can make a comparison between our calculations and those by other colleagues. Moriarty,[18] Mitchell *et al.*,[31] and Nellis *et al.*,[33] had calculated the EOS for Al, Cu, Mo, and Pb at shock pressures up to 2400 GPa based on (i) the cold energies E_c in Eq. (1) were calculated within the framework of local-density approximation (LDA) with augmented plane-wave method, or with linear muffin-tin orbital (LMTO) method employing the atomic-sphere approximation (ASA), to which a so-called combined correction was applied, (ii) the ion-thermal components F_{ion} were obtained from first-principles GPT, where the many-body potentials were expanded in terms of central-force and two-, three-, and four-ion interactions, using quasiharmonic lattice dynamics in the solid and variational perturbation theory based on a soft-sphere reference system in the liquid, and (iii) the thermal excitations of electrons were calculated by the low-temperature expansion in the form of Eq. (20).

In our approach, we employ LAPW-GGA method to calculate E_c and both the cold and thermal parts of the Helmholtz free energy are derived entirely from the 0-K total energies and electronic density of states. With the introducing of Eq. (3), in conjunction with Eqs. (8), (12), and (13), the laborious calculations of the many-body interactions have been successfully circumvented. We mention again that all the integrals involved in the present paper are one dimensional. Such kinds of integrations can be easily evaluated with the modern computer.

F. Temperature, heat capacity, and Grüneisen parameter along the principal Hugoniot

Shown in Figs. 7–9 are the other calculated thermophysical properties along the principal Hugoniot. Note in Fig. 7 that for the highest pressure of 2000 GPa that we have calculated, the temperature has approached to 112 000 K. Shown in Fig. 8 [only for the case that the thermal electronic energy is accurately calculated with Eq. (13)] are the lattice ion only constant-volume heat capacity C_V^{ion} calculated through Eq. (18), the total constant-volume heat capacity C_V by

$$C_V(V,T)=C_V^{ion}(V,T)+\left(\frac{\partial E_{el}(V,T)}{\partial T}\right)_V, \tag{21}$$

and the total constant-pressure heat capacity C_P calculated by

$$C_P(V,T)=C_V(V,T)+VTB_T(V,T)\beta_P^2(V,T). \tag{22}$$

We note that the thermal electronic contribution (the difference between the dashed line and dot-dashed line) to the heat capacity becomes comparable with that due to the lattice ion at high compression. Another interesting result that can be seen from Fig. 8 (see also Fig. 5 and the associated discussions) is that the calculated lattice ion only constant-volume heat capacity C_V^{ion} never exceeds the classical harmonic limit of $3k_B(24.94\ \mathrm{J\,mol^{-1}\,K^{-1}})$ and somewhat decreases with the increasing of the temperature. This result is similar to that of Ref. 6 where metal molybdenum (Mo) had been calculated up to melting point under the ambient pressure and where the anharmonic effect was always negative.

The reductions of shock data to isothermal or isotropic states require specific heat and Grüneisen parameter (γ) values that are not well known. In the absence of experimental constraints, researchers often make the plausible assumption of $\gamma/V=\mathrm{const}$. With the isothermal bulk modulus B_T, the volume thermal-expansion coefficient β_P, and the constant-

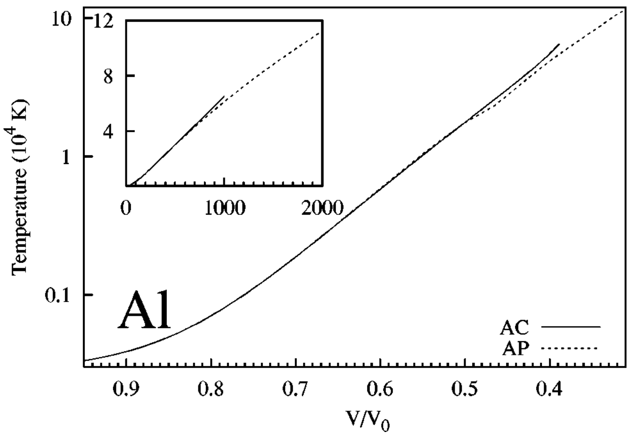

FIG. 7. The calculated temperature along the principal Hugoniot. The solid and the dashed lines represent the cases that evaluate the thermal electronic energy through Eqs. (13) and (20), respectively. The inset shows the curve of T-P.

