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Thermal properties of Al at high pressures and temperatures

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Thermal properties of the face-centered-cubic (fcc) aluminum (Al) crystal including the linear thermal expansion coefficient, specific heat at constant volume, Hugoniot in the *P*-*V* plane, thermodynamic Grüneisen parameter and elastic constants at pressures up to 120 GPa and temperatures to 3300 K have been evaluated by using the full-potential linear muffin-tin orbital (FPLMTO) total-energy method combining with a mean-field model of the vibrational partition function. The mean-field is constructed from the sum of all the pair potentials between the reference atom and the others of the system. The calculated properties are in good agreement with available static and shock-wave experimental measurements.

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I. INTRODUCTION

First-principle electronic-structure methods are routinely used to compute the zero-temperature internal energy, but also can be used to calculate the Helmholtz free energy contributions from the ions and the electrons. They result in a complete equation of state from which the properties such as the thermal expansion coefficients, bulk moduli, specify heat, thermal Grüneisen parameter of the system can be deduced.

The smaller Helmholtz free energy contribution from the electrons usually can be calculated using the finite temperature density functional approach of Mermin.[1] However, the Helmholtz free energy contribution from the ions is difficult to calculate accurately because the volume and temperature dependence of the phonon frequencies and the density of state are complicated. An *ab initio* molecular dynamics simulation, in principle, is the perfect method to deal with this problem. Unfortunately, in spite of recent progress in this field it remains computationally very intensive to deal with this problem in metal. At present there are commonly three other type of methods to handle this problem without using empirical parameters. The first uses the Debye model and may incorporate a volume dependence of the Debye temperature calculated using the first-principle-based methods.[2,3] Infrequently, it is used to calculate such properties as the thermal expansion and thermoelasticity partly because the precision is not high enough to reproduce the experiments data.

The second is based on the quasiharmonic approximation in which the phonon frequencies are functions of the temperature only through their volume dependence. The volume dependence of the phonon frequencies is incorporated either approximately by a Taylor expansion on the volume at zero temperature[4] or directly by calculations of phonon dispersion related to various volumes using a certain simplified total-energy method.[5] Although the quasiharmonic approximation can handle thermal expansion and the Grülseren parameter at a low temperature, it breaks down at sufficiently high temperatures.

A certain mean-field approximation to the thermal contribution to the Helmholtz free energy of crystalline phases is the third type of method, including the-particle-in-a-cell (PIC) model[6,7] and the so-called classical mean-field potential approach.[8,9] The latter is simplified too much to the field and may not have a precision high enough to reproduce such thermal properties as the linear thermal expansive coefficient and elasticity at high pressures and temperatures. The PIC model is essentially an anharmonic Einstein model, and the $3N$-dimensional partition function is reduced to a simple three-dimensional integral.[10] Calculations using this model usually are performed on supercells of several hundreds of atoms for the different lattice with periodic boundary conditions. The PIC model has been demonstrated to match successfully the thermal properties of iron[11] and the high-pressure thermoelasticity of body-centered-cubic tantalum.[10] Although in this model the anharmonic contributions from the potential-energy of the system can included exactly, in principle, without a perturbation expansion, in practice, the computation of the integration over the Wigner-Seitz cell is replaced by integration over the inscribed sphere of radius equal to half the nearest neighbor separation.[11] On the other hand, the total energy of the supercells of several hundreds of atoms can only be performed with such a highly efficient computational method as the so-called tight-binding total-energy method,[12] rather than the full-potential-based total-energy method.

Recently we have calculated the coefficient linear thermal expansion and elastic constants of Na at high pressures and temperatures successfully using a pair-potential-based method.[13] But it is not fit for the study of other extensive thermal properties. In this work we present a pair-potential-based mean-field approximation (PPBMFA) to the thermal contribution to the Helmholtz free energy. Combining a PPBMFA with the FPLMTO total-energy method, a wide range of thermal properties of fcc Al has been studied.

