Hue University Journal of Science
ISSN 1859-1388
Vol. 107, No. 08, 2015, pp. 23-29

TO DEFINE THE THERMODYNAMIC PARAMETERS AND CUMULANTS OF DOPANT CUBIC CRYSTALS BY GENERALIZED ANHARMONIC – CORRELATED EINSTEIN MODEL IN XAFS

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Abstract: A procedure for calculation and analysis of X-ray absorption fine structure (XAFS) cumulants of mixed body center cubic (bcc) crystals has been derived based on quantum statistical theory with generalized anharmonic correlated Einstein model. This study has formulated the expressions that describe asymmetric component for dopant bcc crystals such as the first cumulant or net thermal expansion, the second cumulant or mean square relative displacement (MSRD), the third cumulant, and thermodynamic parameters including the anharmonic effects contributions of body center cubic crystals doped with Einstein frequency, Einstein temperature, and thermal expansion coefficient constant. Numerical results for pure Iron (Fe) and pure Molybdenium (Mo), and Fe doped by Mo (FeMo) were found to be in good agreement with experimental.

Keywords: anharmonic, XAFS, cumulants, thermodynamic, asymmetry

1 Introdution

Today, X-ray Absorption Fine Structure (XAFS) spectra becomes a powerful structural analysis technique, in which the XAFS functions provide information on atomic number of each shell, and their Fourier magnitudes provide information on radius of atomic shell [4]. It is necessary and has been executed to use XAFS theory for studying thermodynamic properties of lattice crystals of a substance. The thermodynamic parameters for pure cubic crystals, and for mixed face centered cubic (fcc) crystals are provided by correlated - anharmonic Einstein model in XAFS theory [3, 6]. However, the thermodynamic parameters for doped body centered cubic (bcc) crystals are not mentioned.

This work is using the generalized anharmonic - correlated Einstein model [4] to formulate effective force constant, thermodynamic parameters, and the cumulant expressions of dopant bcc crystals such as: the first cumulant or net thermal expansion, the second cumulant or mean square relative displacement, the third cumulant, and Einstein frequency and temperature which are contained in the XAFS. In this study, the bcc crystals which contain a dopant atom called as absorbing atom in the XAFS process, its nearest neighbors are host atoms as backscattering atoms. Numerical calculation for Iron (Fe) doped by Molybdenium (Mo) crystal has been carried out to show the thermodynamical effects of bcc crystal under the influence of the doping atom. The calculated results are in good agreement with experimental values.

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Submitted: January 29, 2015; Revised: April 14, 2015; Accepted: September 8, 2015.

2 Fomalism

The expression of anharmonic XAFS spectra is often described by [2]:

$$\chi(k)=F(k)\frac{\exp(-2R/\lambda(k))}{kR^2}\operatorname{Im}\left(\exp(i\Phi(k))\exp\left(2ikR+\sum_n\frac{(2ik)^n}{n!}\sigma^{(n)}\right)\right), \tag{1}$$

where $F(k)$ is atomic backscattering amplitude, $\Phi(k)$ is total phase shift of photoelectron, k is wave number, λ is mean free path of the photoelectron, and $\sigma^{(n)}$ $(n=1,2,3,\ldots)$ are the cumulants to describe asymmetric components. They all appear due to the thermal average of the function e^{-2ikr}, in which the asymmetric terms are expanded in a Taylor series around value $R=\langle r\rangle$ with r is instantaneous bond length between absorbing and backscattering atoms at T temperature.

According to anharmonic correlated Einstein model [4] the interaction between absorber and backscatterer with the effect of neighboring atoms is described via an effective - anharmonic Einstein potential:

$$U_E(x)=\frac{1}{2}k_{eff}x^2+k_3x^3+\ldots+\sum_{i=1,2}\sum_{j\neq i}U\left(\frac{\mu}{M_i}\times\hat{R}_{12}.\hat{R}_{ij}\right) \tag{2}$$

This potential includes: anharmonicity parameter k_3 describing an asymmetry or skew in the pair distribution function and the contributions of a small atom cluster, surrounding the absorbing (is dopant atom) and backscettering atoms (is host atom); therefore, spring constant becomes an effective one k_{eff}. The contributions of such cluster are described in Eq. (2) by the sum of i which is over absorber $(i=1)$ and backscatterer $(i=2)$, and j which is over all their near neighbors, excluding the absorber and backscatterer themselves, because they contribute in the $U(x)$. $\hat{R}$ is the unit bond length vector, μ is reduced mass of absorbing M_1 and backscattering M_2 atoms, respectively, $x=r-r_0$ is deviation of the instantaneous bond length of two atoms from their equilibrium distance or the location of the minimum potential interaction.

