

# ISOTOPE EFFECTS IN DEBYE-WALLER FACTOR AND IN XAFS

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**Abstract.** A new analytical procedure for discover and evaluation of isotope effects in Debye-Waller factor (DWF) and in X-ray absorption fine structure (XAFS) of a crystal has been developed based on the quantum statistical theory. The derived expressions for Debye-Waller, correlated Einstein frequency, correlated Einstein temperature and XAFS depend on the atomic mass number as a variable. The well-known FEFF code has been modified to include the developed expressions. Numerical calculations have been carried out for fcc crystal Ni and its isotopes. The results show several isotope effects of the crystal especially at low temperatures

## I. Introduction

Creation of an artificial isotope can be realized by changing the atomic mass or atom mass number of the crystals. Atomic mass of a crystal and reduced mass of a mixing isotope can be varied as an parameter in the experiment [1, 3]. But it can lead to the variation of several parameters of the crystals like the symmetry or atomic disorders and the others [1, 3]. For example thermal conducting of isotope Ge is increased by 10 times compared to the natural crystal Ge [4]. It is known that XAFS becomes an powerful technique for analysis of thermodynamic and structural information of the substances [5, 8], so that it can be sensitive to the change of the atomic mass number of a crystal or to changing from an isotope to another.

The purpose of this work is to study the isotope effects in the DWF and the XAFS spectra of a crystal. We derive analytical expressions for DWF, correlated Einstein frequency, correlated Einstein temperature and XAFS using quantum statistical theory and correlated Einstein model [8]. They contain the atomic number as an variable. Numerical evaluations have been carried out for fcc crystal Ni and its isotopes. Significant changes of correlated Einstein frequency and temperature, DWF, XAFS spectra and their Fourier transform magnitude for different Ni isotopes have been discovered especially at low temperatures

## II. Formalism

XAFS, i.e., the oscillatory structure in the X-ray absorption coefficient, is produced by the interference between the outgoing and the backscattered waves of the photoelectron emitted from an atom of the crystal under the action of the photon with energy in the

range up to 40keV. For k-edge, i.e., the emitted photoelectron is s-electron, the XAFS function is described by

$$\chi(k) = \sum_j \frac{S_0^2 N_j}{k} F_j(k) \text{Im} \left\{ \left\langle \frac{1}{r_j^2} e^{-2r_j/\lambda} e^{2ikr_j} \right\rangle e^{i\Phi_j} \right\}. \quad (1)$$

Developing further this equation we obtain the expression for the temperature dependent XAFS function

$$\chi(k, T) = \sum_j \frac{S_0^2 N_j}{k R_j^2} F_j(k) e^{-(2k^2 \sigma^2(T) + 2R_j/\lambda(k))} \sin(2kR_j + \Phi_j(k)), \quad (2)$$

where  $F(k)$  is the real atomic backscattering amplitude,  $\Phi$  is the net phase shift,  $k$  and  $\lambda$  are the wave number and the mean free path of the photoelectron, respectively,  $R = \langle r \rangle$  with  $r$  as the instantaneous bond length between absorbing and backscattering atoms and  $\langle \rangle$  denotes a thermal average,  $S_0^2$  is the square of the many body overlap term,  $N_j$  is the atomic number of each shell, and the sum is over all atomic shells. The  $DWF = \exp(-2k^2 \sigma^2)$  is characterized by the mean square relative displacement (MSRD)  $\sigma^2(T)$  describing vibrational disorder in the bond distances due to thermal vibration of the crystal lattice.

In the present approach we apply the correlated Einstein model [8] to the calculation of the MSRD where the effective interacting Einstein potential is given by

$$V_{eff}(x) \cong \frac{1}{2} k_{eff} x^2 + k_3 x^3 + \dots = V(x) + \sum_{j \neq i} V\left(\frac{\mu}{M_i} x \hat{R}_{12} \hat{R}_{ij}\right), \mu = \frac{M_1 M_2}{M_1 + M_2}, \hat{R} = \frac{R}{|R|}. \quad (3)$$

