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Classical mean-field approach for thermodynamics: *Ab initio* thermophysical properties of cerium

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For evaluating the vibrational contribution of the lattice ion to the total free energy, an attempt is made to propose a classical mean-field model without involving any adjustable parameter, where the mean-field potential $g(r,V)$, seen by the lattice ion, is simply constructed in terms of the 0 K total energy. It is shown that as a second-order approximation of the mean-field potential, the well-known Dugdale and MacDonald expression of the Grüneisen parameter $\gamma_{\text{ion}}(V)$ is explicitly deduced. Furthermore, an *ab initio* scheme for calculating the various kinds of thermodynamic properties of a substance is developed. Our approach permits efficient computation. By taking Ce metal as a prototype, the *ab initio* calculated results show that at 590 K, the γ-Ce is more stable than α-Ce, and the experimental 300 K isotherm and the Hugoniot state are reproduced excellently.

Metallic cerium (Ce), which exhibits an extraordinary rich pressure-temperature phase diagram,[1] has inspired numerous theoretical interests.[2–9] Five distinct solid phases are known to exist, having different magnetic and superconducting properties. The most fascinating attraction of Ce is the γ-α isostructural phase transition which, in analogy to the well-known liquid-gas phase transition,[1,2] takes place at room temperature and under a pressure of ~0.7 GPa involving a volume collapse of ~14%. Many attempts have been made to describe such an unusual behavior, such as, the promotional model (PM), the Kondo volume-collapse (KVC) model,[3] and the Mott transition (MT) model.[1] In contrast to the above-mentioned modes, Eriksson *et al.*[4] and Jarlborg *et al.*[5] had shown that by including orbital polarization of the $4f$ electrons in the itinerant bands the isostructural phase transition could be well described theoretically.

In this work, we propose a classical mean-field (CMF) model for evaluating the vibrational contribution of the lattice ion to the total free energy. An *ab initio* scheme for calculating the various kinds of thermodynamic properties of a substance is furthermore developed by means of (i) the accurate calculations of 0 K total-energy curve with the full-potential linearized augmented plane-wave method within the generalized gradient approximation, (ii) the accurate calculation of the thermal excitation of electrons with one-dimensional numerical integration, and (iii) the treatment of the contribution from the magnetic disorder to the free energy by generalizing the Hund's rule. By taking Ce metal as a prototype, our calculated results show that the γ-α isostructural transition can naturally occur. In conjunction with the γ-α isostructural transition, the experimental Hugoniot state (shock-wave compressed state) and the 300 K static equation-of-state (EOS) are also well reproduced.

Let us consider a system with a given averaged atomic volume V. The Helmholtz free-energy $F(V,T)$ per ion can be written as[10]

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

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

We first concentrate our attention to the term F_{ion} in Eq. (1). It is known that the vibrational contribution to the partition function takes the form $Z_{\text{ion}}=\exp(-NF_{\text{ion}}/k_BT)$, where N is the total number of lattice ions. Under the mean-field approximation, the classical form of Z_{ion} can be expressed as[11,12]

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

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 derive the MFP $g(\mathbf{r},V)$. In the well-known free-volume theory,[11] the MFP $g(\mathbf{r},V)$ was derived by means of the averaging of the pair-wise potentials, while in the cell model[12] it was derived by the tight-binding total-energy method. In this work, the MFP $g(\mathbf{r},V)$ is simply constructed in terms of the 0 K total energy $E_c(R)$ as follows

$$g(r,V)=\frac{1}{2}[E_c(R+r)+E_c(R-r)-2E_c(R)], \tag{3}$$

where r represents the distance that the lattice ion deviates from its equilibrium position, R the lattice constant, and $V=R^3/4$ in the case of fcc crystal. Below we demonstrate the physical basis of Eq. (3).