The atomic vibration is calculated based on quantum statistical procedure with approximate quasi - hamonic vibration, in which the Hamiltonian of the system is written as harmonic term with respect to the equilibrium at a given temperature plus an anharmonic perturbation [1], we have:

$$H=\frac{P^2}{2\mu}+U_E(x)=H_0+U_E(a)+\delta U_E(y);\quad H_0=\frac{P^2}{2\mu}+\frac{1}{2}k_{eff}y^2, \tag{3}$$

$$y=x-a,\quad a(T)=\langle x\rangle,\quad \langle y\rangle=0$$

in which a is the net thermal expansion, y is the deviation from the equilibrium value of x at T temperature. The using of interaction potential between each pair of atoms in the single bond can beexpressed by anharmonic Morse potential for cubic crystals. Expanding to third order around its minimum, we have Morse expresion for the bcc pure csystals:

$$U_E(x) = D(e^{-2\alpha x} - 2e^{-\alpha x}) \approx D\left(-1 + \alpha^2 x^2 - \alpha^3 x^3 + \ldots\right) \tag{4}$$

where, D is the dissociation energy by $U(r_0) = -D$, and α is expansion thermal parameter. In the case of dopant crystals, we have expression of the Morse potential formed:

$$U_E(x) = D_{12}\left(-1 + \alpha_{12}^2 x^2 - \alpha_{12}^3 x^3 + \ldots\right) \tag{5}$$

Morse potential parameters in Eq. (5) have been obtained by averaging those of the pure crystals and they are given by [7]:

$$\alpha_{12}^2 = \frac{D_1\alpha_1^2 + D_2\alpha_2^2}{D_1 + D_2}, \qquad \alpha_{12}^3 = \frac{D_1\alpha_1^3 + D_2\alpha_2^3}{D_1 + D_2}, \qquad D_{12} = \frac{D_1 + D_2}{2} \tag{6}$$

From expressions (2), (4) we have effective interaction Einstein potential generalized as:

$$U_E(\chi) = U_E(a) + \frac{1}{2}k_{eff}y^2 + \delta U_E(y), \tag{7}$$

Substituting Eq. (5) with $x = y + a$ into (2) and using Eq. (7) to calculate the second term in Eq. (2) with reduced mass of metals doped:

$$\mu_{12} = \frac{\mu_1\mu_2}{\mu_1 + \mu_2}; \tag{8}$$

The sum of i is over absorbing and backscattering atoms, and the sum of j which is over all their near neighbors, and calculation of $(\hat{R}_{12}.\hat{R}_{ij})$ with lattice bcc crystals, we obtain thermodynamic parameters like effective spring constant k_{eff}, anharmonic parameter k_3, and anharmonic perturbation $\partial U_E(y)$:

$$k_3 = -\frac{5D_{12}\alpha_{12}^3}{4}; k_{eff} = 5D_{12}\alpha_{12}^2 \approx \mu_{12}\omega_E^2; \ \delta U_E(y) = 5D_{12}\alpha_{12}^2\left(ay - \frac{\alpha_{12}y^3}{4}\right) \tag{9}$$

To derive the analytical formulas of cumulants of the bcc crystals, we use perturbation theory [1]. The atomic vibration is quantized as phonon, with consideration of the phonon-phonon interaction for taking into account the anharmonicity, we obtain the cumulants:

$$\sigma^{(1)} = a = \frac{3\hbar\omega_E}{40D_{12}\alpha_{12}}\frac{(1+z)}{(1-z)} \tag{10}$$

$$\sigma^{(2)} = \langle y^2 \rangle = \frac{\hbar\omega_E}{10D_{12}\alpha_{12}^2}\frac{(1+z)}{(1-z)}. \tag{11}$$

$$\sigma^{(3)} = \frac{\hbar^2\omega_E^2}{200D_{12}^2\alpha_{12}^3}\frac{(1+10z+z^2)}{(1-z)^2} \tag{12}$$

where $z \equiv e^{-\beta\hbar\omega_E} = e^{-\theta_E/T}$ is the temperature variable and determined by the $\theta_E = \hbar\omega_E / k_B$ is Einstein temperature, k_B is Bonztmann's constant.

