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 temperature and classical limit at high temperature.

1. Introduction

The XAFS (X-ray Absorption Fine Structure) and their Fourier transform 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

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

where $\sigma^{(1)}$ is the first cumulant or net thermal expansion, $\sigma^2$ 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 characterized by an effective anharmonic potential

$$U_{eff}(y) = \frac{1}{2}k_{eff}y^2 + \delta U(y) \quad y = x - a, \quad x = r - r_0, \quad a = < x >, \quad < y > = 0$$

(2)
where r and \( r_e \) 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 by an plus-averaging of Morse pair potential and is given by

\[
U_{HD}(x) = D_{HD}(-1 + \alpha_{HD}x^2 - \gamma_{HD}x^3 + \ldots)
\]

\[
D_{HD} = \frac{1}{2}(D_H + D_D), \quad \alpha_{HD} = \frac{D_H \alpha_{H1}^2 + \alpha_{D1}^2}{D_H + D_D}, \quad \gamma_{HD} = \frac{D_{H1} \gamma_{H1}^2 + D_{D1} \gamma_{D1}^2}{D_H + D_D},
\]

where the Morse potential parameter \( D_{HD}, \alpha_{HD} \) for the case with impurity have been obtained by averaging those of the host atoms \( D_H, \alpha_H \) and of the dopant atoms \( D_D, \alpha_D \).

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

\[
k_{eff} = 2\left(S_{H1}^2 D_{HH} \alpha_{HH} + \left|1 + S_{H2}^2 D_{HD} \alpha_{HH}\right|\right), \quad \omega_E = \frac{k_{eff}}{\mu}, \quad \Theta_E = \frac{\hbar \omega_E}{k_B}
\]

\[
\delta U(y) = 2\left(S_{H1}^2 D_{HH} \alpha_{HH} + \left|1 + S_{H2}^2 D_{HD} \alpha_{HH}\right|\right) - y^3 \left(\mu_{HD}^2 D_{HH} \gamma_{HH} + \left|1 + \mu_{D1}^2 D_{HD} \gamma_{HD}\right|\right)
\]

where \( \mu_{H1} = \frac{M_H M_D}{M_H + M_D} \), \( \mu_1 = \frac{M_H}{M_H + M_D} = \frac{1}{2} \), \( \mu_2 = \frac{M_D}{M_H + M_D} \)

<table>
<thead>
<tr>
<th>Bravais lattice type</th>
<th>S</th>
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</thead>
<tbody>
<tr>
<td>OF: Face-centered orthorhombic</td>
<td>( 1 + 2\left(\frac{a_1^2 - b_1^2}{a_1^2 + b_1^2}\right)^2 )</td>
<td>OP: Orthorhombic</td>
<td>1</td>
</tr>
<tr>
<td>OI: Body centered orthorhombic</td>
<td>( 7 - 16 \frac{a_2^2 + a_1^2 + b_1^2}{(a_2^2 + b_1^2)^2} )</td>
<td>OC: C-orthorhombic</td>
<td>( 1 + 2\left(\frac{a_2^2 - b_2^2}{a_2^2 + b_2^2}\right)^2 )</td>
</tr>
</tbody>
</table>

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

\[
< y^m > = \frac{1}{Z} \text{tr}(\rho y^m), \quad m = 1, 2, 3, \ldots.
\]

To evaluate the matrix elements in Eq. (7) we express \( y \) in terms of creation and annihilation operators \( \hat{a} \) and \( \hat{a}^+ \) : 

\[
y = y_0 \left(\hat{a} + \hat{a}^+\right), \quad y_0 = \sqrt{\hbar/2\mu \omega_E}.
\]

Hence, we obtain the expressions for:

The first cumulant or net thermal expansion

\[
a = \sigma^{(1)} = \frac{3\left(\mu_{HD}^2 D_{HH} \gamma_{HH} + \left|1 + \mu_{D1}^2 D_{HD} \gamma_{HD}\right|\right)}{6\left(S_{H1}^2 D_{HH} \alpha_{HH} + \left|1 + S_{H2}^2 D_{HD} \alpha_{HH}\right|\right)} \frac{\hbar \omega_E}{1 + \frac{1}{1-z}}
\]
The second cumulant or Debye-Waller factor
\[ \sigma^2 = \frac{1}{4(S\mu_1^2D_{HHH}\alpha_{HHH} + [1 + S\mu_2^2D_{HD\alpha_{HD}}])} \hbar\omega_E \frac{1+z}{1-z} \]
and the third cumulant
\[ \sigma^{(3)} = \frac{\mu_1^3D_{HHH}\gamma_{HHH} + [1 + \mu_2^2D_{HD\gamma_{HD}}]}{16S\mu_1^2D_{HHH}\alpha_{HHH} + [1 + S\mu_2^2D_{HD\alpha_{HD}}]} (\hbar\omega_E)^2 \frac{1 + 10z + z^2}{(1-z)^2} \]

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 \( \alpha \) were taken from Ref. 2. The result are illustrated in Table II. The calculated cumulants are illustrated 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 \( D_{HH}, \alpha_{HH}, \gamma_{HH}, k_{eff}, \omega_E \) and \( \theta_E \) for GaAg

<table>
<thead>
<tr>
<th>Sample</th>
<th>Bond</th>
<th>( D_{HH} ) (eV)</th>
<th>( \alpha_{HH} ) (A^2)</th>
<th>( \gamma_{HH} ) (A^3)</th>
<th>( k_{eff} ) (N/m)</th>
<th>( \omega_E \times 10^{13} ) (Hz)</th>
<th>( \theta_E ) (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ga(Ag)</td>
<td>Ga-Ag</td>
<td>1.537</td>
<td>0.540</td>
<td>0.485</td>
<td>38.95</td>
<td>2.3483</td>
<td>181</td>
</tr>
</tbody>
</table>

Hence, the calculated quantities satisfy all their standard properties appeared in the theory and in experiment.
Fig. 3. Third cumulant of Ga(Ag)

Fig. 4. Single bond potential Ga-Ag

References