

**THERMODYNAMIC PARAMETERS DEPEND ON
TEMPERATURE WITH THE INFLUENCE OF DOPING
RATIO OF THE CRYSTAL STRUCTURE METALS
IN EXTENDED X-RAY ABSORPTION
FINE STRUCTURE**

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Abstract

The effects of the doping ratio and temperature on the cumulants and thermodynamic parameters of alloys metals was investigated by using the anharmonic correlated Einstein model in extended x-ray absorption fine structure (EXAFS) spectra. The analytical expressions for the EXAFS cumulants and thermal expansion coefficient were derived. The parameters of the effective Morse potential and the Debye-Waller factor depend on temperature and the effects of the doping ratio were considered for pure copper (Cu-Cu), silver (Ag-Ag), zinc (Zn-Zn) and their alloys of CuAg, CuZn. The derived anharmonic effective potential includes the contributions of all the nearest neighbours of the absorbing and backscattering atoms, this accounts for three-dimensional interactions and the parameters of the Morse potential to describe single-bond pair atomic interactions. The numerical results of the EXAFS cumulants, thermodynamic parameters and anharmonic effective potential agree reasonably with experiments and other theories.

Keywords and phrases: brackpoint, cumulants, doping ratio, parameter, thermodynamic.

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1. Introduction

Extended x-ray absorption fine structure (EXAFS) spectra has developed into a powerful probe of atomic structures and the thermal effects of substances [1]. The dependence of the thermodynamic properties and cumulants of the lattice crystals of a substance on the temperature with influence doping ratio (DR) was studied by using this technique. The thermodynamic parameters and the EXAFS cumulants for pure cubic crystals, such as crystals of copper doped with silver (CuAg), which depend on DR and temperature have been derived using the anharmonic correlated Einstein model (ACEM) [2] in EXAFS theory. However, the effect of the doping ratio and temperature on the thermodynamic parameters and cumulants of the EXAFS for copper doped with zinc (CuZn), copper doped with silver at a level not above 50%, is yet to be determined.

In this study used anharmonic effective potential from EXAFS theory to formulate thermodynamic parameters, such as the effective force constants, expressions of cumulants, thermal expansion coefficient, correlated Einstein frequency and correlated Einstein temperature, these parameters are contained in the anharmonic EXAFS spectra. The CuAg, CuZn doped crystals contain pure Cu, Ag, and Zn atoms. The Ag, Zn atoms are referred to as the substitute atoms, the Cu atoms are referred to as the host atoms. The expression CuAg72 indicates a ratio of 72% Ag and 28% Cu atoms in the alloy, and CuZn45 indicates a ratio of 45% Zn and 55% Cu atoms in the alloy. The numerical results will be compare with experimental values and other studies.

2. Formalism

In the anharmonic EXAFS function including the anharmonic contributions of atomic vibration is often expressed as:

$$\chi(k) = \frac{S_0^2 N}{kR^2} F(k) \exp\left(-\frac{2R}{\lambda(k)}\right) \text{Im}\left(e^{i\Phi(k)} \exp\left(2ikr_0 + \sum_n \frac{(2ik)^n}{n!} \sigma^{(n)}(T)\right)\right), \quad (1)$$

where $R = \langle r \rangle$ with r is the instantaneous bond length between absorbing and scattering atoms at temperature T and r_0 is its equilibrium value, S_0^2 is the intrinsic loss factor due to many electron effects, N is the atomic number of a shell, $F(k)$ is the atomic backscattering amplitude, k and λ are the wave number and mean free path of the photoelectron, and $\Phi(k)$ is the total phase shift of the photoelectron. In the ACEM, interaction between absorbing and scattering atoms with contributions from atomic neighbours is characterized by an effective potential, to describe the asymmetric components of the interactive potential, the cumulants $\sigma^{(n)}$ ($n = 1, 2, 3, 4, \dots$) are used. To determine the cumulants, it is necessary to specify the interatomic potential and force constant, consider a high-order expanded anharmonic interatomic effective potential, expanded up to fourth order, namely:

$$V(x) \approx \frac{1}{2} k_{eff} x^2 + k_{3eff} x^3 + k_{4eff} x^4 + \dots, \quad (2)$$

where k_{eff} is an effective spring constant that includes the total contribution of the neighbouring atoms, and k_{3eff} and k_{4eff} are effective anharmonicity parameters that specify the asymmetry of the anharmonic effective potential, $x = r - r_0$ is net deviation. The effective potential, given by Equation (2), is defined based on the assumption of an orderly center-of-mass frame for a single-bond pair of an absorber and a backscatterer [3]. For monoatomic crystals, the masses of the absorber and backscatterer are the same, so the effective potential is given by:

$$V_E(x) = V(x) + \sum_{i=0,1} \sum_{j \neq i} V\left(\frac{\mu}{M_i} x \hat{R}_{01} \cdot \hat{R}_{ij}\right), \quad (3)$$

where $V(x)$ includes only absorber and backscatter atoms, i is the sum of the absorber ($i = 1$) and backscatter ($i = 2$) atoms, and j is the sum of all

their near neighbours, excluding the absorber and backscatterer themselves, whose contributions are described by the term $V(x)$, μ is the reduced atomic mass, \hat{R} is the unit bond-length vector. Therefore, this effective pair potential describes not only the pair interaction of the absorber and backscatter atoms but also how their near-neighbour atoms affect such interactions, this is the difference between the effective potential of this study and the single-pair potential [4], which consider only each pair of immediate neighbouring atoms, i.e., only $V(x)$, without the remaining terms on the right-hand side of Equation (3). The atomic vibration is calculated based on a quantum statistical procedure with an approximate quasi-harmonic vibration, in 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:

$$H = \frac{P^2}{2\mu} + V_E(\chi) = H_0 + V_E(a) + \delta V_E(y), \quad H_0 = \frac{P^2}{2\mu} + \frac{1}{2} k_{eff} y^2, \quad (4)$$

with $y = x - a$, $a(T) = \langle x \rangle$, and $\langle y \rangle = 0$, where y is the deviation from the equilibrium value of x at absolute temperature T and a is the net thermal expansion. The potential interaction between each pair of atoms in the single bond can be expressed by the anharmonic Morse potential and expanding to fourth order and considering orderly doped crystals, assign the host atom the indicator 1 and the substitute atom the indicator 2, will have:

$$V_E(x) = D_{12}(e^{-2\alpha_{12}x} - 2e^{-\alpha_{12}x}) \approx D_{12}\left(-1 + \alpha_{12}^2 x^2 - \alpha_{12}^3 x^3 + \frac{7}{12} \alpha_{12}^4 x^4 \dots\right), \quad (5)$$

where D_{12} is the dissociation energy, $V(r_0) = -D_{12}$, and α_{12} describes the width of the potential. For simplicity, assume that the parameters of the Morse potential in Equation (5) at a certain temperature given by approximate:

$$D_{12} = c_1 D_1 + c_2 D_2, \quad \alpha_{12} = \sqrt{(D_1 \alpha_1^2 + D_2 \alpha_2^2) / (D_1 + D_2)}, \quad (6)$$

where c_1, c_2 are the DR (%) of the alloys and $c_1 = 1 - c_2$. Calculation ($\hat{R}_{01} \cdot \hat{R}_{ij}$) in Equation (3) for lattice face-centred cubic (fcc) crystals, substitute Equation (5) with $x = y + a$ into Equation (3) and calculate the sums in the second term of Equation (3) with the reduced mass μ of the doped metals, comparison the results with the factors of Equation (2) and Equation (5) will receive the coefficients k_{eff} , k_{3eff} , and k_{4eff} of the anharmonic effective potential of the Morse potential, namely:

$$k_{eff} = 5D_{12}\alpha_{12}^2, \quad k_{3eff} = \frac{5D_{12}\alpha_{12}^3}{4}, \quad k_{4eff} = \frac{7D_{12}\alpha_{12}^4}{12}. \quad (7)$$