II. COMPUTATIONAL METHODS

A. Helmholtz free energy

For a system with a given averaged atomic volume V and temperature T, The Helmholtz free energy $F(V,T)$ per ion can be written as

$$F(V,T) = E_0(V) + F_{\mathrm{el}}(V,T) + F_{\mathrm{ion}}(V,T), \tag{1}$$

where $E_0(V)$ is the static zero temperature energy, $F_{\mathrm{el}}(V,T)$ is the electronic contribution, and $F_{\mathrm{ion}}(V,T)$ is the vibrational contributions to the free energy. The first two terms on the right-hand side can be calculated using the density functional theory (DFT) generalized to finite temperatures by the Mermin theorem.[1] The charge density is temperature dependent through occupation numbers according to the Fermi-Dirac distribution, giving the electronic entropy from

$$S_{\mathrm{el}} = \sum f_i \ln f_i + (1 - f_i)\ln(1 - f_i), \tag{2}$$

where f_i the Fermi occupation at a certain temperature T for each state i.

B. Vibrational contributions

As an approximate way to evaluate the vibrational contribution NF_{ion} of the system of N ions to the Helmholz free energy, the idea of the the mean-field approximation is that the vibrational contribution to the partition function Z_{WS} can be calculated by having one wanderer particle move in the potential field of an otherwise ideal, static lattice:[6,7]

$$Z_{\mathrm{ion}} = \left[\left(\frac{mk_{\mathrm{B}}T}{2\pi\hbar^2}\right)^{3/2} f(V,T)\right]^N, \tag{3}$$

where

$$f(V,T) = \int_{\mathrm{WS}} dr \exp[-(U(r) - U_0)/(k_{\mathrm{B}}T)], \tag{4}$$

$\hbar$ and k_{B} are Planck's constant and Boltzman's constant, respectively, m is the mass of each ion, U_0 is the potential energy of the system with all ions on ideal lattice sites and $U(r)$ is the potential energy of the system with the wanderer ion displaced by the radius vector r from its equilibrium position. The integration is over the Wigner-Seitz cell WS, centered on the equilibrium position of the wanderer ion.

For each ion the vibrational contribution F_{ion}, according to the relation $NF_{\mathrm{ion}} = -k_{\mathrm{B}}T \ln Z_{\mathrm{ion}}$ and the partition function in Eq. (3), reads as

$$F_{\mathrm{ion}} = -k_{\mathrm{B}}T \ln\left[\left(\frac{mk_{\mathrm{B}}T}{2\pi\hbar^2}\right)^{3/2} f(V,T)\right]. \tag{5}$$

One can see from Eq. (4) and Eq. (5) that the key problem is to determine the change of potential energy of the system of N ions due to the displacement of the wander ion and to calculate the integration over the Wigner-Seitz cell.

In the conventional PIC model the potential energy $U(r)$ are calculated on supercells of several hundreds of atoms for the different lattice with periodic boundary conditions using a tight-binding total-energy method[10,11] for which the parameters were determined by a certain full-potential-based total-energy method. Actually $U(r)$ can be directly constructed in some more physically transparent way rather than from some empirical method,[9] according to the symmetry of lattice, from the pair potential ϕ_{ij} of two ions i and j. Using this pair potential the change of potential energy of the system in Eq. (4) can be written as

$$U(r) - U_0 = \frac{1}{2}\sum_R \phi(\|R - r\|) - \frac{1}{2}\sum_R \phi(\|R\|), \tag{6}$$

where R denotes all the lattice vectors of ion in the system except the wander ion, with the site of wander ion as the zero point of the lattice vector. The sums in Eq. (6) denote the superposition of the pair potential between the reference ion and remaining ions of the system. Using Eq. (6) the integration in Eq. (4) can be expressed as a form of pair potential. If one assumes the pair potential is of the form as

$$\phi(\|R\|) = -x\|R\|^m + y\|R\|^n, \tag{7}$$

where x and y are positive constants and m and n are negative constants, then these parameters in the pair potential can be evaluated by fitting the total energy $E(a)$ of the unit cell with a lattice parameter a to the equation

$$E(a) = \frac{1}{2}\sum_R \phi(\|R\|). \tag{8}$$

Here $E(a)$ can be calculated using a full-potential-based total-energy method.

Once the the pair potentials are obtained from Eq. (8) using only single atom fcc-unit cell calculations with different values of a, the potential energy of the wander ion $U(r)$ and U_0 in Eq. (4) can be constructed according to the symmetry of the lattice. With the potential energy difference $U(r) - U_0$ of the form in Eq. (6) the integration in Eq. (4) and hence the free energy $F_{\mathrm{ion}}(V,T)$ in Eq. (5) can be calculated. In order to simply the calculation, the integration over the Wigner-Seitz cell can be approximately replaced by integration over the inscribed sphere of radius equal to half the nearest neighbor separation. Since pair potential is a scalar function depending only on the distance between two atoms, the integration over the cell is reduced to a two-dimensional (2-D) integration, that is $2\pi\int_0^\pi\int_0^r \sin(\theta) g(\theta,r) d\theta\, dr$, if performed in spherical coordinates.

