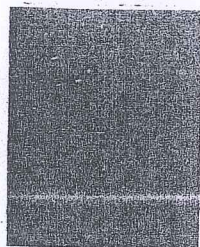


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# ANHARMONIC-CORRELATED EINSTEIN MODEL THERMAL EXPANSION AND XAFS CUMULANTS OF CUBIC CRYSTALS: COMPARISON WITH EXPERIMENT AND OTHER THEORIES

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**Abstract.** *The expressions of anharmonic-correlated Einstein model thermal expansion and XAFS cumulants of cubic crystals have been formulated. This next step is devoted to numerical calculations for fcc crystals Ag, Cu and bcc crystal Fe, and to comparison of their results with experimental values and with those calculated by other procedures. Our calculated values of correlated Einstein temperature for Ag and Cu, second cumulant or Debye-Waller factor, third cumulant, and thermal expansion coefficient for Cu agree well with experimental results, showing some advantages of present procedure in comparison with other theories. These numerical results describe typical thermodynamic properties of fcc and bcc crystals. Correlated Einstein temperature has been identified as the temperature above which the classical limit is applicable, and below which quantum theory must be used.*

## I. INTRODUCTION

Structural information of substances taken from Fourier transform magnitude of the X-ray Absorption Fine Structure (XAFS) spectra can be different at different temperatures due to thermodynamic effects, especially at high temperatures [1-4]. Cumulant expansion approach [1] has been developed to correct these uncertainties. According to this approach the XAFS function contains the cumulants  $\sigma^{(n)}$  [5].

In our previous work [5] using anharmonic-correlated Einstein model [6] we have derived the following values:

- the effective spring constant  $k_{eff}$ , Einstein frequency  $\omega_E$  and temperature  $\theta_E$

$$k_{eff} = c_1 (D\alpha^2 + c_2 a k_3) = \mu \omega_E^2; \quad \theta_E = \frac{\hbar}{k_B} [c_1 (D\alpha^2 + c_2 a k_3) / \mu]^{1/2}, \quad (1)$$

where  $D, \alpha$  are Morse potential parameters,  $k_B$  is Boltzmann's constant,  $\mu$  is reduced mass of absorbing and backscattering atoms,  $k_3 = -5D\alpha^3/4$  is anharmonicity parameter in the interacting potential,



- the first cumulant or net thermal expansion

$$\sigma^{(1)} = a = \sigma_0^{(1)} \frac{1+z}{1-z} = \frac{15\alpha}{4c_1} \sigma^2; \quad \sigma_0^{(1)} = \frac{15\alpha}{4c_1} \sigma_0^2 \quad (2)$$

- the second cumulant or Debye-Waller factor

$$\sigma^2 = \sigma_0^2 \frac{1+z}{1-z}; \quad \sigma_0^2 = \frac{\hbar\omega_E}{2c_1 D\alpha^2}; \quad z = e^{-\theta_E/T}; \quad (3)$$

- the third cumulant

$$\sigma^{(3)} = \sigma_0^{(3)} \frac{3(\sigma^2)^2 - 2(\sigma_0^2)^2}{(\sigma_0^2)^2}; \quad \sigma_0^{(3)} = \frac{5\alpha}{2c_1} (\sigma_0^2)^2; \quad (4)$$

- the thermal expansion coefficient

$$\alpha_T = \alpha_T^0 \left( \frac{c_1 D\alpha^2 \sigma^2}{k_B T} \right)^2 \left[ 1 - \left( \frac{\sigma_0^2}{\sigma^2} \right)^2 \right]; \quad \alpha_T^0 = \frac{15k_B}{4c_1^2 D\alpha^2 r}; \quad (5)$$

and their relations

$$\frac{\alpha_T r T \sigma^2}{\sigma^{(3)}} = \frac{c_1 D\alpha^2 \sigma^2}{2k_B T} \frac{1 - (\sigma_0^2/\sigma^2)^2}{1 - (2/3)(\sigma_0^2/\sigma^2)^2}; \quad (6)$$