The analytical expressions of cumulants will be obtained from perturbation theory in Duc et al. [5], pp. 110-126, the atomic vibration is quantized as phonons, considering the phonon-phonon interactions to account for anharmonicity effects, with correlated Einstein frequency and correlated Einstein temperature:

$$\omega_E = \sqrt{k_{eff} / \mu_{12}}, \quad \theta_E = \hbar \omega_E / k_B, \quad (8)$$

with k_B is the Boltzmann constant. The expressions of the cumulants up to third order, namely:

$$\sigma^{(1)} = \frac{3\hbar\omega_E}{40D_{12}\alpha_{12}} \frac{(1 + \exp(-\theta_E / T))}{(1 - \exp(-\theta_E / T))}, \quad (9)$$

$$\sigma^{(2)} = \frac{\hbar\omega_E}{10D_{12}\alpha_{12}^2} \frac{(1 + \exp(-\theta_E / T))}{(1 - \exp(-\theta_E / T))}, \quad (10)$$

$$\sigma^{(3)} = \frac{3\hbar^2\omega_E^2}{200D_{12}^2\alpha_{12}^3} \frac{(1 + 10 \exp(-\theta_E / T) + (\exp(-\theta_E / T))^2)}{(1 - \exp(-\theta_E / T))^2}. \quad (11)$$

The dependence of the linear thermal expansion coefficient on the absolute temperature T with effects the DR of the doped metals:

$$\alpha_T = \frac{3k_B}{20D_{12}\alpha_{12}r} \frac{\exp\left(-\frac{\theta_E}{T}\right) \left[\ln\left(\exp\left(-\frac{\theta_E}{T}\right)\right) \right]^2}{\left(1 - \exp\left(-\frac{\theta_E}{T}\right)\right)^2}, \quad (12)$$

and the anharmonic factor as:

$$\beta = \frac{9\eta k_B T}{16D_{12}} \left[1 + \frac{3k_B T}{8D_{12}R\alpha_{12}} \left(1 + \frac{3k_B T}{8D_{12}R\alpha_{12}} \right) \right], \quad (13)$$

$$\eta = \frac{2 \exp\left(-\frac{\theta_E}{T}\right)}{1 + \exp\left(-\frac{\theta_E}{T}\right)}.$$

Factor β is proportional to the temperature and inversely proportional to the shell radius, thus reflecting a similar anharmonicity property obtained in experimental catalysis research [6] if R is considered as the particle radius. Equations (9)-(13) describe how the cumulants, thermal expansion coefficient, and anharmonic factor depend on the absolute temperature T and effects of the reduced mass μ_{12} of the doped metals. Therefore, the first cumulant $\sigma^{(1)}$ or net thermal expansion, the second cumulant $\sigma^{(2)}$ also known as the Debye-Waller factor (DWF) or mean-square relative displacement (MSRD), and the third cumulant $\sigma^{(3)}$ describe the asymmetric interactive potential in the XAFS.

3. Results and Discussion

The calculated and experimental parameter values of the Morse potential, D_{12} and α_{12} , for the pure metals and their alloy crystals are given in Table 1.

Table 1. Parameter values of Morse potential for pure metals and their alloy crystals

Crystal	$D_{12}(\text{eV})$ (Present theory)	$D_{12}(\text{eV})$ (Exp.) ⁷	$\alpha_{12}(\text{\AA}^{-1})$ (Present theory)	$\alpha_{12}(\text{\AA}^{-1})$ (Exp.) ⁷
Cu-Cu	0.3429	0.3528	1.3588	1.4072
Ag-Ag	0.3323	0.3253	1.3690	1.3535
Zn-Zn	0.1698	0.1804	1.7054	1.7000
CuAg72	0.3381	–	1.3634	–
CuZn45	0.2650	–	1.4672	–

Substituting the parameters D_{12} and α_{12} from Table 1 into Equation (7), with Boltzmann's constant $k_B = 8.617 \times 10^{-5} \text{eV}\text{\AA}^{-1}$, Planck's constant $\hbar = 6.5822 \times 10^{-16} \text{eV}\cdot\text{s}$, and calculate the values of the anharmonic effective potential in terms of the parameters of the Morse potential, Einstein frequency ω_E , and Einstein temperature θ_E of crystals, as given in Table 2.

