ANHARMONIC CORRELATED EINSTEIN MODEL FOR XAFS CUMULANT OF ORTHORHOMBIC CRYSTALS WITH IMPURITY

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Abstract: Anharmonic correlated Einstein model has been used to study thermodynamic properties of orthorhombic crystals including the case with impurity. Our development is derivation of the analytical expressions for the cumulants. The calculations is based on the quantum statistical theory including anharmonic effects in a small cluster of absorber from an atom sorte and backscatterer from another one including contribution of their nearest neighbours. The derived expressions include quantum effect at low temprature and classical limit at high temprature.

1. Introduction

The XAFS (X-ray Absorption Fine Structure) and their Fourier transfom magnitude provide structural information of substances [4] and the XAFS of substance with impurity has been studied [5]. The purpose of this work is to develop a new procedure for calculating and describing the thermodynamic parameters such as the first, second and third cumulant contained in XAFS spectra. The derivation is based on quantum statistical theory with anharmonic correlated Einstein model [1]. Numerical calculation has been carried out for Ga doped by Ag atom compared to experiment.

2. Theory

To interpret anharmonic contributions in the structural information and to fit the XAFS the cumulant expansion approach [4] has been developed according to which the XAFS function contains the factor

$$e^{w(k)}, \quad w(k) = 2i\sigma^{(1)} - 2k^2\sigma^2 - \frac{4}{3}ik^3\sigma^{(3)} + \cdots \tag{1}$$

where $\sigma^{(1)}$ is the first cumulant or net thermal expansion, σ^2 is the second cumulant or Debye-Waller factor and $\sigma^{(3)}$ is the third cumulant.

Based on anharmonic correlated Einstein model [2] we consider anharmonic vibration between absorbing and backscattering atoms with contributions of their immediate neighbors so that their interaction is characterrized by an effective anharmonic potential

$$U_{eff}(y) = \frac{1}{2}k_{eff}y^2 + \delta U(y) \quad y = x - a, \ x = r - r_o, \ a = <x>, \ <y> = 0 \tag{2}$$

where r and r_o are the instantaneous and equilibrium bond length of the absorbing and backscattering atoms, respectively. The single bond interaction potential for the case with impurity is obtained an plus-averaging of Morse pair potential and is given by

$$U_{HD}(x) \equiv D_{HD}(-1 + \alpha_{HD}x^2 - \gamma_{HD}x^3 + \cdots) \qquad (3)$$

$$D_{HD} = \frac{1}{2}(D_H + D_D), \quad \alpha_{HD} = \frac{D_H\alpha_H^2 + D_D\alpha_D^2}{D_H + D_D}, \quad \gamma_{HD} = \frac{D_H\alpha_H^3 + D_D\alpha_D^3}{D_H + D_D}, \qquad (4)$$

where the Morse potential parameter D_{HD}, α_{HD} for the case with impurity have been obtained by averaging those of the host atoms D_H, α_H and of the dopant atoms D_D, α_D.

Using Eqs. (3, 4) we obtain effective spring constants k_{eff}, Einstein frequency ω_E, Einstein temperature θ_E and the perturbation potential $\delta U(y)$ for impure Orthohombic crystals

$$k_{eff} = 2\left(S\mu_1^2 D_{HH}\alpha_{HH} + \left[1 + S\mu_2^2\right]D_{HD}\alpha_{HD}\right), \quad \omega_E = \sqrt{\frac{k_{eff}}{\mu}} \quad \theta_E = \frac{\hbar\omega_E}{k_\beta} \qquad (5)$$

$$\delta U(y) = 2ay\left(S\mu_1^2 D_{HH}\alpha_{HH} + \left[1 + S\mu_2^2\right]D_{HD}\alpha_{HD}\right) - y^3\left(\mu_1^3 D_{HH}\gamma_{HH} + \left[1 + \mu_2^3\right]D_{HD}\gamma_{HD}\right) \qquad (6)$$

$$\mu = \frac{M_H M_D}{M_H + M_D}, \qquad \mu_1 = \frac{M_H}{M_H + M_H} = \frac{1}{2}, \qquad \mu_2 = \frac{M_H}{M_H + M_D}$$

where M_H and M_D are the mass of the host atoms and dopant atoms, k_β is the Boltzmann constant. S is structure parameter which depends on the structure of the crystal and its derived expressions are presented in Table I..