$$\frac{\sigma^{(1)} \sigma^2}{\sigma^{(3)}} = \frac{1}{2 - (4/3)(\sigma_0^2/\sigma^2)^2}; \quad (7)$$

where  $\sigma_0^{(1)}, \sigma_0^2, \sigma_0^{(3)}$  are zero-point contributions to  $\sigma^{(1)}, \sigma^2, \sigma^{(3)}$ , respectively, and  $r$  is radius of the first shell. The above expressions are different for simple cubic (s.c.), fcc, and bcc structures, separated by the factors  $c_1$  and  $c_2$  as follows

$$c_1 = \begin{cases} 3, & s.c. \\ 5, & fcc \\ 11/3, & bcc \end{cases}; \quad c_2 = \begin{cases} 1, & s.c. \\ 6/5, & fcc \\ 18/11, & bcc \end{cases} \quad (8)$$

The purpose of this work is to carry out numerical calculations of thermodynamic parameters according to the Eqs.(1-8) for fcc crystals Ag, Cu, and bcc crystal Fe to demonstrate our derived quantum statistical procedure for cubic crystals [5], as well as to compare these numerical results with experimental values and with those calculated by other procedures. Through that the advantages of our procedure and the thermodynamic properties of cubic crystals are discussed in details.



## II. NUMERICAL RESULTS AND COMPARISON WITH EXPERIMENT

Now we apply the Eqs.(1-8) to numerical calculations for fcc crystals Ag, Cu, and bcc crystal Fe. The parameters  $D$  and  $\alpha$  of the Morse - pair potential were taken from Ref.7; they were obtained using experimental values for the energy of sublimation, the compressibility, and the lattice constant. The most important parameters contributing to the atomic vibration in our model are effective spring constant  $k_{eff}$ , Einstein frequency  $\omega_E$ , and correlated Einstein temperature  $\theta_E$ . Their values calculated by present procedure and the measured results of  $\theta_E$  from Ref. 8 ( $\theta_E^{Expt}$ ) are presented in Table I. They show a good agreement of our calculated values  $\theta_E$  of with those from the experiment for Ag and Cu. It can lead to the agreement of our other calculated parameters with the experiment because  $\theta_E$  determines the temperature variable  $z$  which plays the main function role in all the above thermodynamic parameters described by Eqs.(1-8). Figure 1 shows the temperature dependence of our calculated first cumulant or net thermal expansion  $\sigma^{(1)} = a$  for Ag, Cu, and Fe. All results are proportional to the temperature  $T$  at high temperatures, and very small, containing zero-point contributions at low temperatures. They describe an asymmetry of the atomic interaction potential of these crystals due to anharmonicity.

Table I: The values of  $k_{eff}\omega_E$  and  $\theta_E$  of calculated by present theory, and the measured results of  $\theta_E^{Expt}$  from Ref.[8] for Ag and Cu.

Sample	Bond	$k_{eff}(N/m)$	$\omega_E (\times 10^{13} Hz)$	$\theta_E(K)$	$\theta_E^{Expt}(K)$
Ag	Ag-Ag	49.891	2.353	176	167(2)
Cu	Cu-Cu	50.748	3.092	236	232(5)
Fe	Fe-Fe	47.275	3.184	243	—