3 Comparison

We applied the expression derived in the previous section to numerical calculation for mixed crystal which is Iron-Molybdenium (FeMo). According to Morse potential parameters for pure Fe, Mo crystals have been known [3, 6], we calculated parameters D_{12} and α_{12} for dopant crystals above, shown on Table 1.

Table 1. Morse potential parameters values for crystals

Crystals	$D_{12}(eV)$	$\alpha_{12}(Å^{-1})$
Fe-Fe	4.821	1.3885
Mo-Mo	6.822	1.4232
Fe-Mo	5.782	1.4029

Substituting D_{12}, α_{12} thermodynamic parameters from Table 1 into Eqs.(8, 9) with Boltzmann's constant $k_B = 8.617\times10^{-5}eVA^{-1}$, Plank's constant $\hbar = 6.5822\times10^{-16} eV s$, we calculated values of other thermodynamic parameters like effective force constant k_{eff}, reduced mass μ_{12}, correlated Einstein frequency ω_E and Einstein temperature θ_E for Fe crystal doped by Mo crystal according to Table 2.

Table 2. Thermodynamic parameters values k_{eff}, μ, ω_E, θ_E

Crystals	k_{eff} (N/m)	$\mu(eV/Å^2.s^{-2})$	$\omega_E(10^{13}Hz)$	θ_E (K)
Fe-Fe	47.275	$0.2919.10^{-26}$	3.184	243
Mo-Mo	107.289	$0.5004.10^{-26}$	3.659	280
Fe-Mo	57.273	$0.3962.10^{-26}$	1.762	134

Substituting values of thermodynamic parameters from Table 2 into Eqs. (10, 11, 12), we received the expressions of cumulants to describe temperature variable $z = e^{-\theta_E/T}$. Next, substituting Einstein temperature value θ_E (K) into expression of z temperature variable, we have the expressions to only illustrate T dependence temperature of cumulants and thermal expansion coefficient constant.

Figure 1 and Figure 3 illustrate the temperature dependence of the first cumulant $\sigma^{(1)}(T)$ or net thermal expansion and third cumulant $\sigma^{(3)}(T)$ of Fe doped by Mo crystal and Fe, Mo pure crystals. Theoretical results of $\sigma^{(1)}(T)$ agree well with the experimental values at 77K, 295K and 700K temperatures for Fe pure crystals [3] and at 300K, 683K temperatures for Mo pure crystal and dopant FeMo crystal. Theoretical results of $\sigma^{(3)}(T)$ are also in good agreement with the experimental values at 295K temperature for Fe pure crystal and Fe doped by Mo crystal, and at 300K temperature for Mo pure crystal [6]. Figure 2 illustrates the temperature dependence of our calculated anharmonic contribution of the second cumulant $\sigma^{(2)}(T)$ or the mean square relative displacement (MSRD) of FeMo mixed crystal and Fe, Mo pure crystals and compared to the measured values at 77K, 295K and 700K temperatures for FeMo [5], and at 10K, 295K and 683K temperatures for Fe and Mo [5] theoretical results also agrees well with experimental ones. Note that the experimental values from XAFS spectra are measured at HASYLAB and BUGH Wuppertal (DESY, Germany) [5]. In the graphs we knowthat at low temperatures the cumulants $\sigma^{(1)}, \sigma^2$, $\sigma^{(3)}$ included zero-point energy contributions, this is quantum effects. At high temperatures, the cumulants $\sigma^{(1)}, \sigma^2$ are linear proportional to the T temperature, and the third cumulant $\sigma^{(3)}$ is proportional to the square temperature (T^2). They agree with results of classical theory and experiment. Figure 4 illustrates the temperature dependence of thermal expansion coefficient constant α_T of Fe, Mo and FeMo in our calculation, they have the form of specific heat, thus reflecting the fundamental of solid state theory, that the thermal expansion is the result of anharmonic effects and is also proportional to specific heat, and α_T factor approach constant values at high temperatures and it is approximate zero at low temperature, thus in agreement with classical theory.