In theory, to calculate the pair potential and construct the mean field from them, the number of R should be of an order of magnitude up to 10^{23}. After a cutoff radius test, we found that it is accurate enough to use the nearest 256 ions from the wanderer ion to evaluate the $\phi(\|R\|)$ and $f(V,T)$ of fcc Al. Here the total energy $E(a)$, if calculated using the finite temperature DFT, can include the zero temperature energy and electron effects of temperature, and hence the couple effect between the electron and the phonon can be partly considered through the temperature- and volume-dependent pair potential. Since the mean-field model treats vibrations classically, it is expected to be a good approximation for temperatures greater than the Debye temperature of the solid but lower than the melting temperature.

C. Thermal properties

From the Helmholtz free energy $F(V,T)$ the thermal properties of the system can be deduced. The isothermal bulk modulus $B_T(V,T)$ and pressure $P(V,T)$ can be obtained by a least-squares fit to the Helmholtz free energy of unit cell

$$F(V+\Delta V)=F(V)+P\Delta V+\frac{B_T}{2V}(\Delta V)^2+\cdots\ , \qquad (9)$$

where ΔV is the small volume change from the balance volume V at the pressure P and temperature T. By definition one can easily obtain the linear thermal expansion coefficient $\alpha_L=(1/3V)(\partial V/\partial T)_P$, specify heat at constant volume $C_V=-T(\partial^2F/\partial T^2)_V$ and at constant pressure $C_P=C_V+9\alpha^2B_TVT$, and thermodynamics Grüneisen parameter $\gamma_{\text{th}}(V,T)=3\alpha_LB_TV/C_V$.

The elasticity of fcc aluminum can be completely described by three elastic constants C_{11}, C_{12}, and C_{44}. To calculate the the shear constant $C_{11}-C_{12}$ one can use the volume-conserving orthorhombic strain tensor,[14]

$$\varepsilon=\begin{pmatrix} x & 0 & 0\\ 0 & -x & 0\\ 0 & 0 & x^2/(1-x^2)\end{pmatrix}, \qquad (10)$$

where x is the magnitude of the strain. Then the the total energy of the strain system can be written as

$$F(x)=F(0)+(C_{11}-C_{12})Vx^2+O(x^4), \qquad (11)$$

where V is the volume of the unit cell and $E(0)$ is the total energy of the unstrained lattice at the volume V. For the elastic constant C_{44} one can use the volume-conserving orthorhombic strain tensor,[14]

$$\varepsilon=\begin{pmatrix} 0 & x & 0\\ x & 0 & 0\\ 0 & 0 & x^2/(1-x^2)\end{pmatrix}, \qquad (12)$$

with the corresponding strain energy

$$F(x)=F(0)+2C_{44}Vx^2+O(x^4). \qquad (13)$$

For isotropic polycrystalline aggregates of cubic crystallites, the calculated C_{ij} can also be used to determined the bulk modulus exactly by

$$B=\frac{1}{3}(C_{11}+2C_{12}), \qquad (14)$$

but only place rather strict bounds on the average isotropic shear modulus. It is a conventional treatment to use the average of the Shtrikman bound and Hashin bound[15] as the shear modulus. Using the elastic constants $C_{11}-C_{12}$, C_{44} and Eq. (14) the elastic constant C_{11} can be determined.

The isothermal bulk moduli B_T computed by the method mention above can converted to adiabatic moduli B_S according to[16]

$$B_S=\frac{C_P}{C_V}B_T, \qquad (15)$$

where α is the thermal expansion coefficient and C_P is the heat capacity at constant pressure. Since in a pure shear the “isothermal” and “adiabatic” moduli are equal, there is no need to adjust the shear moduli.

It should be mentioned here that the crystal anisotropy from the atom vibration vanishes because, if pair potentials are used in the integration $f(V,T)$, the Helmholtz free energy contribution from the ions F_{ion} will not change with the shear strain! But it is still a good approximation for single crystal and especially for polycrystalline aggregates, because the single crystal anisotropy from atom vibration is small and the temperature effect to elastic constants is mainly from the volume expansion,[10] which can be accurately calculated in this method.