Figure 2 illustrates the temperature dependence of our calculated second cumulant or Debye-Waller factor  $\sigma^2$  for Ag, Cu, and Fe, in comparison with the experimental values [9,10] and another theoretical values [11] at 295K, calculated by full lattice dynamical approach for Cu. The good agreement at low temperatures and small differences at high temperatures between our results and the measured values are reasonable. Moreover, all of the techniques of ascertaining the disorder in Ref.9 assume a Gaussian form. Our calculated values  $\sigma^2$  of are proportional to the temperature  $T$  at high temperatures and contain zero-point contribution at the low temperatures. Figure 3 shows the temperature dependence of our calculated third cumulant  $\sigma^{(3)}$  for Ag, Cu, and Fe, in comparison with the measured [10] and theoretical [11] values for Cu. Our results for Cu at 295K agrees very well with the experimental value [10]. Our calculated results of  $\sigma^{(3)}$  are proportional to the quadrate of temperature  $T$  at high temperatures and very small, containing zero-point contributions at low temperatures. The temperature dependence of our calculated thermal expansion coefficient  $\alpha_T$  for Ag, Cu, and Fe and comparison with the measured values [12] are shown in Figure 4. Our results of Cu at 77K and 100K are close to the experimental values [12]. Moreover, our calculated values of  $\alpha_T$  have the form of specific heat



$Cv$ . This agrees with the fundamental of solid states theory, according to which  $\alpha_T$  is proportional to  $Cv$  [13].

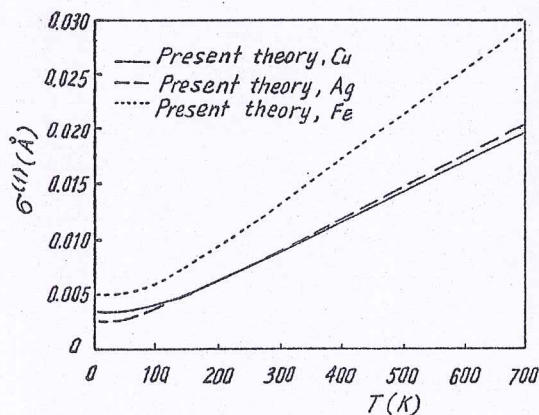


Fig.1 Temperature dependence of our calculated first cumulant or net thermal expansion  $\sigma^{(1)}$  of Cu, Ag, and Fe. All they are proportional to T at high temperatures and contain zero-point contributions  $\sigma_0^{(1)}$  at low temperatures

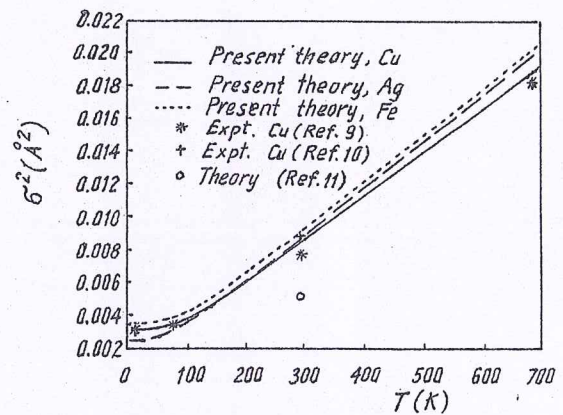


Fig.2. Temperature dependence of our calculated second cumulant or Debye-Waller factors for Ag, Cu, and Fe, and compared with experimental values (Ref.9)(\*) and (Ref.10)(+), and another theoretical value (Ref.10)(o) for Cu. Our calculated values of  $\sigma^2$  are proportional to T at high temperature and contain zero-point contributions low temperatures

From Figures 1, 3, 4 note that first cumulant, third cumulant and thermal expansion coefficient are very small because they describe anharmonic effects which are considerable only at high temperatures, that is why, sometimes they are described by classical theory [3, 4, 14, 15]. The full lattice dynamical approach [11] and the anharmonic single-particle potential procedure [2] also provide the proportionality to T of  $\sigma^2$  and to  $T^2$  of  $\sigma^{(3)}$ , but their calculations are intensive and complicated. Moreover, the results of the full lattice dynamical approach are not so close to the experimental values as ours [Figs. 2, 3], and the anharmonic single-particle potential procedure does not give an accurate description of the situation because it ignores the correlated motion of the atoms. The single-bond spring constant [16] obtained with the Morse potential parameters for Cu [7]  $k_s = 20.3 N/m$  is significantly smaller than the value  $27.9 N/m$  needed to approximate the observed phonon spectra with a single parameter. These differences are indicative of the limitations of a single spring constant model [16] and the possible importance of next-neighbor interactions.



