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**CALCULATION OF THERMODYNAMIC QUANTITIES OF
F.C.C AND B.C.C METALS USING EAM POTENTIALS**

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Abstract

The moment method in the statistical dynamics is used to study the thermodynamic properties of metals taking into account the anharmonicity effects of the lattice vibrations. The effective pair potentials work well for the calculations of metals. For obtaining better agreement of the thermodynamic quantities of metals like Nb, the many body potentials derived from the microscopic electronic theory are used. The theoretical calculations of the thermodynamic properties are in good agreement with the corresponding experimental results.

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1. Introduction

The calculations of thermodynamic quantities of metals are important for fundamental understanding as well as for technological applications.

In order to calculate the thermodynamic quantities of materials, it is highly desirable to establish an analytical method which enables us to evaluate the free energy of the system taking into account both the anharmonicity and quantum mechanical effect of the lattice vibration. So far, the numerical calculation methods, such as the molecular dynamics and Monte Carlo simulation techniques have been presented. However, it is generally difficult to get simple algebraic formula between the thermodynamic quantities and physical insight of the phenomena, within the non - analytical numerical simulation studies. In order to investigate the thermodynamic quantities of metals, we use the moment method in the statistical dynamic [4, 5, 6] to derive the Helmholtz free energy of metallic systems, going beyond the quasi - harmonic approximation of the thermal lattice vibration. The thermodynamic quantities, e.g., the thermal lattice expansion, specific heats and elastic moduli are determined from the explicit expressions of the Helmholtz free energies. In particular, the thermodynamic properties of face - centered cubic (f.c.c) and body centered cubic (b.c.c) metals are investigated within the fourth order moment approximation of the atomic displacement. In metals, the conduction electrons travel from one atom to another and the interaction may be represented by many - body potentials instead of a pairwise potential [1]. The many body potential scheme is similar to the so-called embedded atom method [2], [3]. The numerical calculations are performed for f.c.c Cu, Ag, Au and b.c.c Ta, Nb metals, using the effective pair potentials between the atoms and embedded atom method (EAM) potentials. We will show that the theoretical calculations on the thermodynamic properties are in good agreement with the corresponding experimental results.

In Sec.2, we will make a general derivation of the Helmholtz free energy of the metallic system based on the fundamental principles of quantum statistical mechanics. Some of the numerical examples will be given in Sec.3.

2. Method of calculations

Let us consider a quantum system with the Hamiltonian

$$H = H_0 - \alpha V, \quad (1)$$

in which α is a parameter and V is an operator. In [4] the statistical average of an operator V was found to be

$$\langle V \rangle_\alpha = -\frac{\partial \psi(\alpha)}{\partial \alpha}, \quad (2)$$

where $\langle \dots \rangle_\alpha$ expresses the averaging over the equilibrium ensemble with the Hamiltonian H and ψ denotes the free energy of system. Eq.(2) gives us the general formula

$$\psi(\alpha) = \psi_0 - \int_0^\alpha \langle V \rangle_\alpha d\alpha, \quad (3)$$

in which ψ_0 is the free energy of a system corresponding to the Hamiltonian H_0 . For many cases, $\langle V \rangle_\alpha$ may be given by the moments and thus we may determine it with the aid of the moment formula [4]. Therefore, using (3) the free energy ψ of the system can be determined.

If the Hamiltonian H has a complex form, one can divide it into two more simple parts

$$H = H_0 - \sum \alpha_i V_i. \quad (4)$$

At first, we find the free energy ψ_1 of the "partial" system corresponding to the Hamiltonian $H_1 = H_0 - \alpha_1 V_1$, supposing ψ_0 is known. In this way, one can determine ψ_2, ψ_3, \dots and so on corresponding to Hamiltonian $H_2 = H_1 - \alpha_2 V_2, H_3 = H_2 - \alpha_3 V_3, \dots$. Hence the free energy ψ of the entire system may be determined completely.

