INTRODUCTION

1 Reason for choosing topic

X-ray Absorption Fine Structure (XAFS) gives information about the number of atoms and in a shell Fourier image of the XAFS spectra gives information about the radius of the atomic layer, so XAFS is one of the empirical methods for analyzing and determining the structure of the object.

Initially, XAFS theory formulated as harmonic theory, and it was used to calculate some thermodynamic parameters and give good coincidence with XAFS spectra measured at low temperature. But when the temperature rises, there is an anharmonic effect and if no attention it can get bias of information physics. From that fact, it was necessary to build an anharmonic XAFS theoretical model to study the thermodynamic parameters at high temperatures, and cumulant expansion approximation was born to determine the errors in anharmonic effect. Initially, the cumulant expansion approximation was used mainly to match the theoretical construction spectra with the experimental data measured at high temperatures, and then to derive the physical parameters. The cumulants expansion have been studied by many scientists given different calculation methods, thereby deducing the thermodynamic parameters and crystal structure.

Several theories have been formulated to analyze the cumulants of the XAFS spectra with anharmonic contributions in which the Anharmonic-correlated Einstein model (ACEM) gave experimental results better than the other models. Therefore, the Anharmonic-correlated Einstein model has been of interest to some groups and has been used to study the structure of pure and doped solid objects, in which for simple one ignore dispersion of the phonons in Einstein method. An important development of this method is that the model takes into account the interactions between the absorbing and scattering atoms with neighboring atoms in a small cluster of atoms.

In addition to anharmonic effects of temperature, XAFS spectra are also very sensitive to effects of pressure due to pressure affects on atom displacement. Previous research contents have not seriously considered the dependence on doping ratio and pressure for alloys cubic structure.

2 Research purposes

(1) Continue to develop and generalize Continue to develop and generalize the ACEM model while using the ACDM model to build general expressions for thermal expansion, elastic coefficient, frequency of oscillation and Einstein's correlation temperature, the first

cumulant a representation of the asymmetry of the atomic pair potential or lattice expansion, the second cumulant or the Debye-Waller factor, the third cumulant reflect the phase shift of the XAFS spectra due to the anharmonic effect.

(2) Construct the expression for XAFS with the anharmonic contribution of high temperatures and include the anharmonic XAFS theory at low temperatures.

(3) Build an effective interaction potential with the contribution of neighboring atoms. Theomodynamic parameter, anharmonic contributions to amplitude and phase of the XAFS spectra as well as the XAFS spectra.The calculation applied to the pure cubic crystal structure and alloys, while also considering the effect of pressure on the XAFS spectra. The results were compared with experiment and other theories.

3 Research methods

- The thesis used the quantum statistical method and perturbation method in which Hamilton's operator is written as the sum of the harmonic and anharmonic contribution(as a perturbation). The anharmonic effects are the result of phonon interactions, so the transition between states carried out through the annihilation and creation operators of the secondary quantization method.
- The physical quantities are calculated using the density matrix.
- The analytical results have calculated by Matlab software.

4 Scientific significance and practice of the thesis

The research problems posed by the thesis all come from the problems of modern physics, the obtained results may contribute to perfecting the Anharmonic-correlated Einstein model.

The research results compared with experimental results and other theoretical models published in prestigious journals showed good coincidence and pointed outstanding advantages of the results in the thesis.

The results of the thesis have published in specialized journals and seriously evaluated by the reviewers.

5 New contributions of the thesis

The thesis generalization anharmonic correlated Einstein model, construct general analytical expressions of thermodynamic parameters with anharmonic contributions.

With the quantum statistics method, the thesis uses the expressions obtained in the correct calculation for the entire temperature range. Thermodynamic parameters described through structural parameters, through these structural parameters, we can predict the structure of the crystal and the distribution of the atoms on an atomic shell.

The thesis expands on the calculation of thermodynamic and cumulants parameters

for systems with doped cubic structure and the effect of pressure according to ACEM in the effective anharmonic XAFS spectra. The numerical results show that there is a good agreement between the present theory and the experimental results.

6 The layout of the thesis

Chapter 1. **Overview of the delicate X-ray absorption fine structure**
his program aims to present some general theories about X-rays and Shynchrotron, XAFS spectroscopy and absorption, XAFS spectroscopy, Fourier image and structural information.

Chapter 2. **Construct the cumulant expressions and thermodynamic parameters.**.