Here  $k_{eff}$  is effective spring constant, and  $k_3$  the cubic parameter giving an asymmetry in the pair distribution function. The correlated Einstein model may be defined as an oscillation of a pair of atoms with masses  $M_1$  and  $M_2$  (e.g., absorber and backscattering) in a given system. Their oscillation is influenced by their neighbors given by the last term in the left-hand side of Eq.(3), where the sum is over absorber ( $i = 1$ ) and backscattering ( $i = 2$ ), and the sum is over all their nearest neighbors, excluding the absorber and backscatter themselves. The latter contributions are described by the term  $V(x)$ . We denote  $y = x - a$  to be the deviation from the equilibrium value of  $x$  with  $a(T) = \langle r - r_0 \rangle$  as the net thermal expansion of the bond length and express Eq.(3) as

$$V_{eff}(y) = \frac{1}{2} k_{eff} y^2; \quad (4)$$

Applying the Morse pair potential

$$U(x) = D(e^{-2\alpha x} - 2e^{-\alpha x}) \cong D(-1 + \alpha^2 x^2 - \alpha^3 x^3 + \dots), \quad (5)$$

to the effective potential of the system of Eq(3) (ignoring the overall constant) we obtain

$$k_{eff} = D\alpha^2 \left(S - \frac{15}{2}\alpha a\right) = \mu \omega_E^2 \Rightarrow \omega_E = \sqrt{k_{eff}/\mu}; \theta_E = \frac{\hbar \omega_E}{k_B}, \quad (6)$$

where  $k_{eff}$  is the Boltzmann constant;  $\omega_E, \theta_E$  are the Einstein frequency and temperature, respectively; the Morse potential parameter  $D$  is the dissociation energy, and  $1/\alpha$  corresponds to the width of the potential; the structural parameter [9]  $S = 5$  for fcc and  $S = 11/3$  for bcc.

The MSRD is calculated based on the averaged quantity  $\langle y^2 \rangle$  and according to statistical mechanics [8, 10, 11] it is given by

$$\sigma^2 = \langle y^2 \rangle = \frac{1}{Z} Tr(\rho y^2) \cong \frac{1}{Z_0} Tr(\rho_0 y^2). \quad (7)$$

Here the thermal average is over the statistical density matrix  $\rho = \exp(-\beta H)$ ,  $\beta = 1/k_B T$  and  $Z = Tr \rho$  is the canonical partition function; the corresponding unperturbed quantities are  $\rho_0 = \exp(-\beta H_0)$  and  $Z_0 = Tr \rho_0$ , where  $H$  and  $H_0$  are the perturbed and unperturbed Hamiltonian of the system, respectively. This first order treatment ignores anharmonic contribution as perturbation to  $\sigma^2$  [11].

The trace in Eq.(7) is straightforwardly evaluated using harmonic oscillator state  $|n\rangle$  with eigenvalues  $E_n = \hbar\omega_E$  (zero point energy is set to zero for convenience). Thus we obtain

$$\sigma^2(T) = \frac{1}{Z_0} \sum_n e^{-n\beta\hbar\omega_E} \langle n|y^2|n\rangle, \quad (8)$$

$$Z_0 = \sum_n e^{-n\beta\hbar\omega_E} = \sum_n z^n = \frac{1}{1-z}. \quad (9)$$

To evaluate the matrix elements in Eq.(8) we express  $y$  in terms of creation and annihilation operators  $\hat{a}$  and  $\hat{a}^+$ , i. e.,

$$y = y_0(\hat{a} + \hat{a}^+), y_0 = \sqrt{\hbar/2\mu\omega_E}. \quad (10)$$

Hence, we obtain

$$\sigma^2(T) = \frac{y_0^2}{Z_0} \sum_n z^n (2n+1) = \frac{\hbar\omega_E}{2k_{eff}} \frac{1+z}{1-z}. \quad (11)$$

Using Eqs.(5, 6) we reformed Eq.(11) and obtain the expression for the MSRD

$$\sigma^2(T) = \sigma_0^2 \frac{1+z}{1-z}, \sigma_0^2 = \frac{\hbar\omega_E}{2SD\alpha^2},$$

where  $z = e^{-\theta_E/T}$  is temperature parameter and  $\sigma_0^2$  the zero-point contribution to the MSRD.

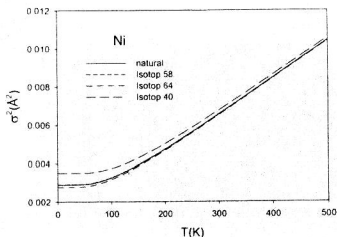
This MSRD contains the correlated Einstein frequency and temperature which depend on the atom mass of the crystal. That is why it will be changed if a crystal is changed into its different isotopes. The MSRD Eq.(12) is included in the XAFS function Eq.(2) so that the XAFS spectra of a crystal and of its isotopes will be different giving thermal and structural information of these substances.