Table 2. Anharmonic effective parameter values

Crystal	$k_{eff}(\text{eVA}^{-2})$ (Present)	$(k_{eff}(\text{eVA}^{-2}))$ (Exp.)	$k_{3eff}(\text{eVA}^{-3})$ (Present)	$k_{3eff}(\text{eVA}^{-3})$ (Exp.)	$k_{4eff}(\text{eVA}^{-4})$ (Present)	$k_{4eff}(\text{eVA}^{-4})$ (Exp.)	ω_E (10^{13} Hz)	θ_E (K)
Cu-Cu	3.1655	3.4931	1.0753	1.2289	0.6646	0.8070	3.0889	236
Ag-Ag	3.1139	2.9797	1.0657	1.0083	0.6809	0.6368	3.3933	176
Zn-Zn	2.4692	2.4348	1.4889	1.0348	0.8378	0.8209	2.6868	206
CuAg72	3.1423	–	1.0710	–	0.6814	–	2.6874	207
CuZn45	2.8522	–	1.0462	–	0.7163	–	2.9161	223

Substituting the values of the thermodynamic parameters from Tables 1 and 2 into Equations (2), (9)-(13), will obtain expressions for the anharmonic effective potential $V(x)$, which depends on T , and the cumulants $\sigma^{(n)}(n)$, which depend on the DR and T .

In Figure 1, the results calculate of anharmonic effective Morse potential (solid lines) has been compared with experimental data (dotted lines) from Pamuk and Halicioğlu [7], for Cu (blue curve with symbol \circ), Ag (red curve with symbol Δ), and Zn (black curve with symbol \square) [8]. The calculated curves of the Morse potential align closely with the experimental curves, indicating that the calculated data for the coefficients k_{eff} , k_{3eff} , and k_{4eff} , from the ACEM, are in good agreement with the measured experimental values. Figure 2 shows how the first three calculated cumulants depend on the DR at a given temperature (300K), for the compound Cu-Ag. The graphs of $\sigma^{(1)}(T)$, $\sigma^{(2)}(T)$, and $\sigma^{(3)}(T)$ illustrate that for DRs of zero to below 50% and from over 50% to 100%, the cumulant values are proportional to the DR. For the second cumulant or DWF, at the point where the ratio of Ag atom decreases to 0% and the ratio of Cu atoms increases to 100% (symbols *, \square), the calculated value is in good agreement with experimental values, at 300K [9, 10]. However, there are breakpoints in the lines at the 0.5 point on the x axis, meaning that we do not have ordered atoms at a DR of 50%. Thus, Cu-Ag alloys do not form an ordered phase at a molar composition of 1:1, i.e., the CuAg50 alloy does not exist, this result is in agreement with the findings of Kraut and Stern [11].

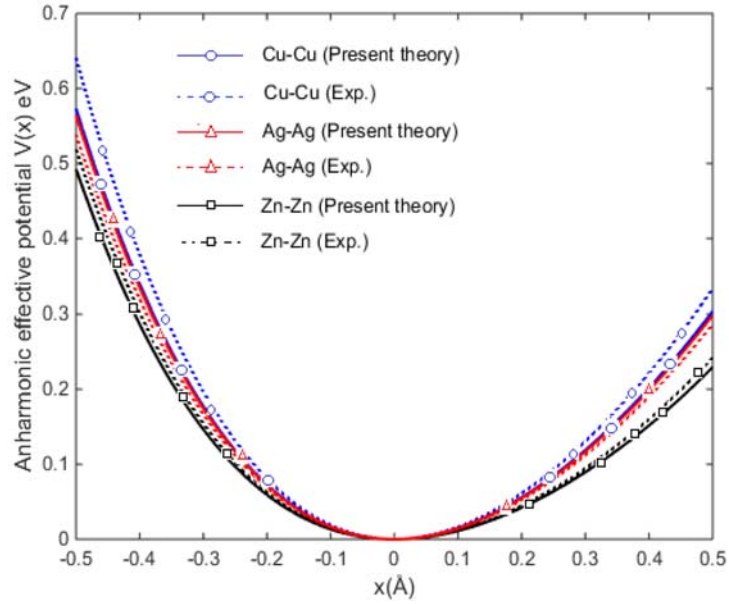


Figure 1. Comparison between present theory and experimental values of anharmonic effective Morse potential.