The thesis presents a number of cumulant calculation models in order to give specific comments on the advantages and disadvantages of the models, thereby giving a plan to overcome the shortcomings, thereby building the optimal method to calculate the cumulants. of the XAFS spectrum. The thesis presents how to calculate the structural coefficients and thereby generalize the Einstein model unconditionally correlated through the structural coefficients, thereby building the computational coefficients of cumulants, thermodynamic parameters through the structural coefficients and the Debye - Waller factor.

Chapter 3. **Theory of the Anharmonic XAFS spectra**.

The dissertation gave the formula of XAFS spectra, including anharmonic effects and described by cumulant expansion approximation. The thesis has also built a new general analytical expression of the anharmonic factor, and the received expressions reflects the anharmonicity of atomic oscillation as obtained from the experiment, from which the thesis calculates the new expressions of the contribution to phase shiff of the anharmonic XAFS spectra, including the cumulants contribution. The thesis has rewritten the expressions of the EXAFS spectra, including the anharmonic effects, and the thesis also expanded to study the pressure dependence and doping ratio of the cumulants and thermodynamic parameter in the anharmonic XAFS spectra.

Chapter 4 **Calculate and discuss the results**.

In this chapter, the thesis has calculated the number for the thermodynamic parameters according to the coefficients obtained in chapters 2 and 3. In this thesis, numerical calculation is applied to some crystals and extended to the doped cube crystal and takes into account the effect of pressure..

Conclusion: Overview the main results obtained and propose research directions in the future..

Chapter 1

Overview of the X-ray absorption spectrum

1.1 X-rays and Synchrotron radiation

Continuous X-ray spectrum and interrupted X-ray spectrum

X-rays were discovered by Wilhelm Conrad Röntgen in 1895 and have made an important contribution to the study of the structure of materials, using X-ray radiation and Synchrotron radiation as the source of photons in interaction with objects. The result of this interaction is the spectrum containing information about the electronic and atomic structure of the solid.

1.2 Spectroscopy XAFS

XAFS spectra with K edge for polycrystalline, has form:

$$\chi(k) = \sum_j \frac{S_0^2 N_j}{k} F_j(k) \times Im\left[\left\langle \frac{1}{r_j^2} \exp\left(2ikr_j - \frac{2r_j}{\lambda}\right)\right\rangle \exp\left(i\delta_j(k)\right)\right]. \qquad (1.1)$$

1.3 Fourier image of the XAFS spectra

It was discovered that the Fourier image of the XAFS spectra gives information about the structure of the object, namely that the peaks of the Fourier image correspond to the radius of the atom layers, so through the Fourier image, we get information about the position r of the atomic shells of the crystal. The Fourier transformation is performed as follows:

$$F(r) = \int \frac{dk}{2\pi} e^{-2ikr} \chi(k) k^n, \ \ n = 1, 2, 3 \ldots \qquad (1.2)$$

Chapter 2

Construct the expressions of the thermodynamic parameters

2.1 Distribution function

XAFS spectra with K:h K edge can be written by the following system:

$$\chi(k) = NF(k) \int \frac{\rho_1(r)}{r^2} e^{-2r/\lambda(k)} \sin[2kr + \delta(k)] dr, \tag{2.1}$$

N is the number of atoms per atomic shell, $F(k), \delta(k)$ is the amplitude and phase of the scattering, including all the contributions of the absorbing atoms, $\lambda(k)$ is the average free step of the photoelectric and depends on the ware-numbe k, $\rho_1(k)$ is the probability distribution of the atoms on the shell and the normalized condition gives $\int \rho_1(r) dr = 1$, $\rho_1(r)$ is related to the three-dimensional distribution $\int \rho(r) d^3 r = 1$, by $\rho_1(r) = 4\pi r^2 \langle \rho(r) \rangle_\Omega$, with $\langle \rangle_\Omega$ represents the average of the angle 4π, $\rho_1(r)$ is zero when $r < 0$. Note that both $\langle \rho(r) \rangle_\Omega$ and $\rho_1(r)$ can be asymmetry for their average distance if $\rho(r)$ is symmetry.

The distribution function can be as follow:

$$P(r, \gamma) \equiv \frac{\rho_1(r)}{r^2} e^{-2\gamma}, \tag{2.2}$$

and Fourier transform the above system to the form:

$$\overline{P}(\overline{r}, \gamma; k) \equiv \int P(r, \gamma) e^{2ik(r-\overline{r})} dr, \tag{2.3}$$

where $\gamma \equiv \lambda^{-1}$ and $\overline{r}$ are the parameters late selected. Rewrite equation (2.1) according to the distribution function

$$\chi(k) = NF(k) Im\left[e^{i(2k\overline{r} + \delta(k))} \overline{P}(\overline{r}, \gamma; k) \right]. \tag{2.4}$$

We define in the formulas for the real amplitude and phase of oscillation satisfying form

$$\chi(k) \equiv A(k) \sin \phi(k),$$

with

$$A(k) = NF(k) \left[\; \overline{P}(\overline{r}, \gamma; k) \right], \tag{2.5}$$

$$\phi(k) = 2k\overline{r} + \delta(k) + \arg \overline{P}(\overline{r}, \gamma; k). \tag{2.6}$$

These expressions correspond to the amplitude and phase equations of the electron spectra obtained through Fourier transform.

