

XAFS CUMULANTS AND THERMAL EXPANSION OF BCC AB BINARY ALLOYS

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Abstract: *A new quantum statistical anharmonic theory has been derived for calculation and analysis of XAFS cumulants and thermal expansion of bcc AB binary alloys systems. This model is developed based on the anharmonic vibration of absorber from atom sorte A and backscatterer from another atom sorte B, including contributions of their nearest neighbours. Atomic pair potential has been taken by plus-averaging of Morse potential. The expressions have been derived for effective spring constant, correlated Einstein frequency, correlated Einstein temperature, first cumulant or net thermal expansion, second cumulant or Debye-Waller factor, third cumulant causing phase change of XAFS spectra, and thermal expansion coefficient. Numerical evaluations have been carried out for $Fe_{1-x}W_x$. The results are temperature dependent and reflect the experiment and fundamental theoretical behaviours of these quantities.*

1. Introduction

The X-ray Absorption Fine Structure (XAFS) spectra and their Fourier transform magnitude provide structural information of substances including alloys. At low temperature the harmonic theory works well [1]. But as the temperature increases due to anharmonic effects the XAFS spectra provide different structural informations at different temperatures [2-7]. To correct these uncertainties the cumulant expansion approach [4] has been developed. According to this theory the XAFS function contains the factor

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

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 providing the phase change of XAFS spectra [3]. Most of the efforts is focused to interpret the measured anharmonic or high-temperature XAFS spectra. Some progresses have been made to calculate the cumulants of the crystals [5,6,10,11], and recently our evaluations for fcc alloys systems have been discussed [9].

This work is our next step of [9] deriving a quantum statistical anharmonic procedure to calculate the cumulants and thermal expansion of bcc binary AB alloys systems in XAFS theory. Our model is based on the local atomic vibration including anharmonic effects in a small cluster of the absorber from an atom sorte (A) and the backscatterer from another one (B) with taking into account of their nearest neighbors' contributions. The

creation and annihilation operators are used to describe phonon interaction, and physical parameters have been derived by averaging calculation using the statistical density matrix. Numerical calculations have been carried out for bcc alloys $Fe_{1-x}W_x$. The results are temperature dependent and reflect the experimental ones and fundamental theoretical behaviours of the above derived quantities.

2. Theory

We consider anharmonic vibration between absorber as atom A and backscatterer as atom B with taking into account the contributions of their immediate neighbors so that their interaction is characterized by an anharmonic effective potential

$$U_{eff}(x) = \frac{1}{2}k_{eff}x^2 + k_3x^3 + \dots, \quad x = r - r_0, \quad (1)$$

where r is spontaneous bond length between absorbing and backscattering atoms, r_0 is its equilibrium value, k_{eff} is effective spring constant, and k_3 is cubic anharmonicity parameter which gives an asymmetry in the pair distribution function.

It is usually sufficient to consider weak anharmonicity, then our derivation of the expressions of cumulants and thermal expansion of bcc alloys systems in XAFS theory is based on quantum statistical theory with quasi-harmonic approximation, according to which the Hamiltonian of the system is written as a harmonic term with respect to the equilibrium at a given temperature, plus an anharmonic perturbation [5]. Using the definition [5,12] $y = x - a$ as the deviation from the equilibrium value of x at temperature T and $a(T) = \langle r - r_0 \rangle$ as the net thermal expansion we express Eq. (1) in the form

$$U_{eff}(y) = \frac{1}{2}k_{eff}y^2 + \delta U(y). \quad (2)$$

The single bond interaction potential between the atoms A and B contained in the effective potential (2) of the system is obtained by an plus-averaging of Morse pair potential and is given by

$$U_{AB}(x) \cong D_{AB}(-1 + \alpha_{AB}x^2 - \alpha'_{AB}x^3 + \dots), \quad (3)$$

$$D_{AB} = \frac{1}{2}(D_A + D_B), \alpha_{AB} = 2\frac{D_A\alpha_A^2 + D_B\alpha_B^2}{D_{AB}}, \alpha'_{AB} = 2\frac{D_A\alpha_A^3 + D_B\alpha_B^3}{D_{AB}}, \quad (4)$$