volume heat capacity C_V in hand, one can evaluate the thermodynamic Grüneisen gamma by

$$\gamma_{th}(T,V)=\frac{VB_T(V,T)\beta_P(V,T)}{C_V(V,T)}. \tag{23}$$

Plotted in Fig. 9 [only for the case that the thermal electronic energy is accurately calculated with Eq. (13)] is our calculated $\gamma_{th}V_0/V_H$. Note that the conventional assumption $\gamma/V=$const for the reductions of shock-wave data is applicable on the whole in the case of Al.

G. 300-K static EOS

Finally we will briefly talk about the static EOS of Al under ambient temperature. 300-K static EOS is largely governed by cold energy curve whereas the thermal energy does not play too much role. The calculated 300-K isotherm together with the measured data by Vaidya and Kennedy,[34] by Syassen and Holzapfel,[35] and by Greene, Luo, and Ruoff[36] are compared in Fig. 10. For the lower compression, the agreements among our calculation, Refs. 34, and 35 are very excellent. The agreements are also great for higher compressions between our calculation and Ref. 36. For the modest pressure of from 20 to 180 GPa, however, the agreements between our calculation and Ref. 36 are not as good as that in the case of lower compression. Boettger and Trickey had calculated static EOS of Al with the linear combination of Gaussian-type orbitals (LCGTO) method,[37] and our calculated results are very similar to theirs. In the light of the agreements of our previous calculations[10,13] with experiments and particularly the agreements between the calculation and the experiment for the Hugoniot state for Al of this paper, we prefer our calculation.

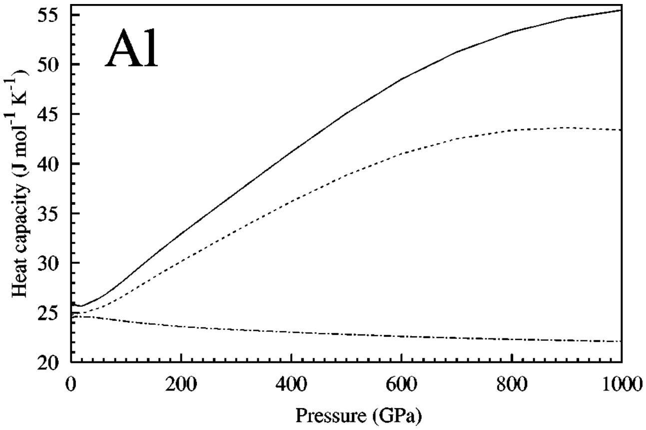

FIG. 8. The calculated heat capacities along the principal Hugoniot [only for the case that the thermal electronic energy is accurately calculated with Eqs. (13)]. The solid, dashed, and dot-dashed curves represent the calculated constant-pressure specific heat C_P, constant-volume specific heat C_V, and the lattice ion only constant-volume specific heat C_V^{ion}, respectively.

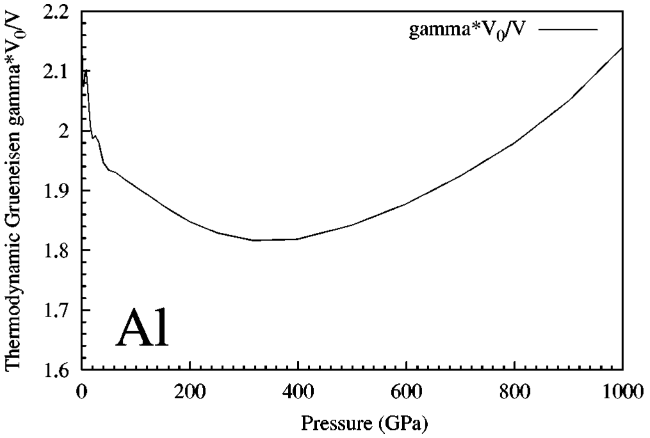

FIG. 9. The calculated $\gamma_{th}V_0/V$ as a function of Hugoniot pressure [only for the case that the thermal electronic energy is accurately calculated with Eq. (13)].