The distribution function $\overline{P}(\overline{r}, \gamma; k)$ can be expanded according to the displacement moments of the form effective distribution

$$\overline{P} = \sum_{n=0}^{\infty} \frac{(2ik)^n}{n!} P_n, \tag{2.7}$$

in which

$$P_n(\overline{r}, \gamma) = \int P(r, \gamma)(r - \overline{r})^n dr. \tag{2.8}$$

If $\overline{r}$ is close to the center of $P(r, \gamma)$, then the ratio $\frac{P_n}{P_0}$ has the same magnitude as the exponent n of the distance extension Δr.

In the above formulas, P_n are functions of $\overline{r}$ and γ, can be seen in the above expansion, at small values of k only low order moment are important, but when k increases, higher order moment will be taken from all contributing orders. The above expansion is essentially an expansion to the powers of $(2k\Delta r)$, Δr the characteristic width in the perturbation of the distribution.

2.2   Cumulant expansion

The cumulant expansion is performed using the following relation:

$$\left\langle e^{\xi x} \right\rangle = \exp \Big[\sum_{n=0}^{\infty} \frac{\xi^n \sigma^{(n)}}{n!} \Big], \qquad (n \geq 0), \tag{2.9}$$

$<>$ is represents the mean of each distribution of the variable x, which will be appropriately discarded. Obviously $\sigma_0 = 0$ if the distribution is normalized. We define the cumulants by the correlation relation

$$\int P(r, \gamma) e^{2ik(r-\overline{r})} dr \equiv \exp \Big[\sum_{n=0}^{\infty} \frac{(2ik)^n}{n!} \sigma^{(n)}(\overline{r}, \gamma) \Big]. \tag{2.10}$$

Expanding the above relation by Taylor series and separating even-order cumulants we will get expressions of the amplitude of the oscillation

$$\ln \frac{A(k)}{NF(k)} = \ln |\overline{P}| = \sum_{n=0}^{\infty} \frac{(-1)^n}{(2n)!} (2k)^{2n} \sigma^{(2n)}, \tag{2.11}$$

and odd order cumulants that describe the phase of the atomic oscillation

$$\phi(k) - \delta(k) = \arg \overline{P} = 2k\overline{r} + \sum_{n=0}^{\infty} \frac{(-1)^n}{(2n+1)!} (2k)^{2n+1} \sigma^{(2n+1)}. \tag{2.12}$$

Since the amplitude and phase of the oscillation depend on k it can't depend on our choice of $\overline{r}$, we see that the cumulant $\sigma^{(n)}$ with $n \neq 1$ is independent of the origin point.

This is also described from the equation (2.10) with relation to $\bar{r}$ with the use of linear dependence on powers of k.

The cumulants equal to or less than the power moments, if $\bar{r} = 0$ we can obtain the formulas

$$\frac{dP_n}{dq} = P_{n+1},$$

and

$$\frac{d\sigma^{(n)}}{dq} = \sigma^{n+1},$$

with $n \geq 0$ and $q \equiv -2\gamma$. According to equations (2.7) (2.8) and (2.10) so

$$\sigma^{(0)}(\gamma) = \ln P_0(\gamma).$$

Combining the above relations, we can write the expansion of cumulants in the following form

$$\sigma^{(1)} = \frac{d\sigma^{(0)}}{dq} = \frac{d\ln P_0}{dq} = \frac{1}{p_0}\frac{dp_0}{dq} = \frac{p_1}{p_0} = p_1, \tag{2.13}$$

and

$$\sigma^{(2)} = \frac{d}{dq}\frac{p_1}{p_0} = p_2 - p_1^2, \tag{2.14}$$

$$\sigma^{(3)} = p_3 - 3p_2p_1 + 2p_1^3, \tag{2.15}$$

$$\sigma^{(4)} = p_4 - 4p_3p_1 - 3p_2^2 + 12p_2p_1^2 - 6p_1^2, \tag{2.16}$$

$$\sigma^{(5)} = p_5 - 5p_1p_4 + 20p_1^2p_3 - 60p_1^3p_2 - 10p_2p_3 + 30p_1p_2^2 + 24p_1^5, \tag{2.17}$$

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2.3 Some models compute cumulants

In this part, the thesis briefly introduces some models currently used to approximate cumulants.