where $D_{A,B}$ and $\alpha_{A,B}$ are the Morse potential parameters

$$U_{A,B}(x) = D_{A,B}(e^{-2\alpha_{A,B}x} - 2e^{-\alpha_{A,B}x}). \quad (5)$$

Considering the contributions of immediate neighbors of absorber and backscatterer, as well as, the atomic distribution in bcc structure, we derive the effective spring constant

$$k_{eff} = 2D_{AB}(C_1\alpha_{AB} - 3C_2a\alpha'_{AB}), \quad (6)$$

the perturbation potential due to anharmonicity

$$\delta U(y) = D_{AB}(2C_1\alpha_{AB}ay - C_2\alpha'_{AB}y^3). \quad (7)$$

Our approach is based on a local vibration picture and a Einstein model is appropriate. From the above relations the correlated Einstein frequency ω_E and correlated Einstein temperature θ_E have been derived, and they are given by

$$\omega_E = \left(\frac{2D_{Ab}}{\mu} [C_1 \alpha_{AB} - 3C_2 a \alpha'_{AB}] \right)^{1/2}, \quad (8)$$

$$\theta_E = \frac{\hbar}{k_B} \left(\frac{2D_{Ab}}{\mu} [C_1 \alpha_{AB} - 3C_2 a \alpha'_{AB}] \right)^{1/2}. \quad (9)$$

In the Eq.(6-9) we used k_B as Boltzmann's constant and the following symbols

$$\begin{aligned} C_1 &= 1 + \frac{5}{3} (\mu_A^2 + \mu_B^2), & C_2 &= 1 + \mu_A^3 + \mu_B^3, \\ \mu &= \frac{M_A M_B}{M_A + M_B}, & \mu_A &= \frac{M_A}{M_A + M_B}, & \mu_B &= \frac{M_B}{M_A + M_B}, \end{aligned} \quad (10)$$

where M_A and M_B are the mass of the absorbing and backscattering atoms, respectively.

The cumulants are derived by averaging the value of y [5,12]. Atomic vibration is quantized as phonon, and anharmonicity is the result of phonon interaction. Therefore, to calculate the matrix elements for these interactions we express y in term of annihilation and creation operators \hat{a} and \hat{a}^+ , i. e. ,

$$y = \sigma_0 (\hat{a} + \hat{a}^+), \quad \sigma_0 = (\hbar/2\mu\omega_E)^{1/2}, \quad (11)$$

and use the harmonic oscillator states $|n\rangle$ as eigenstates and $E_n = n\hbar\omega_E$ as eigenvalue. The cumulants have been derived by averaging procedure, using the statistical density matrix ρ and the canonical partition function Z in the form

$$\langle y^m \rangle = \frac{1}{Z} \text{tr}(\rho y^m), \quad m = 1, 2, 3, \dots, \quad (12)$$

where

$$Z = \text{tr} \rho, \quad \rho = \rho_0 + \delta\rho, \quad Z_0 = \text{tr} \rho_0 \quad (13a)$$

$$\rho_0 = e^{-\beta H_0}, \quad H_0 = \frac{P^2}{2\mu} + \frac{1}{2} k_{eff} y^2, \quad \beta = 1/k_B T, \quad (13b)$$

$$\delta\rho = - \int_0^\beta \rho_0 = e^{-\beta' H_0} \delta \tilde{U}(\beta) = e^{\beta H_0} \delta U e^{-\beta H_0}. \quad (13c)$$

Using Eqs. (12,13) we derived the expressions for the averaging value of y for the even moments m_e

$$\langle y^{m_e} \rangle = \frac{1}{Z_0} \sum_n e^{-n\beta\hbar\omega_E} \langle n | y^{m_e} | n \rangle, \quad m_e = 2, 4, 6, \quad (14)$$

and for the odd moments m_o

$$\langle y^{m_o} \rangle = \frac{1}{Z_0} \sum_{n,n'} \frac{e^{-\beta E_n} - e^{-\beta E_{n'}}}{E_n - E_{n'}} \langle n | \delta U(y) | n \rangle \langle n | y^{m_o} | n \rangle, \quad m_o = 1, 3, 5 \dots \quad (15)$$

In the calculation of transition matrix elements the selection rule has been obeyed. From Eq. (14) we derived the second cumulant or Debye-Waller factor

$$\sigma^2(T) = \frac{\hbar\omega_E}{4C_1 D_{AB} \alpha_{AB}} \frac{1+z}{1-z}, \quad z = e^{-\theta_E/T}. \quad (16)$$