Following this procedure, we derive the free energy of f.c.c and b.c.c metals. In the fourth order approximation, the potential energy of system can be written as

$$U = \frac{N}{2} \left\{ \sum_i \left[\varphi(\vec{a}_i) + \frac{1}{2} \sum_{\alpha, \beta} \left(\frac{\partial^2 \varphi_{i0}}{\partial u_{i\alpha} \partial u_{i\beta}} \right)_{eq} u_{i\alpha} u_{i\beta} + \frac{1}{6} \sum_{\alpha, \beta, \gamma} \left(\frac{\partial^3 \varphi_{i0}}{\partial u_{i\alpha} \partial u_{i\beta} \partial u_{i\gamma}} \right) u_{i\alpha} u_{i\beta} u_{i\gamma} + \right. \right. \\ \left. \left. + \frac{1}{24} \sum_{\alpha, \beta, \gamma, \eta} \left(\frac{\partial^4 \varphi_{i0}}{\partial u_{i\alpha} \partial u_{i\beta} \partial u_{i\gamma} \partial u_{i\eta}} \right)_{eq} u_{i\alpha} u_{i\beta} u_{i\gamma} u_{i\eta} \right] \right\}. \quad (5)$$

Using Eq.(5), the averaging potential energy of the f.c.c and b.c.c crystals is given by

$$\langle U \rangle = U_0 + 3N \left(\frac{k}{2} \langle u^2 \rangle + \gamma_1 \langle u^4 \rangle + \gamma_2 \langle u^2 \rangle^2 \right),$$

where,

$$U_0 = \frac{3N}{2} \sum_i \varphi_{i0} \left(\left| \vec{a}_i \right| \right), \quad (6)$$

$$\gamma_1 = \frac{1}{48} \sum_i \left(\frac{\partial^4 \varphi_{i\alpha}}{\partial u_{i\beta}^4} \right)_{eq}, \gamma_2 = \frac{6}{48} \sum_i \left(\frac{\partial^4 \varphi_{i\alpha}}{\partial u_{i\beta}^2 \partial u_{i\gamma}^2} \right)_{eq}, k = \frac{1}{2} \sum_i \left(\frac{\partial^2 \varphi_{i\alpha}}{\partial u_{i\beta}^2} \right)_{eq}, \alpha \neq \beta = x, y, z. \quad (7)$$

In deriving Eq.(6) we have assumed the symmetry property for the atomic displacements in the cubic lattice : $\langle u_{i\alpha} \rangle = \langle u_{i\beta} \rangle = \langle u_{i\gamma} \rangle = \langle u_{i\eta} \rangle \equiv \langle u_i \rangle$.

To find the free energy of a system, one must further evaluate the integrals

$$\int_0^{\gamma_2} [\langle u^2 \rangle^2]_{\gamma_1=0} d\gamma_2 \quad \text{and} \quad \int_0^{\gamma_1} [\langle u^4 \rangle]_{\gamma_2=0} d\gamma_1. \quad (8)$$

Using moment formulae, one can find the low order moments like the fourth order one $\langle u^4 \rangle$ as [4]

$$\langle u^4 \rangle \approx -\frac{8\theta^2}{3k^2} \left(\frac{a_1}{4} + \frac{\gamma^2 \theta^2}{k^4} a_2 \right) - \frac{2\gamma\theta^3}{k^4} (\coth x + 1) a_1 + \frac{2\gamma^2 \theta^4}{k^6} a_1 (x \coth x + 1) (x \coth x + 5)$$

where

$$a_1 = 1 + \frac{x \coth x}{2}, \quad a_2 = \frac{13}{3} + \frac{47}{6} x \coth x + \frac{23}{6} x^2 \coth^2 x + \frac{1}{2} x^3 \coth^3 x, \quad (9)$$

$$\theta = k_B T, \quad x = \frac{\hbar \omega}{2\theta}, \quad \gamma = 4(\gamma_1 + \gamma_2).$$

Using Eqs. (3) and (8), it is straightforward to find the Helmholtz free energy of the fcc and bcc lattice as:

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

with

$$\psi_0 = 3N\theta[x + \ln(1 - e^{-2x})]. \quad (11)$$

Applying the Gibbs - Helmholtz relation and using Eq.(10) one can find the free energy of the f.c.c and b.c.c crystals. So the specific heat at constant volume C_V has the form

$$C_V = 3N k_B \left\{ \frac{x^2}{sh^2 x} + \frac{2\theta}{k^2} \left[\left(2\gamma_2 + \frac{\gamma_1}{3} \right) \frac{x^3 cth x}{sh^2 x} + \frac{\gamma_1}{3} \left(1 + \frac{x^2}{sh^2 x} \right) - \right. \right. \\ \left. \left. - \gamma_2 \left(\frac{x^4}{sh^4 x} + \frac{2x^4 cth^2 x}{sh^2 x} \right) \right] \right\}. \quad (12)$$