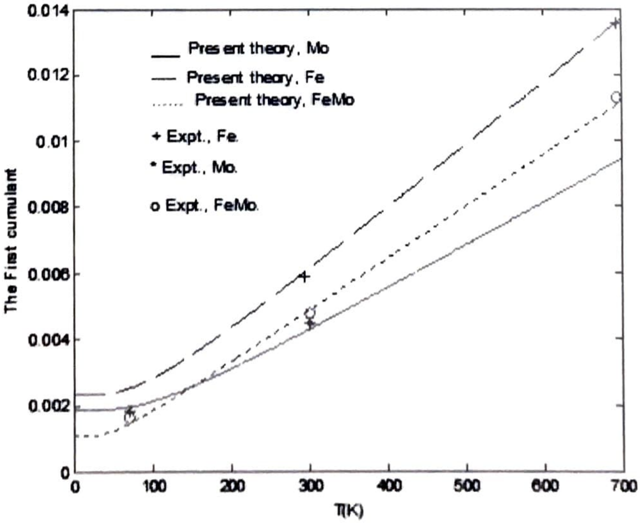

Fig. 1.

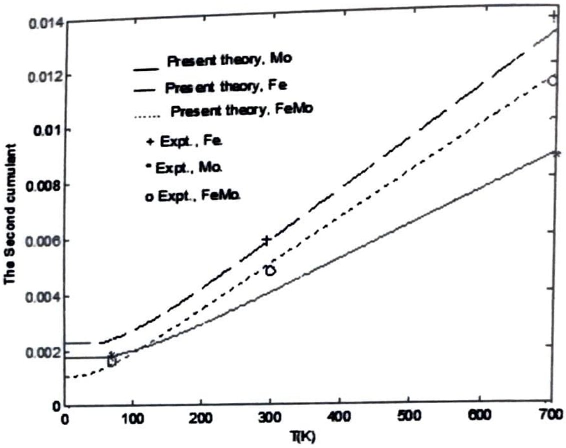

Fig. 2.

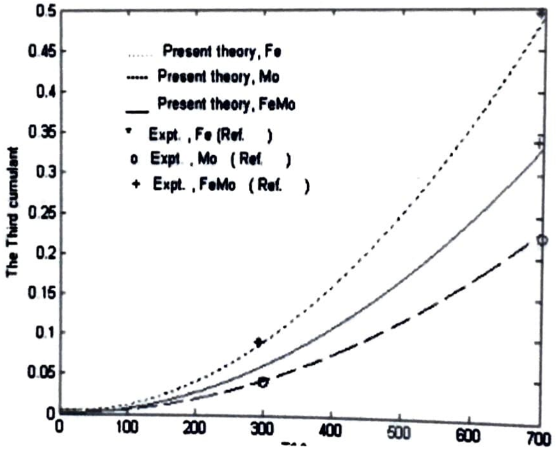

Fig. 3.

4 Conclusions

A new analytical theory for calculation and evaluation of the thermodynamic properties of bcc dopant crystals has been developed based on the quantum statistical theory with the anharmonic correlated Einstein model developed for the doping bcc crystals. In this Einstein model, a method has been derived for the calculation and analysis of the thermodynamic parameters and expanded XAFS Debye-Waller factors described in terms of cumulants of FeMo having bcc structure based on the correlated Debye model in consideration of dispersion relation to take more information of phonons taken from integration over the phonon wave numbers varied in the first Brillouin zone and the anharmonic effective potential involving the contributions of all nearest neighbors of absorber and backscattering atoms to take into account three-dimensional interaction [8]. Morse potential is used for describing the single-pair interatomic interaction. Based on the success of the anharmonic effective potential used in the anharmonic correlated Einstein model in XAFS theory due to taking into account three-dimensional interaction in a simple measures by including the contributions of all nearest neighbors of absorber and backscattering atoms, in this work we develop further such anharmonic effective potential for higher expansion up to the three order.

The expressions for the thermodynamic parameters, effective force constant, correlated Einstein frequency and temperature, the first, second and third cumulants, thermal expansion coefficient constant in anharmonic XAFS spectra of bcc crystals including dopaint crystals agree with all standard properties of these quantities. The quantitative calculation for the doping crystals has the same form as for the pure crystals themselves.

The good agreement between the results of calculated theory and the experimental values demonstrates the possibility that we can use the present developed theory in XAFS data analysis.

Acknowledgment

The author thanks Prof. Sci.Ph.D Nguyen Van Hung and Prof. Ronnald R. Frahm for useful discussions and for authorizing the author to use some results published.

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