III. CALCULATION DETAILS AND RESULTS

In this work to calculate the total energy of the unit cell at different temperatures we used the accurate full-potential linear muffin-tin orbital method (FPLMTO).[22] The generalized gradient approximation (GGA)[23] is used for the exchange-correlation potential. The calculations were all-electron, nonrelativistic, and employed no shape approximation for the charge density or potential. The basis set is comprised of augmented linear muffin-tin orbitals with *s*, *p*, *d* momenta. Integration over the Brillouin Zone was done using the linear tetrahedron method. In the irreducible wedge of the fcc Brillouin Zone, 256 *k* points were used for no strain crystal. The number of *k* points was recalculated for the symmetry of the distorted crystal.

The pair potential fcc Al was obtained by fitting unit cell total energies, calculated using zero temperature DFT, for relative volume V/V_0 from 1 to 0.65 in 0.01 increments to its relationship with the pair potential expressed with the nearest neighbor 256 ions. The integration $f(V,T)$ was performed by a dense sampling of two-dimensional grids in the $\theta-r$ plane.

The calculated linear expansion coefficients as a function of temperature at various pressures are compared to the available experimental data[17] in Fig. 1, which shows good agreement at zero pressure, in particular for temperatures greater than the Debye temperature but lower than the melting temperature. The calculated thermal expansion coefficients decreases sharply with pressure and increases with temperature, which are well known feathers of metals.

The calculated specific heat (electronic and ionic) at constant volume $V(T=293\ K,P=P)$ and per atom as a function of temperature is shown in Fig. 2. The constant-volume specific heat at zero pressure, deduced from the experimental data of Forsblom *et al.*,[18] is reproduced by our calculation. The temperature contribution to anharmonic effects shown by the deviation of constant-volume specific heat due to the lattice atom from its classical harmonic value $3k_B$ diminishes with pressure.

To compare our results of the equation of state of Al at high compression and high temperatures with those derived from the shock data, we calculated the pressures P_{H} and

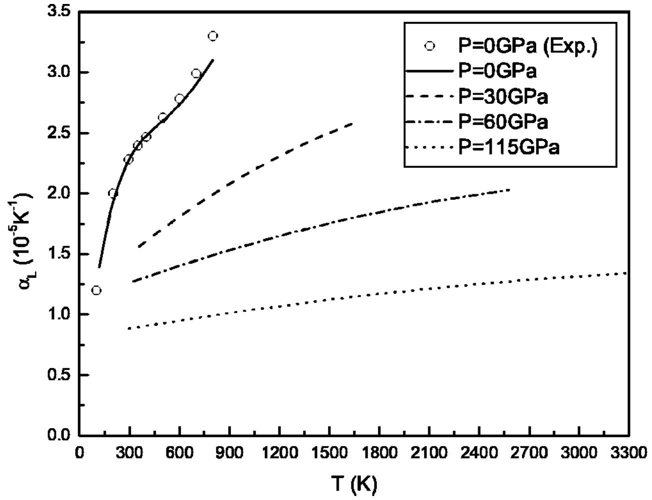

FIG. 1. Calculated linear thermal expansion coefficients α_L of fcc Al. The available experimental results (Ref. 17) at zero pressure are shown by circles. The curves correspond (from bottom to top) to decreasing pressures $P=115$, 60, 30, and 0 GPa.

temperatures T_H on the Hugoniot for a set of relative volumes ranging from 1 to 0.6 by solving the Rankin-Hugoniot equation:[24]

$$P_H(V_0 - V) = 2(E_H - E_0), \tag{16}$$

where E_H is internal energy along the Hugoniot, and E_0 and V_0 are, respectively, zero-pressure and room-temperature energy and volume of the FPLMTO results. For a given volume V, the temperature on the Hugoniot is varied until Eq. (16) is satisfied. The agreement of the calculated Hungoniot with experimental data[19] is better than that from the Debye-model-based method[3] (Fig. 3).