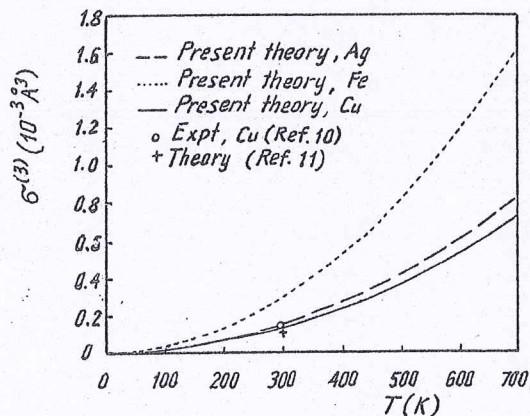


Fig.3. Temperature dependence of our calculated third cumulants  $\sigma^{(3)}$  for Ag, Cu, and Fe, and compared with value (Ref.11)(+) for Cu. Our calculated value of  $\sigma^{(3)}$  are proportional to the quadrate of temperature  $T$  at high temperatures and contain zero-point contributions at low temperatures

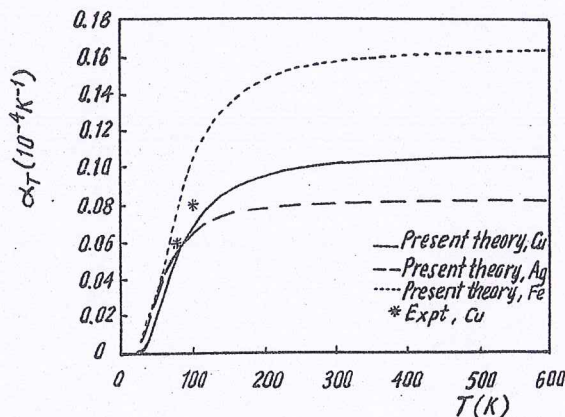


Fig.4. Temperature dependence of our calculated thermal expansion coefficient  $\sigma_T$  for Ag, Cu and Fe, and compared with the experimental values (Ref.12)(\*) for Cu. Our calculated values of  $\sigma_T$  approach the constant value  $\sigma_T^0$  at high temperatures and vanish exponentially with  $\theta_T/T$  at low temperatures

Figures 5 and 6 demonstrate the temperature dependence of the relations  $\sigma_T r T \sigma^2 / \sigma^{(3)}$  and  $\sigma^{(1)} \sigma^2 / \sigma^{(3)}$  respectively, for Ag, Cu and Fe. The quantum theory works for any temperature, but reduece of our calculaed thermal ces to classical limit at high temperature when  $\sigma^2 \gg \sigma_0^2$ , and our above relations approach the classical expression of 1/2. These results reflect the conclusion of the classical method and experiment [3,15]. Therefore, we can use these relations as a criterion to identify the temperature above which the classical limit is applicable. Figures 5 and 6 show that below Einstein temperature ( $\theta_E = 176K$  for Ag, 236K for Cu, and 243K for Fe ) the classical result loses validity.

In our computer program coded to calculate thermodynamic parameters according to the Eqs. (2-9) we have mainly to calculate Debye-Waller factor, the other parameters are obtained in conjunction with. It is the advantage and simplicity of our description.

### III. CONCLUSIONS

The expressions of anharmonic-correlated Einstein model thermal expansion and XAFS cumulants of cubic crystals derived in our previous work [5] have been for fcc



crystals Ag, Cu, and bcc crystal Fe numerically demonstrated, compared with experimental results and with those calculated by other theories.