### III. Numerical results and discussion

Now we apply the expressions developed in previous section to numerical calculations for fcc crystal Ni and its isotopes. The Morse potential parameter  $D = 0.4205\text{eV}$  and  $\alpha = 1.4199\text{\AA}^{-1}$  of Ni were from [12]. The values of our calculated correlated Einstein frequency  $\omega_E$  and temperature  $\theta_E$  are presented in Table 1, where the atom mass number is written in the brackets. The correlated Einstein frequency and temperature are increased as the atom mass number of the crystal is decreased. Figure 1 shows the temperature dependence of our calculated MSRSD of Ni and its isotopes 64, 58 and 40. They are different especially at low temperatures and contain zero-point contributions. At high temperatures they are linearly proportional to the temperature  $T$ .

**Table 1.** The values of  $\omega_E$  and  $\theta_E$  of Ni and its isotopes calculated by present procedure.

Ni	Isotope(64)	Natural(58.7)	Isotope(58)	Isotope(40)
$\omega_E(\times 10^{13}\text{Hz})$	2.5205	2.632	2.648	3.177
$\theta_E(\text{K})$	192.534	201.041	202.248	243.535



*Figure 1:* Temperature dependence of MSRSD of natural Ni and of its isotopes 64, 58 and 40.

We have modified the well-known FEFF code [13] to include our developed DWF containing the atom mass number as a parameter. It is convenient for consideration of isotope effects of a crystal with different atomic masses. The scattering amplitudes of the first shell for single scattering of natural Ni and of its isotopes 64, 58 and 40 calculated by the present procedure are presented in Figure 2. They are different especially at high  $k$ -values. Figure 3 illustrates our calculated total XAFS spectrum of Ni at 25 K. This fine structure contains the structural and thermal information of the crystal.

Note that the main contribution to the XAFS is given by the first shell [14]. This is why only the calculated XAFS of the first shell for single scattering has been used for the

discussion. The generalization to the other shells is straightforward. Figure 4 shows our calculated XAFS spectra of the first shell for single scattering of Ni isotopes 64, 58 and 40 at 25 K. They are different especially at high  $k$ -values. Fourier transform magnitude of XAFS spectra presented in Figures 3 and 4 on the range  $3\text{\AA}^{-1} < k < 19.6\text{\AA}^{-1}$  are shown in Figures 5 and 6. They are different for different isotopes of Ni and for its natural crystal.

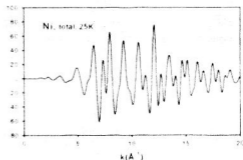
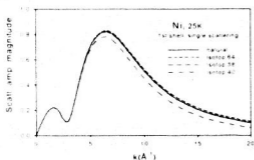


Figure 2: Scattering amplitude of the first shell for single scattering of natural Ni and its isotopes 64, 58 and 40 at 25 K. Figure 3: Calculated total XAFS spectrum of natural Ni at 25 K.

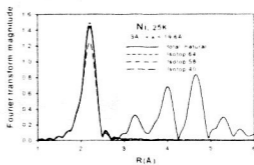
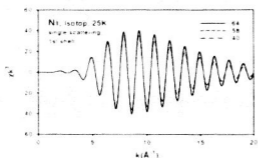


Figure 4: Calculated XAFS spectra of the first shell for single scattering of Ni isotopes 64, 58 and 40.

Figure 5: Fourier transform magnitude of XAFS of natural Ni (total) and of its isotopes 64, 58 and 40 (first shell).

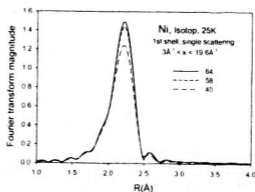


Figure 6: Fourier transform magnitude of XAFS spectra of the first shell for single scattering of Ni isotopes 64, 58 and 40 (Fig. 4)

In the present approach we considered only the DWF or the 2<sup>nd</sup> cumulant, that is why only the amplitude of the XAFS spectra and the height of their Fourier transform magnitude peaks are changed when the atom mass number of the crystal is changed. The phase of the XAFS can also be changed if the first and the third cumulants are included using the procedure described in [15].

#### IV. Conclusions

In this work a new procedure for calculation and analysis of XAFS, DWF, correlated Einstein frequency and temperature of isotopes of a crystal has been developed based on the quantum statistical theory and the correlated Einstein model.

Containing the atom mass number our developed expressions are convenient for consideration of the structural and thermodynamic property information of isotopes.

Correlated Einstein frequency and temperature are increased as the atom mass number of a crystal is decreased. DWF is linearly proportional to the temperature at high temperatures and different for different isotopes, especially at low temperatures. It is also followed that the isotope effects appear more clearly at low temperatures.

The well-known code FEFF has been modified by including our expressions for numerical calculations. The results of Ni show several isotope effects.

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