Using Eq. (15) and the condition $\langle y \rangle = 0$ we derived the first cumulant or net thermal expansion

$$a(T) = \sigma^{(1)}(T) = \frac{3C_2 \hbar\omega_E \alpha'_{AB}}{8C_1^2 D_{AB} \alpha_{AB}^2} \frac{1+z}{1-z}, \quad (17)$$

and the third cumulant

$$\sigma^{(3)}(T) = \frac{C_2 (\hbar\omega_E)^2 \alpha'_{AB}}{16C_1^3 D_{AB}^2 \alpha_{AB}^3} \frac{1+10z+z^2}{(1-z)^2}. \quad (18)$$

The parameter $a(T)$ describes an asymmetry of the pair potential or the thermal expansion of the bond length r_{AB} between the two atoms A and B due to the anharmonicity, that is why from Eq.(17) we derived the thermal expansion coefficient

$$\alpha_T(T) = \frac{3C_2 k_B \alpha'_{AB} \theta_E^2}{4C_1^2 D_{AB} \alpha_{AB}^2} r_{AB} \frac{z}{[(1-z)T]^2}. \quad (19)$$

To get the above simplified formulas several mathematical expressions have been used.

From the above expressions it is easy to receive the following relation

$$\frac{\alpha_T r T \sigma^2}{\sigma^{(3)}} = \frac{3z(1+z) \ln(1/z)}{(1-z)(1+10z+z^2)}. \quad (20)$$

In order to define the behaviours of the above obtained thermodynamic quantities in temperature dependence we derived them in the low temperature ($T \rightarrow 0$) and high temperature ($T \rightarrow \infty$) limits. The results are presented in Table I.

Table I. The values of $\sigma^{(1)}$, σ^2 , $\sigma^{(3)}$, α_T and $\alpha_T r T \sigma^2 / \sigma^{(3)}$ for an alloys AB at low temperature ($T \rightarrow 0$) and high temperature ($T \rightarrow \infty$) limits.

Value	$T \rightarrow 0$	$T \rightarrow \infty$
$\sigma^{(1)}$	$3C_2 \alpha'_{AB} \hbar\omega_E (1+2z) / 8C_1^2 D_{AB} \alpha_{AB}^2$	$3C_2 \alpha'_{AB} k_B T / 4C_1^2 D_{AB} \alpha_{AB}^2$
σ^2	$\hbar\omega_E (1+2z) / 4C_1 D_{AB} \alpha_{AB}$	$k_B T / 2C_1^2 D_{AB} \alpha_{AB}$
$\sigma^{(3)}$	$C_2 \alpha'_{AB} (\hbar\omega_E)^2 (1+12z) / 16C_1^3 D_{AB}^2 \alpha_{AB}^3$	$3C_2 \alpha'_{AB} (k_B T)^2 / 4C_1^3 D_{AB}^2 \alpha_{AB}^3$
α_T	$3C_2 k_B \alpha'_{AB} z (\ln z)^2 (1+2z) / 4C_1^2 D_{AB} \alpha_{AB}^2 r_{AB}$	$3C_2 k_B \alpha'_{AB} / 4C_1^2 D_{AB} \alpha_{AB}^2 r_{AB}$
$\alpha_T r T \sigma^2 / \sigma^{(3)}$	$3z \ln(1/z)$	$1/2$

3. Numerical results

Now we apply the above derived expressions to numerical calculations for the bcc binary alloys $Fe_{1-x}W_x$. The Morse potential parameters $D_{A,B}$ and $\alpha_{A,B}$ were taken from Ref. 8. The calculated values of $D_{AB}, \alpha_{AB}, \alpha'_{AB}, k_{eff}, \omega_E, \theta_E$ for the alloys FeW are given in Table II.

Table II. The calculated values of $D_{AB}, \alpha_{AB}, \alpha'_{AB}, k_{eff}, \omega_E, \theta_E$ for the alloys FeW .

Sample	Bond	$D_{AB}(eV)$	$\alpha_{AB}(\text{\AA}^{-2})$	$\alpha'_{AB}(\text{\AA}^{-3})$	$k_{eff}(N/m)$	$\omega_E(\times 10^{13} Hz)$	$\theta_E(K)$
FeW	Fe-W	0.708	1.9734	2.7725	92.1962	3.5896	274

The vibration characterizing quantities for the alloys bond $Fe - W$, calculated by present procedure are different from those for the single crystal bond $Fe - Fe$ and $W - W$, calculated by the procedure presented in Ref. 14. This can be seen in the Table III.