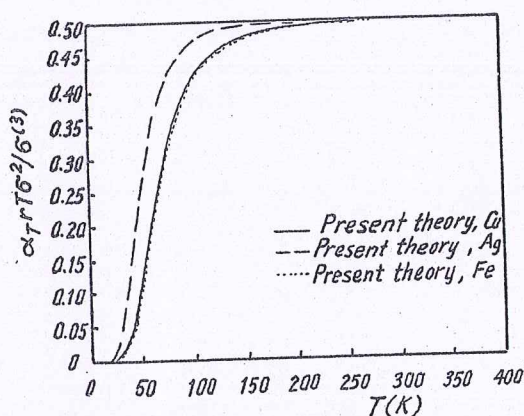


Fig.5. Temperature dependence of the relation  $\alpha_T r T^2 / \sigma^{(3)}$  for Cu, Ag, and Fe as criterion to identify the temperature above which this relation approaches the classical ( Refs.3,15) of 1/2 and the classical limit is applicable. This temperature is about correlated Einstein Temperature ( $\theta_E = 176K$  for Cu, and 243K for Fe)

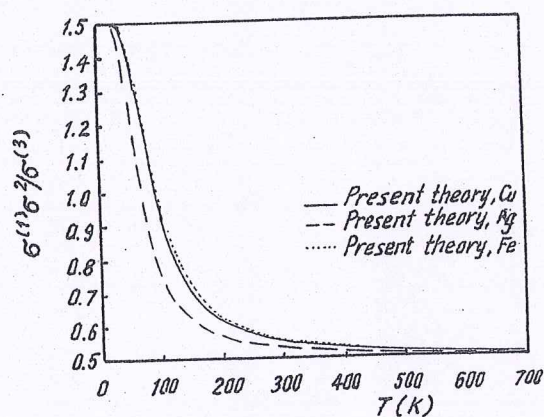


Fig.6. Temperature dependence of the relation  $\sigma^{(1)} \sigma^{(2)} / \sigma^{(3)}$  for Ag, Cu, and Fe as a criterion to identify the temperature above which this relation approaches the classical expressions ( Refs.3,15) of 1/2 and the classical limit is applicable. This temperature is about correlated Einstein Temperature ( $\theta_E = 176K$  for Cu, and 243K for Fe).

Our calculated correlated Einstein temperature  $\theta_E$  of Ag and Cu, second cumulant or Debye-Waller factor  $\sigma^2$ , third cumulant  $\sigma^{(3)}$ , and thermal expansion coefficient  $\alpha_T$  of Cu agree well with the experimental results [9,10,12].

The figures show the proportionality to  $T$  of  $\sigma^{(1)}$ ,  $\sigma^2$ , and to  $T^2$  of  $\sigma^{(3)}$ , and the approaching to constant value of thermal expansion coefficient  $\alpha_T$  at high temperatures, as well as, the containing zero-point contributions of  $\sigma^{(1)}$ ,  $\sigma^2$ , and the exponential vanishing with  $\theta_E/T$  of  $\alpha_T$  at low temperatures. The figure of  $\alpha_T$  shows its proportionality to specific heat, thus reflecting the fundamental of solid state theory.

The discussion has been carried out with the full lattice dynamical approach [11], the anharmonic single-particle potential theory [2], and the single-bond model [16], showing the advantage of present procedure in reflecting the experimental results and the real motion situation of atoms in the crystals. Our description of thermal expansion and XAFS cumulants in terms of Debye-Waller factor is advantageous for reducing the numerical calculations and measurements.

Numerical results of the relations  $\alpha_T r T^2 / \sigma^{(3)}$  and  $\sigma^{(1)} \sigma^{(2)} / \sigma^{(3)}$  approach the classical expression of 1/2, thus reflecting the conclusion of the classical method and experiment [3,15]. Therefore, these relations can serve as a criterion to identify the correlated Einstein temperature to be the temperature above which the classical limit is applicable,



and below it the quantum theory must be use ( $\theta_E = 176\text{K}$  for Ag,  $236\text{K}$  for Cu, and  $243\text{K}$  for Fe ).

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