Thermodynamic properties and structural phase transition of cerium under high pressure

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ABSTRACT

The pressure effects on thermodynamic properties as well as the structural phase transition of the rare-earth metal cerium have been investigated by using the statistical moment method in quantum statistical mechanics. The analytical expressions of Helmholtz free energy, thermal expansion coefficient, and bulk modulus of α-Ce have been derived. Numerical calculations of these above thermodynamic quantities give good and reasonable results comparing to experiments as well as other theoretical works. This research also proposes the efficiency of the statistical moment method for determining the relative change of the phase transition temperature of the process γ-Ce $\rightarrow$ δ-Ce under pressure.

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1. Introduction

Cerium is a rare-earth metal with most unusual properties and complicated structural phase diagram [1,2]. As the first rare earth metal with one 4f-electron, cerium exhibits at least 5 recorded allotropic forms of cerium: α-Ce (face-centered cubic − fcc), β-Ce (hexagonal closed pack − dhcp), γ-Ce (fcc), $\in$-Ce (Body-centered tetragonal − bct) and δ-Ce (body-centered cubic − bcc). In particular, this metal is best known for its isostructural solid−solid phase transition between the two α and γ phases with a volume (V) collapse of about 15% [3−6]. Apart from this isostructural phase transition, however, to our best knowledge, only a few works have been done to investigate the $\gamma \rightarrow \delta$ phase transition of cerium.

Besides a direct study of the electronic properties, numerous efforts have been devoted to deeply understand the lattice dynamics of the δ phase of cerium. Using inelastic neutron scattering, growing the single crystals in situ on the spectrometer, Nicolaus et al. [7] measured the phonon dispersion of high-temperature δ-Ce. By performing lattice dynamical calculations in the angular force model, Deligöz et al. [8] computed dispersion curves, frequency spectra, lattice specific heat and Debye temperature of bcc cerium. For the γ phase, the phonon dispersion has been studied by

Stassis et al. [9,10], as well as the elastic constants by Greiner et al. [11]. Recently, Huang and Chen [12] and Sun et al. [13] investigated the lattice dynamics of the α and γ phases of cerium via the first-principles plane wave method. However, according to the literature, the values of thermodynamic quantities of α-Ce are still currently under debate, with very different conclusions reached by different authors.

In this paper, with the aim of contributing to the knowledge about thermodynamic properties of the α phase of cerium, using the statistical moment method (SMM) in quantum statistical mechanics [14−16], we derive the Helmholtz free energy, then the bulk modulus and linear thermal expansion coefficient of a crystalline system in analytical forms. Furthermore, based on thermodynamic considerations, we determine the phase transition temperature of the process $\gamma \rightarrow \delta$ of cerium as a function of pressure.

2. Theory

2.1. Summary of statistical moment method

In the first part of this section, we summarize the main results of SMM which has been derived for crystalline materials [14,16]. At finite temperature, the thermal lattice vibration plays an important role in determining the thermodynamic properties of materials. Let us firstly consider the system with Hamiltonian as

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$$\widehat{H} = \widehat{H}_0 - \alpha\widehat{V}, \tag{1}$$

where $\widehat{H}_0$ is the lattice Hamiltonian in the harmonic approximation and the second term is due to the anharmonicity of thermal lattice vibrations. As reported by Tang & Hung [14] and Masuda-Jindo et al. [16], the Helmholtz free energy at temperature T of the above quantum system is given by

$$\psi = \psi_0 - \int_0^{\alpha} \langle\widehat{V}\rangle_{\alpha} d\alpha, \quad \langle\widehat{V}\rangle_{\alpha} = -\partial\psi/\partial\alpha, \tag{2}$$

in which ψ_0 is the free energy of the system corresponding to the Hamiltonian $\widehat{H}_0$, $\langle\ldots\rangle_{\alpha}$ expresses the expectation values at thermal equilibrium with the anharmonic Hamiltonian $\widehat{H}$. If the Hamiltonian $\widehat{H}$ has a complex form, we divide it into two more simple parts,

$$\widehat{H} = \widehat{H}_0 - \sum_i \alpha_i\widehat{V}_i, \tag{3}$$

At first we find the free energy ψ_1 of the system corresponding to the Hamiltonian $\widehat{H}_1 = \widehat{H}_0 - \alpha_1\widehat{V}_1$. Afterwards we find the free energy ψ_2 of the system corresponding to $\widehat{H}_2 = \widehat{H}_1 - \alpha_2\widehat{V}_2$, and so on. In this way we can find the expression of the free energy ψ of the system with Hamiltonian $\widehat{H}$. The thermodynamic quantities of the harmonic crystal (harmonic Hamiltonian) will be treated in the Einstein approximation.