If we make a Taylor expansion of Eq. (3), we have

$$g(r,V)=k(V)r^2+O(r^4), \tag{4}$$

where $k(V)=\partial^2E_c(R)/\partial R^2$ and $O(r^4)$ represents the term higher than the third order. Furthermore, the Grüneisen parameter $\gamma_{\text{ion}}(V)$ from Debye-Grüneisen theory[13,14] can be estimated by $\gamma_{\text{ion}}(V)=-\partial\ln\nu/\partial\ln V$, where ν stands for the phonon frequency. Since $\nu\simeq(k(V)/m)^{1/2}$, we obtain

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$$\gamma_{\mathrm{ion}}(V)=-\frac{1}{3}-\frac{V}{2}\frac{\partial^2(P_cV^{2/3})/\partial V^2}{\partial(P_cV^{2/3})/\partial V}, \tag{5}$$

where $P_c(V)=-\partial E_c(V)/\partial V$ is the so-called cold pressure. This is exactly the expression of Dugdale and MacDonald.[15]

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

$$F_{\mathrm{ion}}(V,T)=-k_BT\left(\frac{3}{2}\ln\frac{mk_BT}{2\pi\hbar^2}+\ln v_f(V,T)\right), \tag{6}$$

where

$$v_f(V,T)=4\pi\int \exp\left(-\frac{g(r,V)}{k_BT}\right)r^2dr. \tag{7}$$

With Eq. (6) in conjunction with Eq. (7), the free-energy due to the lattice ion is now evaluated in form of one-dimensional integration which is more accurate than the conventional way of using the second-order derivative of the cold energy to the lattice constant. Eq. (3) is also supported by the good asymptotic behaviors of the well-known free-volume theory (see Ref. 11 by Vashchenko and Zubarev), where in the case of low temperature Eq. (6) will be reduced to that of the classical harmonic theory and in the case of very high temperature Eq. (6) will be reduced to that of the ideal gas. We note also that Eq. (4) does not contain the third (or the odd) order term and $O(r^4)$ may in part account for the so-called softening of phonon.

Let us turn our attention to the term F_{el} in Eq. (1), the free-energy due to one-particle thermal excitation of the electrons from their ground states. It is known that $F_{\mathrm{el}}=E_{\mathrm{el}}-TS_{\mathrm{el}}$, where the bare electronic entropy S_{el} takes the form[5]

$$S_{\mathrm{el}}(V,T)=-k_B\int n(\epsilon,V)[f\ln f+(1-f)\ln(1-f)]d\epsilon, \tag{8}$$

where $n(\epsilon,V)$ is the electronic density of states (DOS) and f is the Fermi distribution. With respect to Eq. (8), the energy E_{el} due to the electron excitations can be expressed as

$$E_{\mathrm{el}}(V,T)=\int n(\epsilon,V)f\epsilon d\epsilon-\int^{\epsilon_F}n(\epsilon,V)\epsilon d\epsilon, \tag{9}$$

where ϵ_F is the Fermi energy.

Consecutively, let us consider the term F_{mag} in Eq. (1). To our best knowledge, no accurate expression exists for the magnetic free-energy F_{mag}. In this work, we only consider the magnetic entropy which arises from the γ-α isostructural transition involving the magnetic disorder. By only considering the magnetic multiplicity, we introduce F_{mag} as

$$F_{\mathrm{mag}}(V,T)=-k_BT\ln[M_S(2L-M_S)+1], \tag{10}$$

where $\ln[M_S(2L-M_S)+1]$ is the magnetic entropy, M_S is the total spin magnetic moment, and L is $4f$ orbital moment with $L=3$. Since Hund's rule can be expressed by the total angular moment as $J=M_S(2L-M_S)/2$ with integer M_S, it is obvious that Eq. (10) can be regarded as a generalization of Hund's rule. For the case of Ce, a gradually increased magnetic disorder has been described by the present author in this way.

Since the integrands in v_f, S_{el}, and E_{el} are all one dimensional, the integrals in Eqs. (7)–(9) can be easily evaluated by modern computational techniques without further shape approximation. In practice, all the thermodynamic quantities reported in this work are calculated by one-dimensional numerical integration or difference on a PC-266 computer with the time consuming of only a few minutes. Thus, the present CMF model permits efficient computation of the thermal properties.