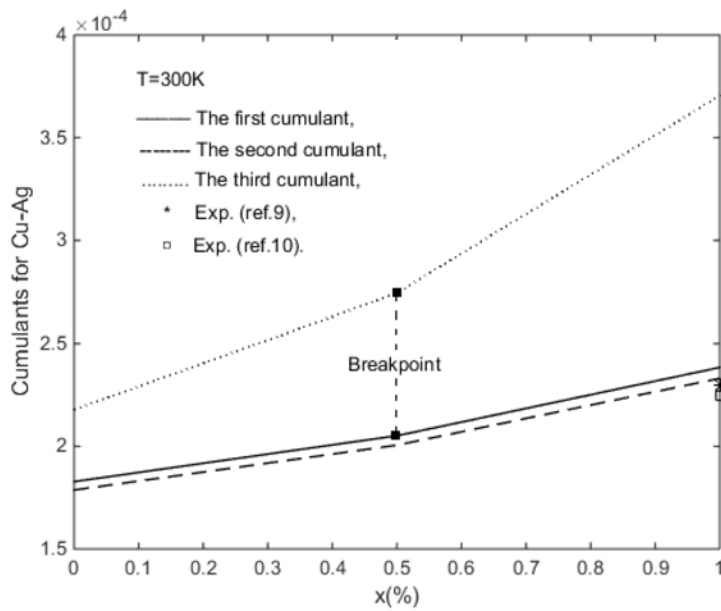


Figure 2. Dependence of cumulants on doping ratio (DR) CuAg50.

Figure 3 shows the temperature dependence of the calculated first cumulant $\sigma^{(1)}$ for Cu, Ag, CuAg72 (the alloy with 28% Cu atoms and 72% Ag atoms, referred to as CuSil or UNS P07720), and CuZn45 (the alloy with 55% Cu atoms and 45% Zn atoms referred to as the *brass*, a yellow alloy of copper and zinc). Figure 4 illustrates the temperature dependence of the calculated second cumulant or DWF $\sigma^{(2)}$, for Cu-Cu, Ag-Ag, Zn-Zn, their alloys CuAg72, CuZn45 and comparison with the experimental values. There good agreement at low temperatures and small differences at high temperatures and the measured results between the results for CuAg72 and CuZn45 with Cu values are reasonable. Calculated values for the first cumulant (Figure 3) and the DWF (Figure 4) with the effects of the DRs are proportional to the temperature at high temperatures. At low temperatures there are very small and contain zero-point contributions, which are a result of an asymmetry of the atomic interaction potential of these crystals due to anharmonicity. Figure 5 shows the temperature dependence of the calculated third cumulant $\sigma^{(3)}$ for Cu-Cu, Ag-Ag, Zn-Zn and their alloys CuAg72, CuZn45, the calculated results are in good agreement with the experimental values. The curves in Figures 3, 4, and 5 for CuZn45 and CuAg72 are very similar to the Cu-Cu curve, illustrating the fit between theoretical and experimental results. The calculated three - first cumulants contain zero-point contributions at low temperatures are in agreement with established theory. Furthermore, the calculations and graphs demonstrate that the alloys of two Cu-Zn elements with Zn content less than or equal 45% enhances the durability and ductility of copper alloys, when the Zn content exceeds 50% in the Cu-Zn alloy, it becomes hard and brittle. CuAg72 is an eutectic alloy, primarily used for vacuum brazing [12]. Also, alloy CuZn45 is often used as heat sinks, ducts and stamping parts because of its high viscosity [13].