2.3.1 Statistical Moment Method - SMM

SMM has been developed to study the temperature dependence of the spacing between atoms and the thermodynamic properties of materials. To describe the relationship between MSRD and MSD for DWF, SMM represents MSRD by form:

$$\sigma^2 = \left\langle \left[(\mathbf{u}_i - \mathbf{u}_0).\mathbf{R}\right]^2 \right\rangle = \left\langle (\mathbf{u}_i.\mathbf{R})^2 \right\rangle + \left\langle (\mathbf{u}_0.\mathbf{R})^2 \right\rangle - 2\left\langle (\mathbf{u}_i.\mathbf{R})(\mathbf{u}_0.\mathbf{R}) \right\rangle. \tag{2.18}$$

Using the expressions of the second moment in SMM we get the expression for MSD and from there we have:

$$\sigma^2(T) \approx \frac{4\gamma^2\beta^3}{B^5}\left(1 + \frac{Z}{2}\right)\left(Z + 1\right) + \frac{2\beta Z}{k} + 2\beta\frac{k - B}{kB} \tag{2.19}$$

2.3.2 Path-Integral Effective Potential-PIEP

PIEP has been applied to calculate the cumulants in XAFS anharmonic for multidimensional systems with many degrees of freedom. PIEP is an accurate and efficient method for calculating cumulants.This method includes quantum effects, anharmonic effect and computable effects for three-dimensional crystals, as well as systems with many degrees of freedom. However, the cumulative calculation according to the PIEP method is very complicated, with many calculation steps with many parameters.

2.3.3 ACDM - Anharmonic Correlation Einstein Model

The ACDM builds on the main ideas is: (1) Consider the correlation contributions of the neighboring atoms and take into account the dispersion of the phonons. (2) The anharmonic effective potential contains the contributions of anharmonic components. (3) The anharmonic components is considered perturbation and is the result of the phonon-phonon interaction, in which the lattice displacement is represented by the operator. The cumulant approximation of the anharmonic XAFS function has form:

$$\chi(k) \sim Im\{e^{i\Phi(k)} exp\big(2ikR + \sum_{n} \frac{(2ik)^n}{n!} \sigma^{(n)}(T)\big)\} \tag{2.20}$$

Expansion of the interaction potential for a system consisting of one type of atom up to the 4th order:

$$U_{eff}(x) \approx \frac{1}{2} k_{eff} x^2 + k_3 x^3 + k_4 x^4, \tag{2.21}$$

The effective anharmonic bonding potential can be determined by

$$U_{eff}(x) = U(x) + \sum_{i=0,1} \sum_{i\#j} U\big(\frac{1}{2} x \hat{R}_{01}.\hat{R}_{ij}\big) \tag{2.22}$$

Compare (2.22) with (2.21) we define the effective constants. Due to the dispersion of the phonon, express the parameter x through the phonon displacement operator containing the statistical component according to the phonon oscillation frequencies. Consider the oscillation system of the object N oscillating with a frequency in the range from 0 to maximum Debye frequency ω_D. In a one-dimensional system consisting of only one type of atom, we have;

$$\omega(q) = 2\sqrt{\frac{k_{eff}}{M}} |sin\big(\frac{qa}{2}\big)|, |q| \leq \frac{\pi}{a}, \tag{2.23}$$

At the border of the first Brillouin (BZ) we have

$$\omega_D = 2\sqrt{\frac{k_{eff}}{M}}, \theta_D = \frac{\hbar \omega_D}{k_B} \tag{2.24}$$

displacement u_n is related to the phonon A_q shift operator by expression:

$$x_n = \sum_{q} e^{iqan} f(q) A_q, f(q) = \sqrt{\frac{\hbar}{2NM\omega(q)}} \big(e^{iqa} - 1\big). \tag{2.25}$$

The Hamiltonian of the system is rewritten as the sum of the non-harmonic H_0 and the H_a non-harmonic components, in which the non-harmonic component H_a consists of the 3rd and 4th components.