For obtaining the 0 K total energy curve different philosophies exist. Within the MT model assumption, Johansson *et al.*[9] chose to describe α-Ce by regarding all the $4f$ electrons as delocalized valence electrons and chose to describe γ-Ce by regarding one $4f$ electron as fully localized by treating it as part of the inert core, and to align the energies of the two phases of Ce, an energy shift ΔE^{γ} was introduced for technical reasons rather than as a matter of principles. Within the KVC model assumption, Laegsgaard and Svane[3] chose to treat the $4f$ electrons by a combination of the self-interaction-corrected local-density approximation (SIC-LDA) and the Anderson impurity model where the values for U (*f*-level Coulomb repulsion) and the *f*-level positions were obtained from spectroscopic fits. In contrast to the above two representative works, Jarlborg *et al.*[5] chose to describe the both phases as itinerant band solids. Our physical principle to calculate the 0 K total-energy curve is close to that of Eriksson *et al.*[4] and that of Jarlborg *et al.*, i.e., the spin-polarized calculation is employed without *a priori* assumption for the nature of $4f$ electrons. The self-consistent, relativistic (without considering the spin-orbit coupling), full-potential, and spin-polarized, linearized augmented plane-wave (LAPW) method[16] within the generalized gradient approximation[17] is employed. The calculations span a wide lattice-constant (L_C) range of from 7.1 a.u. to 18.0 a.u. by fcc crystal structure. A constant muffin-tin radius (R_{mt}) of 2.50 a.u. is used for all lattice constants. The plane-wave cutoff K_{cut} is determined by $R_{\mathrm{mt}}\times K_{\mathrm{cut}}=10.0$. The basis sets include the $5s$, $5p$, $6s$, $6p$, $5d$, and $4f$ partial waves. All these orbitals are defined within one energy panel, i.e., they are all allowed to hybridize. 256 k points in the irreducible part corresponding to 8000 points in the full zone are used.

Figure 1 shows the calculated 0 K isotherm for Ce metal. Note that the magnetic state naturally develops for $L_C\geqslant 9.7$ a.u. by the LAPW calculation. As the lattice parameter increases, the spin magnetic moment rises continuously, though very steeply.

To demonstrate the γ-α isostructural transition of cerium, we show the LAPW calculated energy points coupled with the calculated total free-energy curves at $T=300$, 590, and 900 K in Fig. 2(a). At 300 K, a metastable state emerges apparently at $L_C=9.71$ a.u. (33.9 Å^3 by atomic volume). This state is related to the magnetic disorder and surely corresponds to the γ-Ce. At 590 K, the calculated γ-Ce becomes stable with atomic volume of 34.7 Å^3 (the experimental transition temperature lies in the range 200–300 K with atomic volume of 34.36 Å^3). Our calculated volume collapse of the γ-α isostructural transition is 6.8 Å^3 compared with the experimental value of 6.2 Å^3 from Ref. 9. Depicted in Fig. 2(b) is the calculated pressure-temperature phase diagram, where T_P represents the pseudoequilibrium line and T_E represents the minimum temperature at which the γ-Ce can exist.

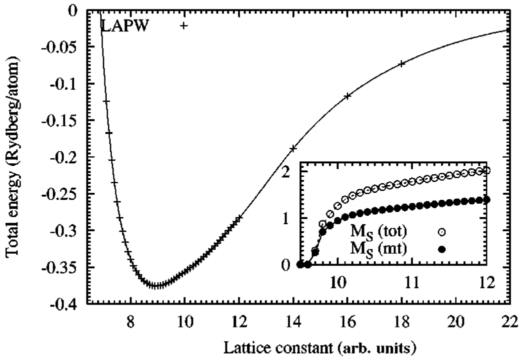

FIG. 1. The calculated 0 K total energies vs lattice constants for fcc Ce. The crosses are the LAPW points. The solid line between 7.1 a.u. and 18.0 a.u. is derived by cubic spline interpolation, and that smaller than 7.1 a.u. and that greater than 18.0 a.u. are derived by extrapolations by means of Morse function. The inset shows the total (tot) and in the muffin-tin sphere (mt) spin magnetic moments vs lattice constants.

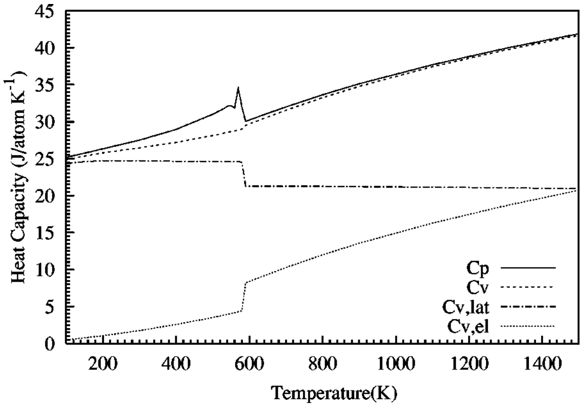

FIG. 3. The calculated heat-capacity vs temperature curves. The solid, dashed, dot-dashed, and dotted lines represent the calculated constant-pressure specific heat C_P, constant-volume specific heat C_V, the lattice ion only constant-volume specific heat $C_{V,\mathrm{lat}}$, and the electron only constant-volume specific heat $C_{V,\mathrm{el}}$, respectively.