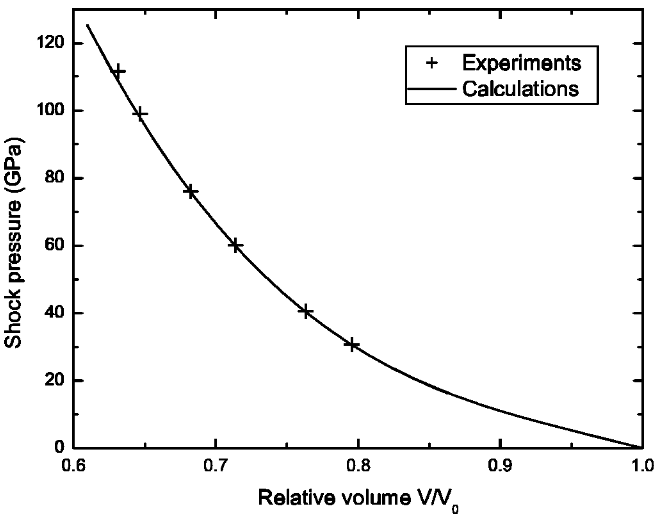

FIG. 3. Hugoniot for the fcc Al in the P-V plane. The solid line is the calculated Hungoniot and the pluses are experimental values (Ref. 19).

The calculated thermodynamics Grüneisen parameter γ_{th} (Fig. 4) in the range of low shock compression qualitatively agrees with the conventional assumption $\gamma_{\text{th}}/V=\text{const}$, such as in the semi-empirical equation of state of Al.[20] In range of high shock compression the conventional assumption dose not hold.

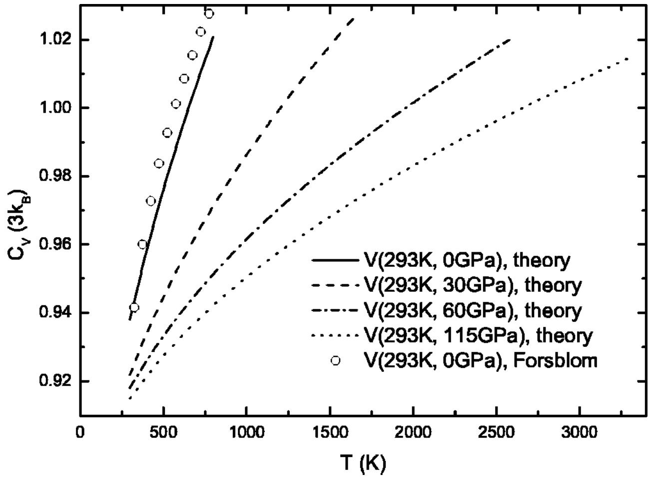

FIG. 2. The calculated specify heat at constant volume $V(T=293\,K, P=P)$ and per atom. The curves correspond (from bottom to top) to increasing initial volume at pressures $P=115$, 60, 30, and 0 GPa. The circles are deduced from experimental data on the enthalpy by Forsblom *et al.* (Ref. 18).

The isothermal elastic constants of fcc Al as functions of temperature at various pressures are presented in Fig. 5. The elastic constants of fcc Al elevates with the increasing pressure value and declines with the increasing temperature value.

In order to compare the theoretical results with the experimental ones, we also calculated, at room temperature and zero pressure, the adiabatic elastic constants C_{11}, C_{12}, and C_{44} of a single crystal, the bulk moduli B and shear moduli G of polycrystalline aggregates of fcc Al (Table I), and along the Hungoniot the moduli B (Fig. 6) and G (Fig. 7). The experimental moduli on the Hungoniot are determined by the sound data[21] according to Navier's equation as follows:[16]

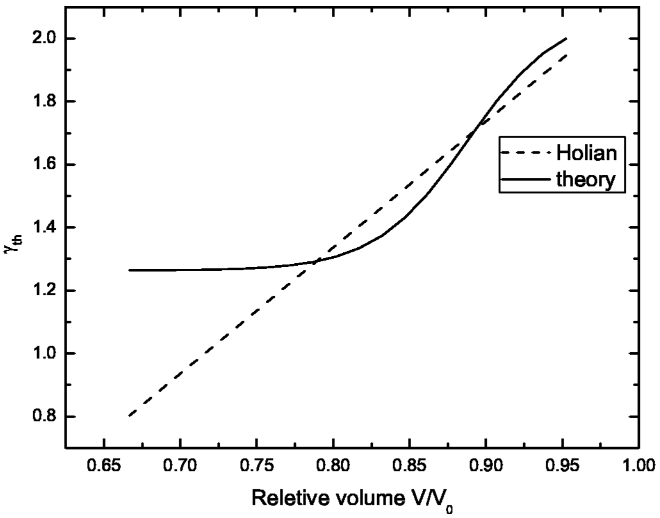

FIG. 4. Thermodynamic Grüneisen parameter γ. The solid line denotes our calculations and the dashed line shows data from the semi-empirical EOS (Ref. 20).