In order to derive the Helmholtz free energy of the crystalline material, we assume that the potential energy of the system composed of N atoms can be written as

$$U = \frac{N}{2}\sum_i \varphi_{i0}(|r_i + u_i|) \tag{4}$$

where r_i is the equilibrium position of the i-th atom, u_i its displacement, and φ_{i0} the effective interaction energy between zero-th and i-th atoms. We expand the potential energy $\varphi_{i0}(|r_i + u_i|)$ in terms of the displacement up to the fourth-order terms and evaluate the vibrational coupling parameters.

$$U = \sum_i \left\{ \varphi_{i0}(|r_i|) + \frac{1}{2}\sum_{\alpha,\beta}\left(\frac{\partial^2\varphi_{i0}}{\partial u_{i\alpha}\partial u_{i\beta}}\right)_{eq} u_{i\alpha}u_{i\beta} \right.$$
$$+ \frac{1}{6}\sum_{\alpha,\beta,\gamma}\left(\frac{\partial^3\varphi_{i0}}{\partial u_{i\alpha}\partial u_{i\beta}\partial u_{i\gamma}}\right)_{eq} u_{i\alpha}u_{i\beta}u_{i\gamma}$$
$$\left. + \frac{1}{24}\sum_{\alpha,\beta,\gamma,\eta}\left(\frac{\partial^4\varphi_{i0}}{\partial u_{i\alpha}\partial u_{i\beta}\partial u_{i\gamma}\partial u_{i\eta}}\right)_{eq} u_{i\alpha}u_{i\beta}u_{i\gamma}u_{i\eta} + \ldots \right\} \tag{5}$$

Using Eq. (5), the thermal average of potential energy of the system is given in terms of the power moment $\alpha = \frac{k_B\chi_T}{3}\left(\frac{\partial P}{\partial\theta}\right)_V = -\frac{\sqrt{2}k_B\chi_T}{3r_1^2}\frac{1}{3N}\frac{\partial^2\psi}{\partial\theta\partial r}$. of the thermal atomic displacements and harmonic parameter k, and anharmonic expansion coefficients γ_1 and γ_2 as [15].

$$\langle U\rangle = U_0 + 3N\left[\frac{k}{2}\langle u^2\rangle + \gamma_1\langle u^4\rangle + \gamma_2\langle u^2\rangle^2 + \ldots\right], \tag{6}$$

where

$$k = \frac{1}{2}\sum_i\left(\frac{\partial^2\varphi_{i0}}{\partial u_{i\alpha}^2}\right)_{eq} \tag{7}$$

$$\gamma_1 = \frac{1}{24}\sum_i\left(\frac{\partial^4\varphi_{i0}}{\partial u_{i\alpha}^4}\right)_{eq}, \quad \gamma_2 = \frac{6}{24}\sum_i\left(\frac{\partial^4\varphi_{i0}}{\partial u_{i\alpha}^2\partial u_{i\beta}^2}\right)_{eq}, \tag{8}$$

with $\alpha \neq \beta = x, y$ or z. In the above equation (6), eq indicates the thermal averaging over the equilibrium ensemble.

In order to derive the expression of the Helmholtz free energy, we need to evaluate analytically the following integrals

$$I_1 = \int_0^{\gamma_1} \langle u_i^4\rangle d\gamma_1 \quad, \quad I_2 = \int_0^{\gamma_2} \langle u_i^2\rangle_{\gamma_1=0}^2 d\gamma_2 \tag{9}$$

Then the final Helmholtz free energy of the system with N atoms is given by [15]

$$\psi = U_0 + \psi_0 + \frac{3N\theta^2}{k^2}\left\{\left[\gamma_2 X^2 - \frac{2\gamma_1}{3}\left(1 + \frac{X}{2}\right)\right]\right.$$
$$\left. + \frac{2\theta}{k^2}\left[\frac{4}{3}\gamma_2^2 X - 2\left(\gamma_1^2 + 2\gamma_1\gamma_2\right)(1 + X)\right]\left(1 + \frac{X}{2}\right)\right\} \tag{10}$$

where $x = \hbar\omega/2\theta$, $X = x\coth x$, $\theta = k_B T$ (k_B is the Boltzmann constant), and ω is the atomic vibration frequency which can be approximated in most cases (especially for obtaining the thermodynamic quantities at high temperatures) by the Einstein frequency $\omega_E = \sqrt{k/m}$; $U_0 = \sum_i \varphi_{i0}(r_i)$ denotes the total pair interaction energy $\varphi(r_{0i})$ on the 0th atom, $\psi_0 = 3N\theta[x + \ln(1 - e^{-2x})]$ is the anharmonicity contribution to the free energy.

The Helmholtz free energy ψ is going to be used to calculate the various thermodynamic quantities (such as the thermal expansion coefficient, and bulk modulus which are closely related to the anharmonicity of thermal lattice vibrations) as well as to investigate the fcc $\rightarrow$ bcc phase transition of the cerium element.

Let us now consider the isothermal compressibility of the solid phase with fcc structure. According to the definition of the isothermal compressibility χ_T, it is given in terms of the volume V and pressure P as

$$\chi_T = -\frac{1}{V_0}\left(\frac{\partial V}{\partial P}\right)_T = \frac{1}{B_T}, \tag{11}$$

where B_T is the isothermal bulk modulus and the pressure P can be determined from the free energy ψ of the crystal by

$$P = -\left(\frac{\partial\psi}{\partial V}\right) = -\frac{r_1}{3V}\left(\frac{\partial\psi}{\partial r}\right). \tag{12}$$

The final expression of isothermal compressibility is given by

$$\chi_T = -\frac{3(r_1/r)}{2P + \frac{\sqrt{2}}{r_1}\frac{1}{3N}\left(\frac{\partial^2\psi}{\partial r^2}\right)}, \tag{13}$$

where $r_1(T)$ is the nearest-neighbor distance (NND) between two intermediate atoms at temperature T which can be determined as

$$r_1(T) = r_0 + y_0(T), \tag{14}$$

here, r_0 is the value of NND $r_1(T)$ at zero temperature. This value can be evaluated from experiment or from the minimum condition of the potential energy of the crystal, the average atomic displacement $y_0(T)$ which takes into account the anharmonicity effects of thermal lattice vibrations at temperature T as [15,14]