Let us now consider the compressibility of the f.c.c and b.c.c lattice. According to the definition of the isothermal compressibility, one has the following relation

$$\chi_T = -\frac{1}{V_o} \left(\frac{\partial V}{\partial P} \right)_T. \quad (13)$$

Since the pressure P is given by

$$P = -\left(\frac{\partial \psi}{\partial V} \right)_T = -\frac{a}{2V} \left(\frac{\partial \psi}{\partial a} \right)_T, \quad (14)$$

the isothermal compressibility is obtained in the form

$$\chi_T = \frac{3 \left(\frac{a}{a_o} \right)^3}{2P + \frac{a^2}{V} \cdot \frac{1}{3N} \left(\frac{\partial^2 \psi}{\partial a^2} \right)_T}. \quad (15)$$

On the other hand, the linear thermal expansion coefficient is derived as

$$\alpha = \frac{k_B \chi_T}{3} \left(\frac{\partial P}{\partial V} \right)_V \quad \text{or} \quad \alpha = -\frac{\sqrt{2}}{3a^2} k_B \chi_T \cdot \frac{1}{3N} \left(\frac{\partial^2 \psi}{\partial a \cdot \partial \theta} \right). \quad (16)$$

The specific heat C_P at constant pressure and the adiabatic compressibility χ_S and χ_T are determined from the well established thermodynamic relations

$$C_P = C_V + \frac{9TV\alpha^2}{\chi_T}, \quad \chi_S = \frac{C_V}{C_P} \chi_T. \quad (17)$$

If the compressibility χ_S and χ_T are known, one can determine straight forwardly the related quantities, i.e., the isothermal and adiabatic bulk moduli β_T and β_S

$$\beta_T = \frac{1}{\chi_T}, \quad \beta_S = \frac{1}{\chi_S}. \quad (18)$$

3. Results of numerical calculations

We first calculate the thermodynamic quantities of metallic systems with f.c.c and b.c.c structures using the effective pair potentials between the atoms [7]. The effective pair potentials between the atoms is chosen by the power law form (similar to Lennard - Jones potentials):

$$\varphi(r) = \frac{D}{(n-m)} \left[m \left(\frac{r_o}{r} \right)^n - n \left(\frac{r_o}{r} \right)^m \right], \quad (19)$$

where, D and r_0 are determined to fit the experimental data (e.g., cohesive energy and elastic modulus) and $m \approx 10$ and $n \approx 5$. For the f.c.c metals like Au, Ag and Cu and b.c.c metals like Ta, Nb, the potential parameters D , r_0 , m and n are taken from ref.[7].

For f.c.c and b.c.c metals, we take into account both the first and second nearest - neighbor interactions. The thermodynamic quantities at zero pressure ($P = 0$) and finite temperature T are obtained. The numerical results of the specific heats C_V and C_P , the thermal expansion coefficient α , the isothermal compressibility χ_T , ... are presented in Table (2). The calculation of the thermodynamic quantities of metals by the present statistical moment method is of great significance in the sense that the thermodynamic quantities are directly determined from the closed analytic expressions and it does not use certain (artificial) averaging procedures, as done in the usual computer simulation studies based on the molecular dynamics and Monte Carlo method.

One may ask here whether the phenomenological pair potentials are adequate to describe the change in physical properties like specific heats, permittivity etc in the metals. However, it is to be noted that atomic displacements, due to thermal vibration, are relatively small and many body interaction effects do not play a dominant role in determining the change in total electronic energies of the system due to the atomic displacements. In order to check this point, we have also used the more sophisticated many body potentials derived from the electronic theory [1].

The many body potential scheme is similar to the so-called embedded atom method [8]. In the EAM, each atom in a solid is viewed as an atom embedded in a host comprising of all the other atoms. A simple approximation to embedding function F is the so-called local approximation, whereby the embedded atom experiences a locally uniform electron density. This can be viewed as the lowest - order term of an expansion involving the successive gradients of the density. The functional F is then approximated to yield

$$E = F_i(\rho_i(r_i)) + 1/2 \sum_j \phi_{ij}(r_{ij}), \quad (20)$$

where, ϕ_{ij} is a pair potential representing the electrostatic interaction, r_{ij} is the distance between atom i and j and F_i denotes the embedding energy of atom into electron density ρ_i .