$$H_c = k_3 x^3 = \sum_{q_{1,2,3}} U(q_{1,2,3}) A_{q_1} A_{q_2} A_{q_3} = \sum_{q_1, q_2, q_3} U(q_1, q_2, q_3) A_{q_1} A_{q_2} A_{q_3}, \qquad (2.26)$$

$$H_q = k_4 x^4 = \sum_{q_{1,2,3}} U(q_{1,2,3,4}) A_{q_1} A_{q_2} A_{q_3} A_{q_4} = \sum_{q_1, q_2, q_3, q_4} V(q_1, q_2, q_3, q_4) A_{q_1} A_{q_2} A_{q_3} A_{q_4},$$

$$(2.27)$$

Replace (2.25) to (2.26), 2.27 and the transformation we get;

$$U_{(q_{123})} = k_3 \left(\frac{\hbar}{2NM}\right)^{3/2} \left(\sum_n e^{i(q_1, q_2, q_3)an}\right) \frac{(e^{iq_1 a} - 1)(e^{iq_2 a} - 1)(e^{iq_3 a} - 1)}{\sqrt{\omega(q_1)\omega(q_2)\omega(q_3)}} \qquad (2.28)$$

$$U(q_{1234}) = k_4 \left(\frac{\hbar}{2NM}\right)^2 \left(\sum_n e^{i(q_1+q_2+q_3+q_4)an}\right) \frac{(e^{iq_1 a} - 1)(e^{iq_2 a} - 1)(e^{iq_3 a} - 1) + (iq_4 a - 1)}{\sqrt{\omega(q_1)\omega(q_2)\omega(q_3)\omega(q_4)}}$$

$$(2.29)$$

2.4 Anharmonic-correlated Einstein model-ACEM

Anharmonic-correlated Einstein model (ACEM) is based on the beam correlation contribution nearest neighboring atoms, in which the dispersion of phonons in Einstein's method has been omitted for simplicity. An important development in this approach is that the model takes into account the interactions between the absorbing and scattering atoms with neighboring atoms in a small cluster of atoms. Therefore, ACEM is described through a form of effective interaction potential

$$U_E(x) \approx \frac{1}{2} k_{eff} x^2 + k_3 x^3 + \dots, \qquad (2.30)$$

With $x = r - r_0$ is the instantaneous bonding deviation between two atoms in an equilibrium position, k_{eff} is the effective elastic coefficient because it includes all contributions of neighboring atoms, k_3 is the third order parameter that characterizes the anharmonicity and creates the asymmetry of the interaction potential. Anharmoniccorrelated Einstein model is determined by the oscillation of a bond pair of atoms with mass M_1 and M_2 (the absorbing and scattering atoms, respectively). Their vibrations are influenced by neighboring atoms, so the effective interaction potential in ACEM has a form

$$U_E(x) = U(x) + \sum_{j \neq i; i = 0, 1} U\left(\frac{\mu}{M_i} x \hat{R}_{01}.\hat{R}_{ij}\right), \qquad (2.31)$$

with $\mu = \frac{M_1 M_2}{M_1 + M_2}$ is called reduced mass, $\hat{R}$ is the unit vector, $U(x)$ characterizes the pair potential between the absorbing and scatering atoms has form:

$$U(x) = D\left[-1 + \alpha^2 x^2 - \alpha^3 x^3 + \frac{1}{2}\alpha^4 x^4 + \dots\right]. \qquad (2.32)$$

Vibrations of the atoms are calculated according to quantum statistics with standard harmonic approximation, in which the Hamiltonian operator of the system is written as;

$$H = \frac{P^2}{2\mu} + U_E(x) = \frac{P^2}{2\mu} + \frac{1}{2}k_{eff}x^2 + k_3 x^3 + \cdots =$$

$$= \frac{P^2}{2\mu} + \left(\frac{1}{2}k_{eff}a^2 + k_3 a^3\right) + y\left(k_{eff}a + 3k_3 a^2\right) + y^2\left(\frac{1}{2}k_{eff} + 3k_3 a\right) + k_3 y^3 + \cdots . \quad (2.33)$$

Transform the expression (2.33) we have

$$H = H_0 + U_E(a) + \delta U_E(y), \quad (2.34)$$

From (2.34) we have anharmonic effective potential according to ACEM can be written in form;

$$U_E(y) = U_E(a) + \frac{1}{2}k_{eff}y^2 + \delta U_E(y). \quad (2.35)$$

Chapter 3

Theory of the anharmonic XAFS spectra

3.1   XAFS spectroscopy and characteristic quantities

At low temperatures, the calculation of XAFS spectra can be performed in harmonic approximation since the anharmonic contributions of the thermal vibrations of the atom are small and can be ignored. But as the temperature rises, the thermal fluctuations of the atoms cease to be harmonic, and the interaction potential between atoms becomes asymmetric because of the appearance of anharmonic effects. Thus, we need to build a way to determine the XAFS spectra, including the contribution of the anharmonic effects. An approximate cumulant expansion approach often describes the formulation of the XAFS spectra, including the anharmonic effects. Accordingly, the XAFS oscillator function is usually written as follows