Johansson *et al.*[9] had mentioned a nearly linear dependence of the transition pressure with temperature and the existence of a critical point. In our calculation, the salient features of P-T linearity is reproduced and the ratio of linearity can be also comparable with that of the experiment whereas the critical point is lost. The loss of the critical point and the higher transition temperature can be ascribed to the calculation of the 0 K total energy, because the evaluation for the critical point requires the 0 K total energy too precise to be obtained from an *ab initio* calculation at present without any empirical parameter.

Plotted in Fig. 3 are the calculated heat capacities versus temperature under ambient pressure. Before the transition ($T=580$ K), the calculated constant-volume heat capacities from the lattice ion ($C_{V,\mathrm{lat}}$) and the thermal electron are 24.57 J/atom and 4.42 J/atom, respectively. After the transition ($T=590$ K), the two values become 21.30 J/atom and 8.21 J/atom, respectively.

The decreases from 24.57 J/atom to 21.30 J/atom in $C_{V,\mathrm{lat}}$ can demonstrate the physical difference between Eq. (3) and the quasiharmonic approximation since the classical harmonic value of $C_{V,\mathrm{lat}}$ is just 24.94 J/atom $(3k_B)$. This can be clearly seen in Fig. 1 where an evident change in the curvature of the energy lattice curve appears near $L_c=9.8$ a.u. The calculated variations of the heat capacities near the transition temperature shown in Fig. 3 support the assertion that the transition is very similar to a liquid-gas phase transition as mentioned by Johansson[1] and by Min *et al.*[2]

Figure 4 shows the calculated 300 K static EOS of Ce based on the calculated metastable γ-Ce as well as the experimental results.[19,20] Notice that a very good agreement between the calculation and the experiment is obtained.

Shock-wave dynamic compression is a common way to study the thermodynamic properties of a substance under extreme condition such as high-temperature and high-pressure environments. From its derived Hugoniot state one can deduce much useful information such as EOS at feasible temperature range. In fact, the various static EOS experiment by the diamond-anvil cell is usually calibrated by the data from the reductions of the Hugoniot data. Illustrated in Fig. 5 is the calculated Hugoniot by solving the Rankine-Hugoniot conservation equation[12] $P_H(V_0-V)/2=E_H-E_0$, where P_H is called Hugoniot pressure and E_H is the internal energy

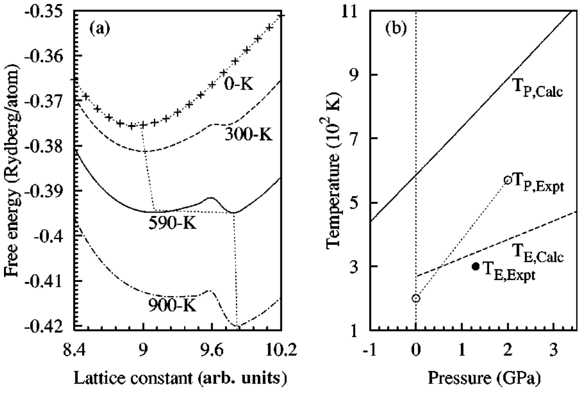

FIG. 2. (a) The calculated total free-energy vs lattice-constant curves at $T=300$, 590, 900 K coupled with 0 K LAPW total energy points (crosses). The vertical light dotted line marks the global minimum along the total free-energy curve. (b) The calculated pressure-temperature phase diagram, where T_P represents the pseudo-equilibrium line (for the experimental T_P see Ref. 18) and T_E represents the minimum temperature that the γ-Ce can exist (the experimental T_E is taken from Ref. 19).