V. SUMMARY

In conjunction with our previous work,[10,13] we have suggested a classical mean-field potential (MFP) approach to the first-principles calculation of thermodynamic properties of a metal. The major physics lies in the construction of MFP $g(r,V)$ in Eq. (3) in terms of the 0-K total energy. The major time-consuming parts involved in the thermodynamic calculations of the present MFP approach are the three integra-

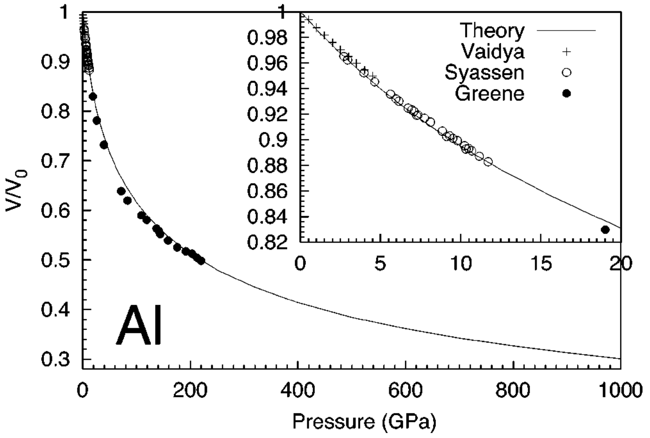

FIG. 10. The calculated 300-K isotherm (solid line) together with the measured data by Vaidya and Kennedy, (Ref. 34) by Syassen and Holzapfel (Ref. 35) and by Greene, Luo, and Ruoff (Ref. 36). The inset shows the lower compression region.

tions in Eqs. (8), (12), and (13). However, since these integrations are all one dimensional, our approach permits efficient computation of thermal properties. Taking aluminum (Al) as a prototype, we demonstrate that our scheme correctly describes most of the thermodynamic properties, such as static compression, shock-wave compression, thermal expansion, bulk modulus, and anharmonic effect.

We expect that the present MFP approach is not just limited to the case of metal. It seems that the MFP approach can also be applied to other systems with the quasimonatomic crystal types, such as NaCl, CsCl, and CaF_2.

ACKNOWLEDGMENTS

Valuable comments on this work by Professor Wanxiang Zhang and Professor Xiangeng Zhao are gratefully acknowledged. This work is supported by National PAN-DENG Project (Grant No. 95-YU-41).

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[1] S.K. Saxena, L.S. Dubrovinsky, P. Häggkvist, Y. Cerenius, G. Shen, and H.K. Mao, Science **269**, 1703 (1995).

[2] C.S. Yoo, J. Akella, A.J. Campbell, H.K. Mao, and R.J. Hemley, Science **270**, 1473 (1995).

[3] M. Körling and J. Häglund, Phys. Rev. B **45**, 13 293 (1992).

[4] V. Ozolins and M. Körling, Phys. Rev. B **48**, 18 304 (1993).

[5] V.L. Moruzzi, J.F. Janak, and K. Schwarz, Phys. Rev. B **37**, 790 (1988).

[6] J.A. Moriarty, Phys. Rev. B **49**, 12 431 (1994).

[7] E. Wasserman, L. Stixrude, and R.E. Cohen, Phys. Rev. B **53**, 8296 (1996).

[8] J.G. Kirkwood, J. Chem. Phys. **18**, 380 (1950); W.W. Wood, *ibid.* **20**, 1334 (1952); Z.W. Salsburg and W.W. Wood, *ibid.* **37**, 798 (1962).

[9] V.Y. Vashchenko and V.N. Zubarev, Fiz. Trerd. Tela (Leningrad) **3**, 886 (1963) [Sov. Phys. Solid State **5**, 653 (1963)].