$$\chi(k) = F(k)\frac{e^{-2R/\lambda(k)}}{kR^2} \times Im\left\{ e^{i\phi(k)} \exp\left[2ikR + \sum_n \frac{(2ik)^n}{n!}\sigma^{(n)} \right] \right\}, \qquad (3.1)$$

in the expression, $F(k)$ represents atomic scattering amplitude, $\phi(k)$ is the total phase shift displacement of the photoelectron, k is the number of waves and $\lambda(k)$ is the average free distance of the photoelectron, $\sigma^{(n)}$, $n = 1, 2, 3, ...$ are cumulants, they appear due to function averaging $\left\langle e^{ikr} \right\rangle$, where the asymmetric terms are expanded in the Taylor series around the $R = < r >$ value, with r is the average distance between the absorbing and scattering atoms at temperature T and then the asymmetric components are written in the form of cumulants.

Expression (3.1) of the XAFS oscillator function includes anharmonic effects that contain the coefficient DWF due to the effects of thermal oscillation of the atoms. The extinction factor of the XAFS spectra would be $e^{w(k)}$ with

$$w(k) = 2ik\sigma^{(1)}(T) - 2k^2\sigma^2(T) - \frac{4ik\sigma^2(T)}{R}\left(1 - \frac{R}{\lambda(k)} \right) -$$

$$-\frac{4}{3}ik^3\sigma^{(3)}(T) + \frac{2}{3}k^4\sigma^{(4)}(T) + ... \qquad (3.2)$$

Because the anharmonic effect is usually small, XAFS analysis only requires third or fourth order cumulants, higher order cumulants can be ignored because their contribution to thermal oscillation is very small.

In the formula (3.2) only second (DWF) and the fifth term contributes to the amplitude change, while the first, third and fourth terms contribute to the phase shift of the XAFS spectra due to the anharmonic effect.

In which the phase of the XAFS spectrum is defined as:

$$\phi_A(T, k) = 2k\left[\sigma^{(1)}(T) - 2\sigma_A^2(T)\left(\frac{1}{R} - \frac{1}{\lambda(k)}\right) - \frac{2}{3}\sigma^{(3)}(T)k^2\right]. \tag{3.3}$$

It is evident from the above expression that the phase displacement $\phi_A(T)$ will rapidly decrease at low temperatures because the anharmonic values $\sigma^{(1)}, \sigma^{(3)}, \beta$ are insignificantly small.

3.2 Anharmonic XAFS spectra and applications

Temperature dependent XAFS spectroscopy including anharmonic effects are written as:

$$\chi(k, T) = \sum_j \frac{S_0^2 N_j}{kR_j^2}F_j(k)e^{-\left(2k^2\left(\sigma_H^2(T)+\sigma_A^2(T)\right)+\frac{2R_j}{\lambda(k)}\right)} \times$$

$$\times \sin\left[2kR_j + \phi(k) + \phi_A^j(k, T)\right]. \tag{3.4}$$

In the above equation S_0^2 is the term specific to the polypartic system, N_j is the number of atoms on the j shell, and the sum sign is for all atomic shells.

3.2.1 The pressure dependence of DWF in the anharmonic XAFS spectra

To consider the pressure dependence of cumulants including DWF we derive from the expression Gr$\ddot{u}$neisen.

$$\beta(T) = 2\gamma_G\frac{\Delta V}{V}, \tag{3.5}$$

factor γ_G factor depends on volume and through that is pressure, transform (3.5) we get the volume dependent of γ_G for form crystals:

$$\frac{\gamma_G\big(V(P)\big)}{V(P)} = -\frac{\gamma_G\big(V_0\big)}{V} = const, \tag{3.6}$$

with V and V_0 are the volume of a crystal at pressure P and zero.

From expressions (3.5) and (3.6), we will get Einstein correlation frequency and Einstein correlation temperature depending on pressure:

$$\omega_E\big(V(P)\big) = \omega_E(V_0)\exp\left[\gamma_G(V_0)\big(1 - \frac{V(P)}{V_0}\big)\right], \tag{3.7}$$

$$\theta_E\big(V(P)\big) = \frac{\hbar\omega_E\big(V(P)\big)}{k_B}, \tag{3.8}$$

$$\frac{V(P)}{V_0)} = \frac{r^3(P,T)}{r^3(0,0),} \tag{3.9}$$

here, $r(P,T)$ is the instantaneous distance between the two nearest atoms at a pressure of P and the absolute temperature T, $r(0,0)$ is the instantaneous distance between the two nearest atoms at zero pressure and zero temperature.