The total energies of metals are given by a sum over all individual contributions

$$E_{tot} = \sum_i F_i(\rho_{hi}) + 1/2 \sum_{i,j(i \neq j)} \phi_{ij}(r_{ij}), \quad (21)$$

where, the host density ρ_{hi} at atom i is closely approximated by a sum of the atomic densities ρ_j of the all other constituent atoms. The embedding function F is given by

$$F(\rho_i) = D\rho_i \ln \rho_i, \quad \rho_i = \sum_j f(r_{ij}), \quad (22)$$

and the functional forms are assumed

$$\phi_{ij}(r_{ij}) = A_1(r_{c1} - r_{ij})^2 \exp(-C_1 r_{ij}), \quad (23)$$

$$f_{ij}(r_{ij}) = A_2(r_{c2} - r_{ij})^2 \exp(-C_2 r_{ij}). \quad (24)$$

For f.c.c metals, $f(r_{ij})$ and $\phi(r_{ij})$ are smoothly truncated at r_{c1} and r_{c2} respectively such that, r_{c1} was chosen to be $1.65d$ and r_{c2} was chosen to be $1.95d$ where d is the nearest neighbor distance. Here $\phi(r_{ij})$ was cut off between the second and the third nearest neighbor for a perfect crystal. This means $f(r_{ij})$ was cut off between the third and fourth nearest neighbor, d was normalized to be unity. For b.c.c metals $f(r_{ij})$ and $\phi(r_{ij})$ are smoothly truncated at r_c , where r_c was chosen to be $1.4d$ while $f(r_{ij})$ and $\phi(r_{ij})$ were cut off between the second and the third nearest neighbor for a perfect crystal.

The potential functions described in Eqs.(22) - (24) contain five parameters A_1, A_2, C_1, C_2 and D . These are determined to reproduce the Born stability, cohesive energy, elastic constants, the formation energy of a vacancy and stacking fault energy. The potential parameters determined for Nb are summarized in Table (1) [1].

Table 1. Parameters for Nb metal [1]

A_1	43.8714013508282476
A_2	1.21346376862356462
C_1	3.15264023140411085
C_2	0.88086659918361343
D	29.8475444853668736

We have also calculated the thermodynamic quantities of Nb metal using the many body potentials derived from the microscopic electronic theory. The calculated results are presented in Table (2), together with the corresponding experimental results [9]. In the present study, we have used effective pair potential and the many

body potentials for metal atoms to demonstrate the utility of the present theoretical scheme based on the moment method in the statistical dynamics.

In general, we have obtained good agreement between the theoretical calculations and experimental results in the thermodynamic quantities.

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Table 2. Thermodynamic properties of Nb metal

T(K)	100	300	600	800	1200	1600	2000
$a, \text{ }^{\circ}\text{A}$	*) 2.7211	2.7259	2.7333	2.7383	2.7484	2.7586	2.7690
	**) 2.7210	2.7255	2.7324	2.7371	2.7466	2.7562	2.7659
$\alpha \cdot 10^{-5} \cdot \text{K}^{-1}$	*) 0.87	0.90	0.92	0.93	0.96	0.99	1.01
	**) 0.82	0.85	0.86	0.87	0.89	0.92	0.95
	$\alpha_{\text{exp}} \cdot 10^{-5} \cdot \text{K}^{-1}$ [9]	0.47	0.71	0.79	0.83	0.89	0.99
C_v (cal/ mol . K)	*) 3.563	5.604	5.859	5.898	5.925	5.935	5.939
	**) 3.562	5.604	5.859	5.898	5.925	5.935	5.939
C_p (cal/ mol . K)	*) 3.61	5.83	6.31	6.49	6.79	7.05	7.25
	**) 3.60	5.81	6.28	6.45	6.73	6.97	7.17
	$C_{p, \text{exp}}$ (cal/ mol .K) [9]	-	5.95	6.24	6.43	6.81	-
$\chi_T \cdot 10^{-13}(\text{cm/ dyn}^2)$	*) 5.330	3.619	3.700	3.856	4.269	4.798	5.457
	**) 5.070	3.404	3.470	3.610	3.981	4.455	5.043
$\beta_T \cdot 10^{12}(\text{dyn}^2/\text{cm})$	*) 1.876	2.763	2.702	2.592	2.342	2.084	1.832
	**) 1.972	2.937	2.881	2.769	2.511	2.244	1.983

*) Results of numerical calculations correspond to using pair potential

**) Results of numerical calculations correspond to using embedded atom potentials