[10] Y. Wang, Phys. Rev. B **61**, R11 863 (2000).

[11] P. Blaha, K. Schwarz, and J. Luitz, WIEN97, Vienna University of Technology, 1997. [Improved and updated Unix version of the original copyrighted WIEN code, which was published by P. Blaha, K. Schwarz, P. Sorantin, and S.B. Trickey, Comput. Phys. Commun. **59**, 399 (1990).]

[12] J.P. Perdew, S. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).

[13] Y. Wang, D. Chen, and X. Zhang, Phys. Rev. Lett. **84**, 3220 (2000).

[14] J. C. Slater, *Introduction to Chemical Physics* (McGraw-Hill, New York, 1939).

[15] J.S. Dugdale and D.K.C. MacDonald, Phys. Rev. **89**, 832 (1953).

[16] J.C. Boettger and D.C. Wallace, Phys. Rev. B **55**, 2840 (1997).

[17] T. Jarlborg, E.G. Moroni, and G. Grimvall, Phys. Rev. B **55**, 1288 (1997).

[18] J.A. Moriarty, High Press. Res. **13**, 343 (1995).

[19] C. Kittel, *Solid State Physics* (John Wiley & Sons, Inc., New York, 1976).

[20] Y. S. Touloukian, R. K. Kirby, R. E. Taylor, and P. D. Desai, *Thermophysical Properties of Matter* (Plenum, New York, 1975), Vol. **12**.

[21] P.S. Ho and A.L. Ruoff, J. Appl. Phys. **40**, 3151 (1969).

[22] J.L. Tallon and A. Wolfenden, J. Phys. Chem. Solids **40**, 831 (1979).

[23] P.D. Desai, Int. J. Thermophys. **8**, 621 (1987).

[24] U. Schmidt, O. Vollmer, and R. Kohlhaas, Z. Naturforsch. A **25**, 1258 (1970).

[25] Los Alamos Shock Hugoniot Data, edited by S. P. Marsh (University of California Press, Berkeley, 1980).

[26] A.C. Mitchell and W.J. Nellis, J. Appl. Phys. **52**, 3363 (1981).

[27] L.V. Al'tshuler, S.B. Kormer, A.A. Bakanova, and R.F. Trunin, Zh. Éksp. Teor. Fiz. **38**, 790 (1960) [Sov. Phys. JETP **11**, 573 (1960)].

[28] S.B. Kormer, A.I. Funtikov, V.D. Urlin, and A.N. Kolesnikova, Zh. Éksp. Teor. Fiz. **42**, 686 (1962) [Sov. Phys. JETP **15**, 477 (1962)].

[29] A.P. Volkov, N.P. Voloshin, A.S. Vladimirov, V.N. Nogin, and V.A. Simonenko, Pis'ma Zh. Éksp. Teor. Fiz. **11**, 623 (1980) [JETP Lett. **31**, 588 (1980)].

[30] R.F. Trunin, Phys. Usp. **37**, 1123 (1994).

[31] A.C. Mitchell, W.J. Nellis, J.A. Moriarty, R.A. Heinle, N.C. Homes, R.E. Tipton, and G.W. Repp, J. Appl. Phys. **69**, 2981 (1991).

[32] C.E. Ragan III, Phys. Rev. A **25**, 3360 (1982).

[33] W.J. Nellis, J.A. Moriarty, A.C. Mitchell, M. Ross, R.G. Dandrea, N.W. Ashcroft, N.C. Holmes, and G.R. Gathers, Phys. Rev. Lett. **60**, 1414 (1988).

[34] S.N. Vaidya and G.C. Kennedy, J. Phys. Chem. Solids **31**, 2329 (1970).

[35] K. Syassen and W.B. Holzapfel, J. Appl. Phys. **49**, 4427 (1978).

[36] R.G. Greene, H. Luo, and A.L. Ruoff, Phys. Rev. Lett. **73**, 2075 (1994).

[37] J.C. Boettger and S.B. Trickey, Phys. Rev. B **53**, 3007 (1996).