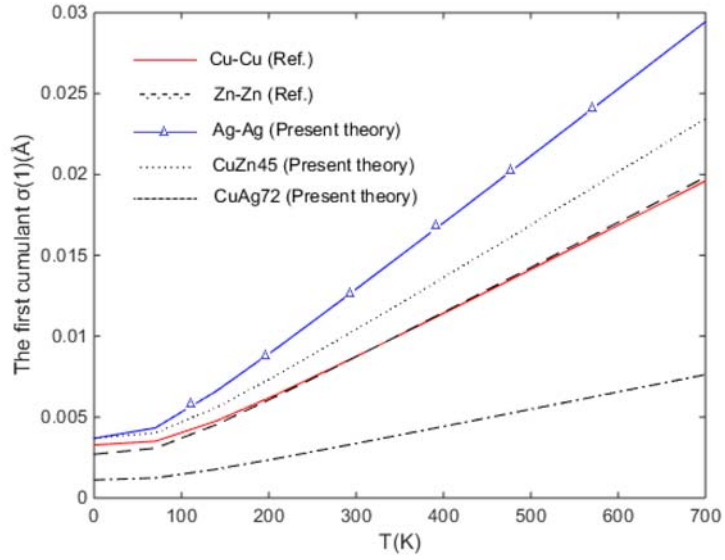


Figure 3. Temperature dependence of the first cumulant for Cu, Ag, Zn, and their alloys, with the effect of DR.

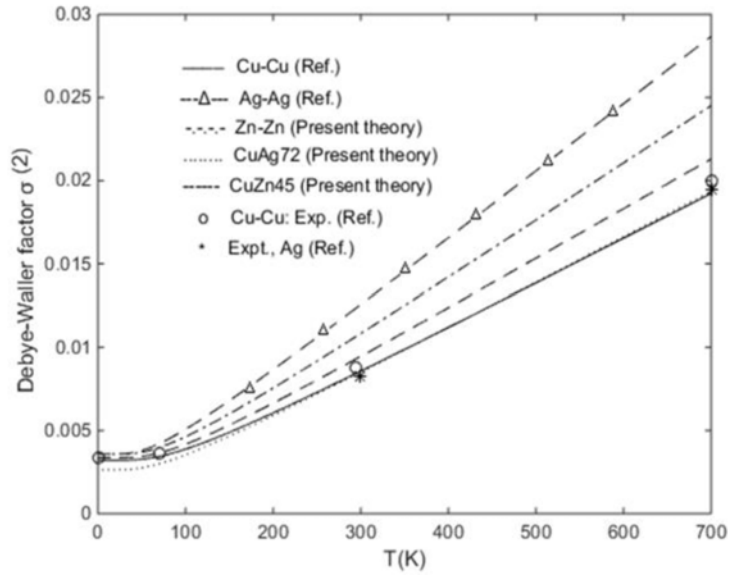


Figure 4. Temperature dependence of the Debye-Waller factor for Cu, Ag, Zn, and their alloys, with the effect of DR.