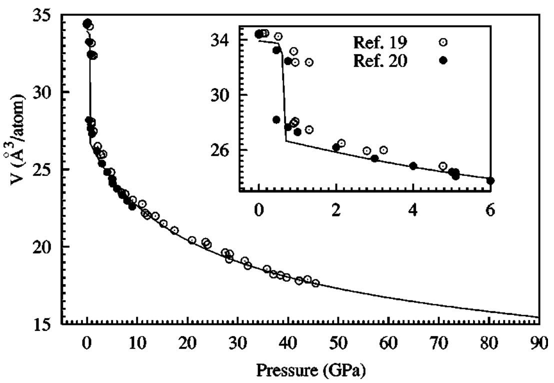

FIG. 4. The calculated 300 K static equation of state of Ce compared with experiment (Refs. 19 and 20). The inset demonstrates the lower compression region.

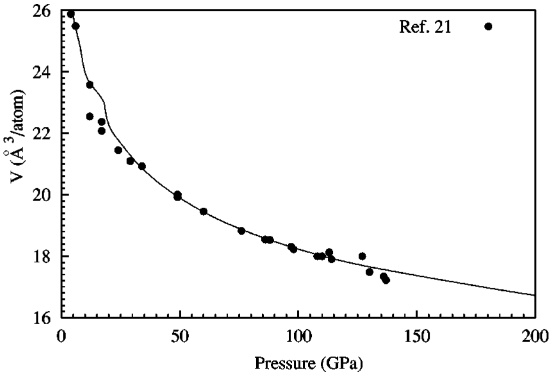

FIG. 5. The calculated Hugoniot ($P-V$) of Ce compared with experiment.[21]

along the Hugoniot, and V_0 and E_0 refer to the atomic volume and energy under ambient condition, respectively, where we take them from the calculated metastable γ-Ce. The present *ab initio* results fall well within the experimental uncertainties.

In summary, we have developed an *ab initio* scheme for calculating the various kinds of thermodynamic properties of a substance without any adjustable parameter. The major physics lies in the construction of MFP $g(r,V)$ in terms of the 0 K total energy in Eq. (3). By taking Ce metal as a prototype, the calculated results show that at 590 K the γ-Ce is more stable than α-Ce (the experimental transition temperature lies in the range 200–300 K), and the experimental 300 K isotherm and the Hugoniot state are well reproduced. Furthermore, the variation of the heat capacity near the transition temperature indicates that the transition is very similar to a liquid-gas phase transition as mentioned by Johansson[1] and Min *et al.*[2]

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[1] B. Johansson, Philos. Mag. **30**, 469 (1974).

[2] B. I. Min, H. J. F. Jansen, T. Oguchi, and A. J. Freeman, Phys. Rev. B **34**, 369 (1986).

[3] J. Laegsgaard and A. Svane, Phys. Rev. B **59**, 3450 (1999).

[4] O. Eriksson, M. S. S. Brooks, and B. Johansson, Phys. Rev. B **41**, 7311 (1990).

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

[6] P. Söderlind, O. Eriksson, J. Trygg, B. Johansson, and J. M. Wills, Phys. Rev. B **51**, 4618 (1995).

[7] P. Ravindran, L. Nordström, R. Ahuja, J. M. Wills, B. Johansson, and O. Eriksson, Phys. Rev. B **57**, 2091 (1998).

[8] Z. Szotek, W. M. Temmerman, and H. Winter, Phys. Rev. Lett. **72**, 1244 (1994).

[9] B. Johansson, I. A. Abrikosov, M. Aldén, A. V. Ruban, and H. L. Skriver, Phys. Rev. Lett. **74**, 2335 (1995).

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

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

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

[13] C. Kittel, *Solid State Physics* (Wiley, New York, 1976).

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

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

[16] 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)].

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

[18] From Ref. 5, Jarlborg *et al.* had summarized, ‘‘At zero pressure, the α-γ transition begins at 200 K (where a hexagonal β phase comes in between), and ends in a critical point at about 570 K and 20 kB (=2 GPa).’’

[19] J. S. Olsen, L. Gerward, U. Benedict, and J.-P. Itié, Physica B **133**, 129 (1985).

[20] W. H. Zachariasen and F. H. Ellinger, Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr. **33**, 155 (1977).

[21] W. J. Carter, J. N. Fritz, S. P. March, and R. G. McQueen, J. Phys. Chem. Solids **36**, 741 (1975).