Table III: Comparison of the values $k_{eff}, \omega_E,$ and θ_E of the single crystal bond with those of the alloys bond of FeW .

Sample	Bond	$k_{eff}(N/m)$	$\omega_E(\times 10^{13} Hz)$	$\theta_E(K)$
Fe	Fe-Fe	47.2748	3.1836	243
W	W-W	115.9597	2.7481	210
FeW	Fe-W	92.1962	3.5896	274

Fig. 1 shows the temperature dependence of our calculated net thermal expansion $\sigma^{(1)}$ of FeW compared with those of its components Fe and W . Fig. 2 shows the temperature dependence of our calculated Debye-Waller factor σ^2 of FeW in comparison with those of its components Fe and W .

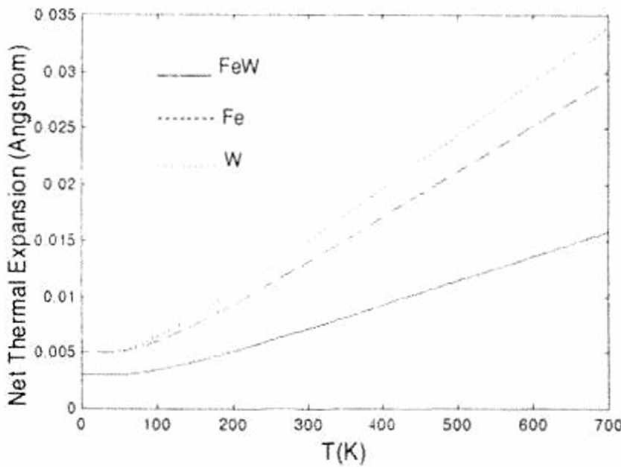


Fig. 1: Net thermal expansion $\sigma^{(1)}$ (\AA) of FeW compared with those of its components Fe and W .

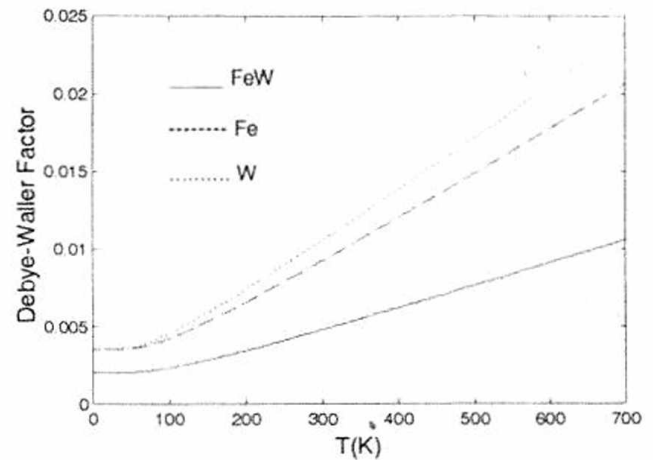


Fig. 2: Debye-Waller factor σ^2 (\AA^2) of FeW compared with those of its components Fe and W .

Fig. 3 illustrates the temperature dependence of our calculated third cumulant $\sigma^{(3)}$ of FeW in comparison with those of its components Fe and W . Fig. 4 shows the temperature dependence of thermal expansion coefficient α_T of $Fe_{0.88}W_{0.12}$ compared with those of its components Fe and W . Fig. 5 demonstrates the temperature dependence of our calculated cumulants relation $\alpha_T r T \sigma^2 / \sigma^{(3)}$ of FeW compared with those of its components Fe and W .

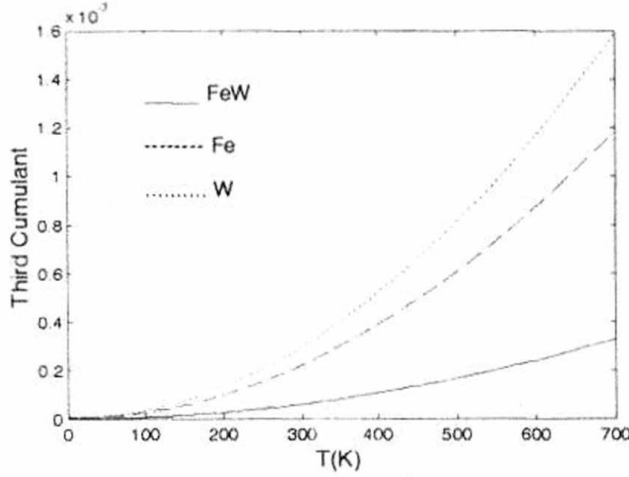


Fig. 3: Third cumulant $\sigma^{(3)}$ (\AA^3) of FeW in comparison with those of its components Fe and W .