Table I: Calculated value of S with a,b, c as the non-coplanar lattice vector

Bravais lattice type	S	Bravais lattice type	S
OF: Face-centered orthorhombic	$1 + 2\left(\dfrac{a^2 - b^2}{a^2 + b^2}\right)^2$	*OP*: Orthorhombic	1
OI: Body centered orthorhombic	$7 - 16\dfrac{a^2b^2 + a^2c^2 + b^2c^2}{\left(a^2 + b^2 + c^2\right)^2}$	*OC*: C-orthorhombic	$1 + 2\left(\dfrac{a^2 - b^2}{a^2 + b^2}\right)^2$

The cumulants have been derived by averaging procedure, using the statistical density matrix ρ and the canonical partition function Z in the form

$$<y^m> = \frac{1}{Z}tr(\rho y^m), \quad m = 1, 2, 3, \cdots. \qquad (7)$$

To evaluate the matrix elements in Eq. (7) we express y in terms of creation and annihilation operators $\hat{a}$ and $\hat{a}^+$: $y = y_0(\hat{a} + \hat{a}^+)$, $y_o = \sqrt{\hbar/2\mu\omega_E}$. Hence, we obtain the expressions for:

The first cumulant or net thermal expansion

$$a = \sigma^{(1)} = \frac{3\left(\mu_1^3 D_{HH}\gamma_{HH} + \left[1 + \mu_2^3\right]D_{HD}\gamma_{HD}\right)}{8\left(S\mu_1^2 D_{HH}\alpha_{HH} + \left[1 + S\mu_2^2\right]D_{HD}\alpha_{HD}\right)^2}\hbar\omega_E \frac{1 + z}{1 - z} \qquad (8)$$

The second cumulant or Debye-Waller factor

$$\sigma^2 = \frac{1}{4\left(S\mu_1^2 D_{HH}\alpha_{HH} + \left[1 + S\mu_2^2\right]D_{HD}\alpha_{HD}\right)}\hbar\omega_E\frac{1+z}{1-z} \qquad (9)$$

and the third cumulant

$$\sigma^{(3)} = \frac{\left(\mu_1^3 D_{HH}\gamma_{HH} + \left[1 + \mu_2^3\right]D_{HD}\gamma_{HD}\right)}{16\left(S\mu_1^2 D_{HH}\alpha_{HH} + \left[1 + S\mu_2^2\right]D_{HD}\alpha_{HD}\right)^3}\left(\hbar\omega_E\right)^2\frac{1+10z+z^2}{\left(1-z\right)^2} \qquad (10)$$

3. Numerical results and discussions

Now we apply the above derived expressions to numerical calculations for orthorombic crystal Ga doped by an Ag atom. The Morse potential parameters D and α were taken from Ref. 2. The result are illutrated in Table II . The calculated cumulants is ilustrated in Figures 1-4. They are found to be in a reasonable agreement with experiment [4] and show the following properties:
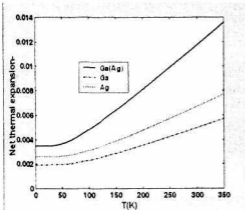
Net thermal expansion and Debye-Waller factor contain zero-point contributions as quantum effects at low temperature and are linear proportional to the temperature at high temperature.

Third cumulant describing the phase change of XAFS spectra due to anharmonicity contains zero-point contribution as quantum effect at low temperature and is proportional to the square of temperature at high temperature.
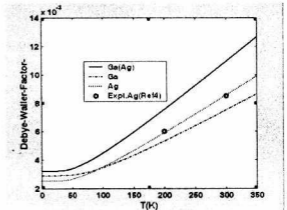
Table II: Calculated values of D_{HD}, α_{HD}, γ_{HD}, k_{eff}. ω_E and θ_E for GaAg

Sample	Bond	D_{HD} (eV)	α_{HD} (A^{-2})	γ_{HD} (A^{-3})	k_{eff} (N/m)	ω_E ($\times10^{13}$ Hz)	θ_E (K)
Ga(Ag)	Ga-Ag	1.537	0.540	0.485	38.95	2.3483	181

Hence, the calculated quantities satisfy all their standard properties appeared in the theory and in experiment.

Fig.1. Net thermal expansion of Ga(Ag)

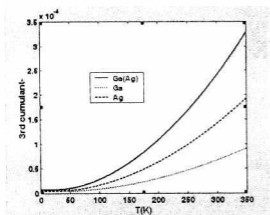**Fig.2.** Debye-Waller factor of Ga(Ag)
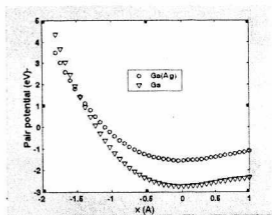
Fig.3. Third cumulant of Ga(Ag)

Fig.4. Single bond potential Ga-Ag

References

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