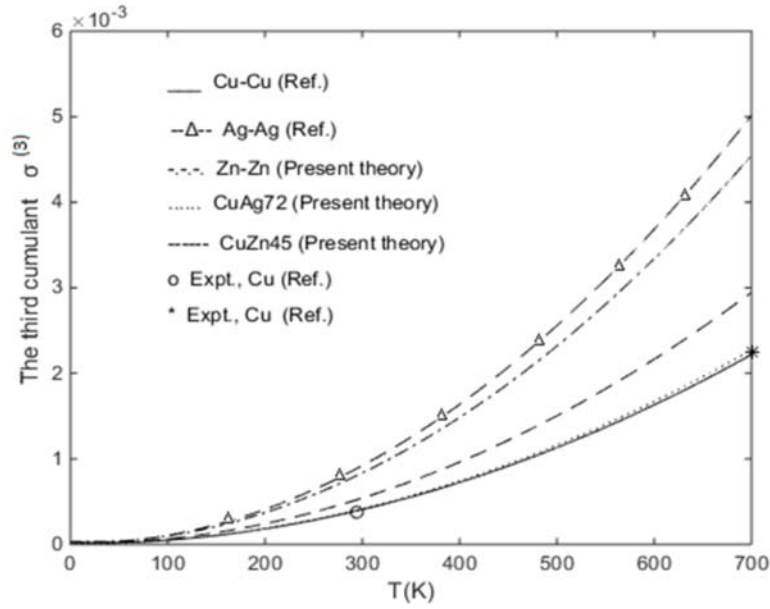


Figure 5. Temperature dependence of the third cumulant for Cu, Ag, Zn, and their alloys, with the effect of DR.

Figure 6 description dependence of the thermal expansion coefficient α_T on temperature and effects DR for Cu-Cu, Ag-Ag, Zn-Zn, CuAg72, and CuZn45, with the absolute temperature T , the thermal expansion coefficient α_T have the form of the specific heat C_V , thus reflecting the fundamental principle of solid state theory that the thermal expansion results from anharmonic effects and is proportional to the specific heat C_V [14], the calculated values of α_T approach the constant value α_T^0 at high temperatures and vanish exponentially with θ_E/T at low temperatures, which agrees with the findings of other research [15].

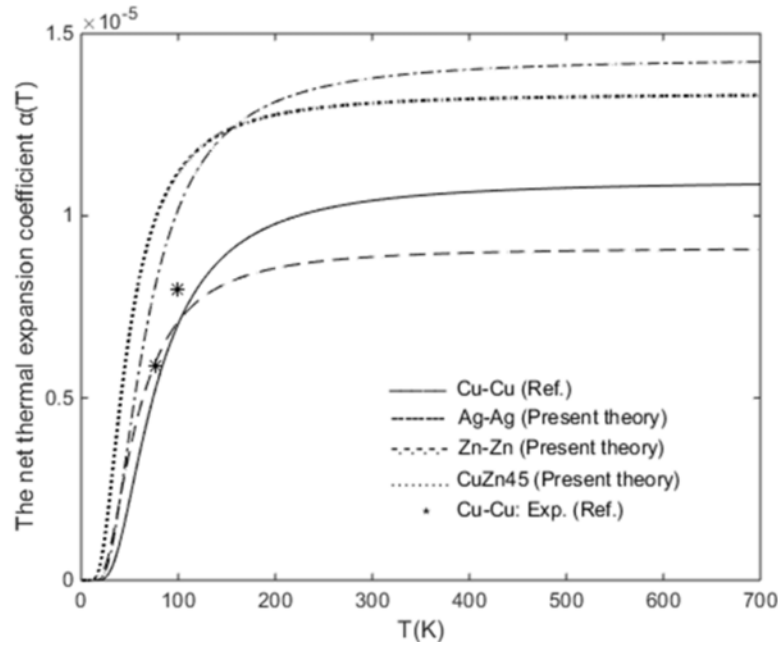


Figure 6. Dependence of thermal expansion coefficient on temperature and effect of DR.

4. Conclusion

A new analytical theory for calculating and evaluating the thermodynamic properties of Cu, Ag, and Zn, taking into consideration the effects of the DRs in alloys was developed based on quantum statistical theory with the effective anharmonic Einstein potential. The expressions for the thermodynamic parameters, effective force constant, correlated Einstein frequency and temperature, and cumulants expanded up to third order for Cu, Ag, and Zn crystals and their alloys agree with all the standard properties of these quantities. The expressions used in the calculations for the orderly doped crystals have similar forms to those for pure crystals. Figures 1-6 show the dependence of thermodynamic parameters on temperature and effects the DR for the crystals, they reflect the properties of anharmonicity in EXAFS and agree well with

results obtained in previous studies. Reasonable agreement was obtained between the calculated results and experimental and other studies of Cu, Ag, Zn, CuAg72, and CuZn45, this indicates that the method developed in this study is effective for calculating and analyzing the thermodynamic properties of doped crystals based on the ACEM in EXAFS theory.

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