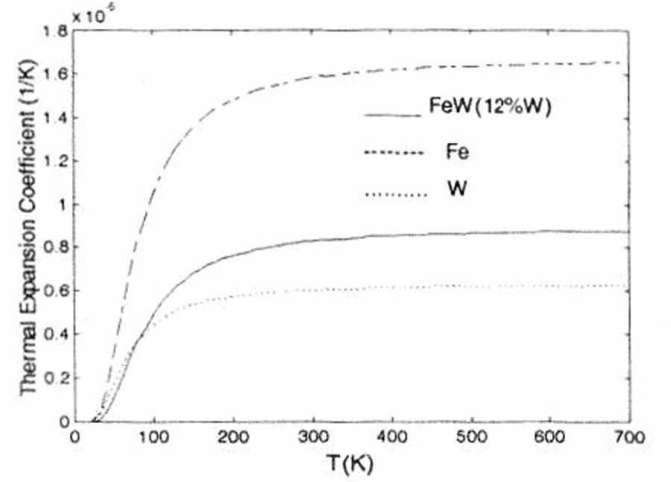


Fig. 4: Thermal expansion coefficient α_T (K^{-1}) of FeW in comparison with those of its components Fe and W .

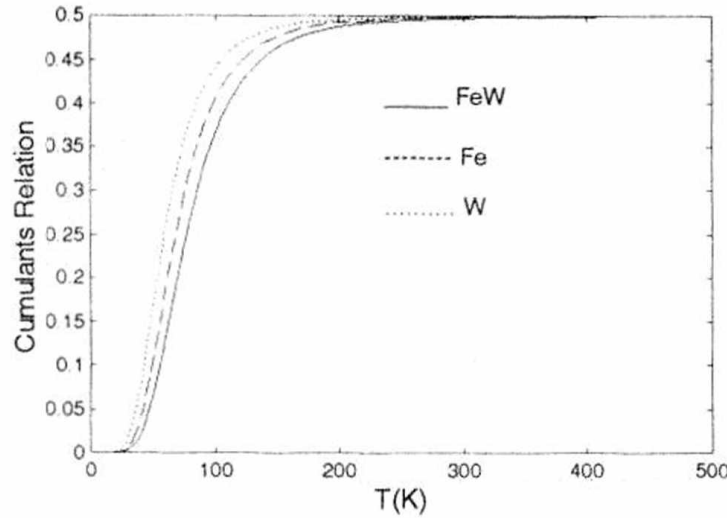


Fig. 5: Cumulants relation $\alpha_T r T \sigma^2 / \sigma^{(3)}$ of FeW in comparison with those of its components Fe and W .

4. Discussions and conclusions

- In this work the expressions of XAFS cumulants and thermal expansions of the two components bcc alloys systems in temperature dependence have been derived based on quantum statistical theory.

- The net thermal expansion $\sigma^{(1)}$, Debye-Waller factor σ^2 and third cumulant $\sigma^{(3)}$ contain zero-point contributions as quantum effects at low temperature, and contain the

classical limits at high temperature, where $\sigma^{(1)}, \sigma^2 \sim T$, and $\sigma^{(3)} \sim T^2$. These behaviours are similar to those of the results of theories [5,6,10] and by experiments [2,13] for the single crystals.

- Thermal expansion coefficient has the form of specific heat which approaches to a constant value at high temperature as the Dulong-Petit rule and vanishes at low temperature obeying the cubic temperature rule.

- The cumulants relation $\alpha_T \tau T \sigma^2 / \sigma^{(3)}$ approaches the classical and experimental value [2] of 1/2 at θ_E (Fig. 5). This denotes the Einstein temperature as the limit above which the classical approach can be applicable and below which the quantum theory must be used as it was defined for the single crystals [5].

- This approach can also be applied to the research of thermodynamic properties of nano systems.

Acknowledgments. This work is supported in part by the basic science research programs No 410 801.

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