Use the results (3.7), (3.8) and (3.9), we obtain the pressure dependent expression of k_{eff}:

$$k_{eff}\big(V(P)\big) = \mu\omega_E^2\big(V(P)\big). \tag{3.10}$$

From expressions (3.7) - (3.10),We will get the DWF expression in XAFS of crystals as a function of pressure at a specified temperature:

$$\sigma^2(P,T) = \sigma_0^2\big(V(P)\big)\frac{1 + z\big(V(P),T\big)}{1 - z\big(V(P),T\big)}, \tag{3.11}$$

$$\sigma_0^2\big(V(P)\big) = \frac{\hbar\omega_E\big(V(P)\big)}{2k_{eff}\big(V(P)\big)}, \tag{3.12}$$

$$z\big(V(P),T\big) = \exp\left(\frac{-\theta_E\big(V(P)\big)}{T}\right). \tag{3.13}$$

From the 1st and 3rd cumulant expressions in section (2.8), we can write the pressure dependent functions at a given temperature:

$$\sigma^{(1)}(P,T) = \sigma_0^{(1)}\big(V(P)\big)\frac{1 + z\big(V(P),T\big)}{1 - z\big(V(P),T\big)}, \quad \sigma_0^{(1)}\big(V(P)\big) = \frac{3c_3\alpha}{c_1}\sigma_0^2\big(V(P)\big), \tag{3.14}$$

$$\sigma^{(3)}(P,T) = \sigma_0^{(3)}\big(V(P)\big)\frac{3\big(\sigma^2\big(V(P),T\big)\big)^2 - 2\big(\sigma_0^2\big(V(P)\big)\big)^2}{\big(\sigma_0^2\big(V(P)\big)\big)^2}, \tag{3.15}$$

$$\sigma_0^{(3)}\big(V(P)\big) = \frac{3c_3\alpha}{c_1}\big(\sigma_0^2\big(V(P)\big)\big)^2,$$

with $\sigma_0^{(1)}\big(V(P)\big)$, $\sigma_0^2\big(V(P)\big)$ and $\sigma_0^{(3)}\big(V(P)\big)$ are the pressure dependence of the zero contribution to the 1st, 2nd, and 3rd cumulants. These are described by the zero-point contribution function of the 2nd cumulant $\sigma_0^2\big(V(P)\big)$ and c_1, c_2, c_3 parameters.

3.2.2 The dependence on the doping ratio of the cumulants and the thermodynamic parameters in the anharmonic XAFS spectra

The interaction between pairs of atoms in the Anharmonic-correlated Einstein model is described by the effective interactive potential expression of the Morse anharmonic pair

potential with the instantaneous deviation of x of the atoms known by the expression (2.32).

Assume that the fusion of new atoms does not change the structure of the material, denoted the index of the original atom as 1 and the substitution atom is 2, we rewrite the relation (2.32) with the dissociation energy D instead D_{12} and parameters α replaced with α_{12}, would be:

$$U_E(x) = D_{12}\left[-1 + \alpha_{12}^2 x^2 - \alpha_{12}^3 x^3 + ... \right]. \tag{3.16}$$

For simplicity, the Morse potential parameters of the alloy are roughly determined using the following mean expressions:

$$D_{12} = \frac{C_1 D_1 + C_2 D_2}{2}, \tag{3.17}$$

$$\alpha_{12}^2 = \frac{D_1 \alpha_1^2 + D_2 \alpha_2^2}{D_1 + D_2}; \quad \alpha_{12}^3 = \frac{D_1 \alpha_1^3 + D_2 \alpha_2^3}{D_1 + D_2}. \tag{3.18}$$

With C_1, C_2 is the doping rate in a compound.