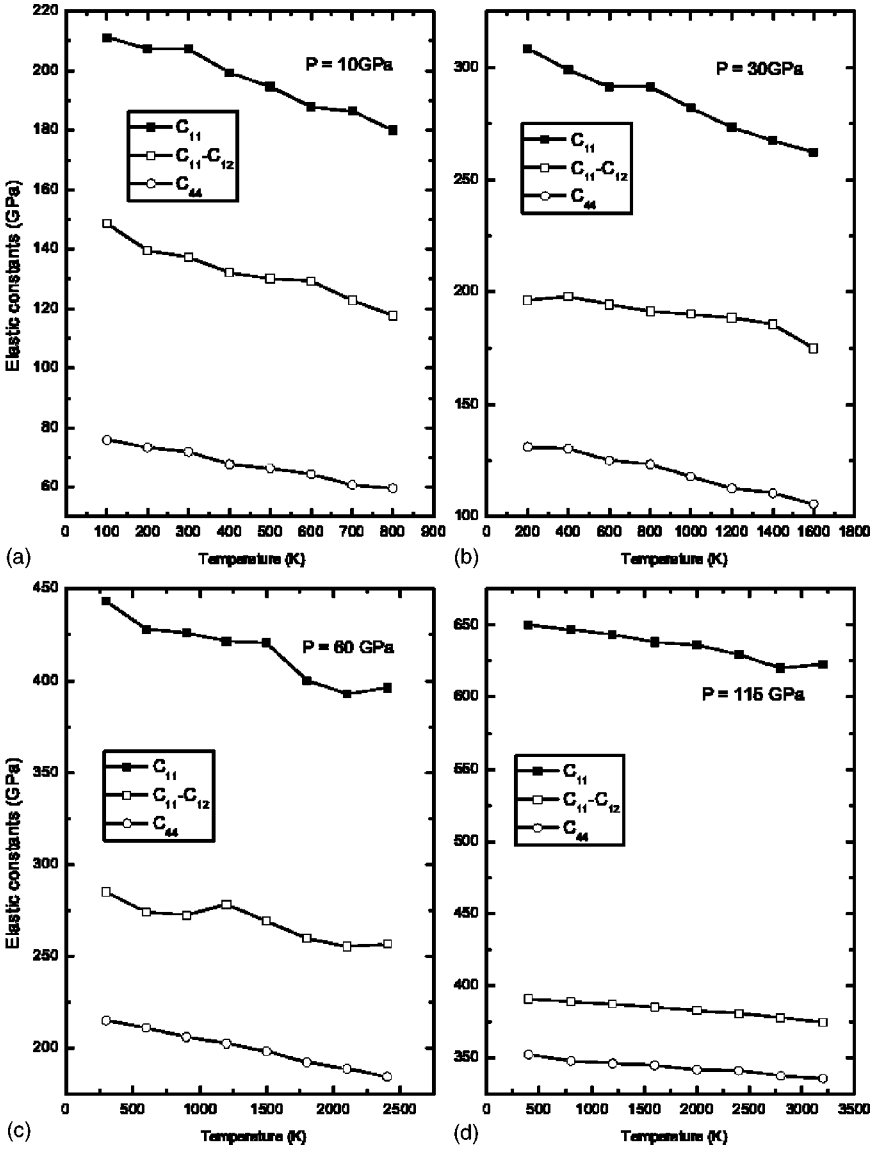

FIG. 5. The calculated isothermal elastic constants of fcc Al as a function of temperature. The pressure for (a), (b), (c), and (d) are 10, 30, 60, and 115 GPa, respectively.

$$v_l = \left(\frac{B + 4G/3}{\rho}\right)^{1/2}, \tag{17}$$

and

$$v_b = \left(\frac{B}{\rho}\right)^{1/2}, \tag{18}$$

where v_l and v_b are the longitudinal and bulk sound velocity of the polycrystalline aggregates of Al, respectively.

TABLE I. The calculated and experimental volume (in Å^3) of the primitive unit cell, the adiabatic moduli C_{11}, C_{12}, C_{44}, B, and G (in GPa) under ambient conditions for fcc Al.

	V_0	C_{11}	C_{12}	C_{44}	B	G
Calculations	16.75	114.8	63.0	31.6	80.3	29.2
Experiments	16.61[a]	106.9[b]	60.8[b]	28.2[b]	75.5[c]	26.1[c]

[a] From Reference 25.
[b] From Reference 26.
[c] From Reference 27.

Table I shows that the calculated volume of the primitive unit cell, the adiabatic moduli C_{11}, C_{12}, C_{44}, B, and G under ambient conditions for fcc Al are well reproduced. From Fig. 6 and Fig. 7 one can see that the bulk moduli and shear moduli obtained by our method fall well in the experimental uncertainties at the pressures below 100 Gpa on Hugoniot (the temperature ranges from 300 to 3600 K). If the pressure increases up to 120 GPa, that means the temperature approaches the melting point and shear modulus should decrease rapidly at the pressure, our method does not work very well anymore. This shows in one way that our method is not fit for a melting study because we have not consider the contribution of fault to Helmholtz free energy which is important at high temperature near the melting point.

IV. SUMMARY

In this work a pair-potential-based mean-field approximation (PPBMFA) to the thermal contribution to the Helmholtz free energy is presented. Combining PPBMFA with the

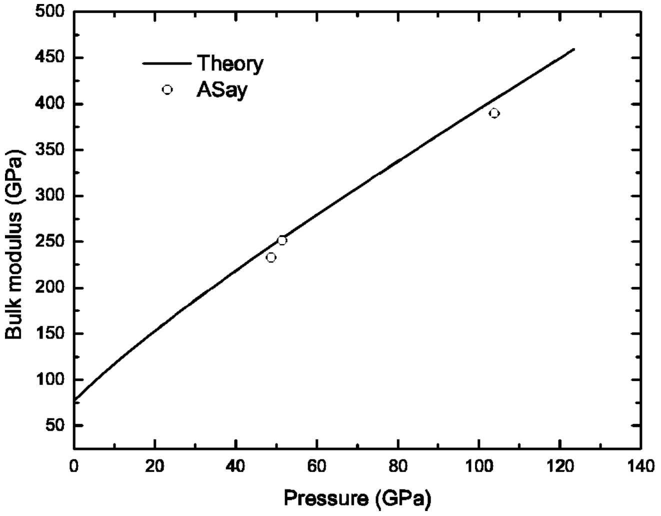

FIG. 6. Bulk moduli VS pressure of Hungoniot. The solid line denotes theory result and the circles are deduced from the experimental data on the bulk sound velocity (Ref. 21).

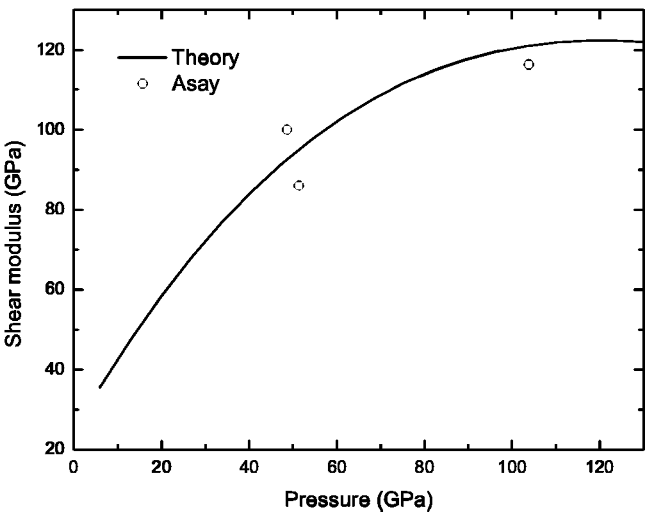

FIG. 7. Shear modulus VS pressure of Hungoniot. The solid line denotes theory result and the circles are deduced from the experimental data on the compressional and bulk sound velocity (Ref. 21).

FPLMTO total-energy method the thermal properties of fcc Al as a prototype were studied. The linear thermal expansion coefficient, specific heat at a constant volume, Hugoniot in the *P-V* plane, thermodynamic Grüneisen parameter, and elastic constants that we calculated at pressures up to 120 GPa and temperature to 3300 K for the fcc Al are in a good agreement with available static and shock-wave experimental measurements. The results also show that our method is not fit for thermal properties near the melting point. We suppose this method may be used to calculate the thermal properties of the solid state of another metal.

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