From expressions (2.31) and (3.17), (3.18) they will have an effective Einstein interaction:

$$U_E(x) = U_E(a) + \frac{1}{2}k_{eff}y^2 + \delta U_E(y). \tag{3.19}$$

Use potential Morse parameters in expressions (3.17), (3.18) and perform calculations for cubic crystal, we get k_{eff} and k_{3eff} of the alloy:

$$k_{eff} = c_1 D_{12}\alpha_{12}^2, \quad k_{3eff} = -c_3 D_{12}\alpha_{12}^3. \tag{3.20}$$

(1) The expression depends on the doping ratio of the cumulants

The analytical expressions of the cumulants depending on the temperature and the doping rate for cubic crystals have the following form:

$$\sigma^{(1)} = \frac{3c_3\hbar\omega_E}{2c_1^2 D_{12}\alpha_{12}} \frac{(1+z)}{(1-z)}, \tag{3.21}$$

$$\sigma^2 = \frac{\hbar\omega_E}{2c_1 D_{12}\alpha_{12}^2} \frac{(1+z)}{(1-z)}, \tag{3.22}$$

$$\sigma^{(3)} = \frac{c_3\hbar^2\omega_E^2}{4c_1^3 D_{12}^2\alpha_{12}^3} \frac{(1+10z+z^2)}{(1-z)^2}, \tag{3.23}$$

with $z = e^{-\beta\hbar\omega_E}$ is the temperature variable and is determined by the Einstein correlation frequency:

$$\omega_E = \sqrt{\frac{k_{eff}}{\mu_{12}}}, \tag{3.24}$$

and Einstein correlation temperature:

$$\theta_E = \frac{\hbar \omega_E}{k_B} = \frac{\hbar}{k_B}\sqrt{\frac{k_{eff}}{\mu_{12}}}, \Rightarrow \quad z = \exp\left(-\frac{\hbar}{k_B T}\sqrt{\frac{k_{eff}}{\mu_{12}}}\right) \tag{3.25}$$

Due to the reduce mass μ_{12} in the expression (3.25) is proportional to the atomic number of matter, so it depends on the doping ratio n, therefore the temperature variable z depends on both the absolute temperature T and the doping ratio n, the resulting cumulants are also dependent on the absolute temperature T and the doping ratio n.

For each alloy considered at a defined absolute temperature, for the n doping ratio of an alloy ranging from 0% to 100% in expressions (3.21)-(3.23) and represented graphically, we will have a line showing the dependence of the cumulants on the n doping ratio of matter with a doped cubic structure. In addition, we can also examine the case that cumulants are both temperature dependent and dependent on the doping ratio by (3.21), (3.22) and (3.23).

(2) The expression depends on the doping ratio of the thermodynamic parameters

Thermal expansion coefficient

The thermal expansion coefficient is dependent on the absolute temperature T and the doping ratio n of a cubic crystal is written as:

$$\alpha_{T,n} = \frac{3c_3 k_B}{c_1^2 D_{12} \alpha_{12} r} \frac{z(\ln z)^2}{(1-z)^2}. \tag{3.26}$$

Thermal expansion coefficient in (3.26) depends on z should follow the expression (??), it also depends on absolute temperature T and n of materials.

Anharmonic factor

Anharmonic factor β of the XAFS spectra for a doped system with a cubic structure:

$$\beta(n,T) = \frac{3c_1 c_2 \eta(T,n) k_B T}{32 D_{12}}\left[1 + \frac{c_2 c_3 k_B T}{4 D_{12} \alpha_{12} R}\left(1 + \frac{c_2 c_3 k_B T}{4 D_{12} \alpha R}\right)\right], \tag{3.27}$$

with:

$$\eta(T,n) = \frac{2\exp(-\frac{\theta_E}{T}) - \exp(-\theta_E)}{\left[1 - exp(-\theta_E)\right]\left[1 + \exp(-\frac{\theta_E}{T})\right]}. \tag{3.28}$$

Follow the expression (3.25), temperature correlation Einstein θ_E dependent μ_{12} therefore also depends on the doping rate n of crystals. From the expressions (3.27) and (3.28), we can see the anharmonic factor of the XAFS spectra also depends on T and the doping ratio n of materials.

Phase shift of the XAFS spectra

Phase expression ϕ_A of the XAFS spectra depends on the temperature determined by the expression (3.3), the cumulants are derived from equations (3.21), (3.22) and (3.23). Because the cumulants depend on the doping ratio n, so ϕ_A of XAFS phase shift also affected by the change of the doping ratio in the alloy namely:

$$\phi_A(T,k,n) = 2k\left[\sigma^{(1)}(T) - 2\sigma_A^2(T)\left(\frac{1}{R} - \frac{1}{\lambda(k)}\right) - \frac{2}{3}\sigma^{(3)}(T)k^2\right]. \tag{3.29}$$

Chapter 4

Calculation and discussion the results

4.1 Calculate the cumulants and thermodynamic parameters for the crystalline system with temperature and pressure dependent radial cubic structure by ACDM

Applying the theory mentioned in section (ref ACDM) for crystals with cubic structure fcc radial, the thesis has specifically calculated with Au and Pt crystals to confirm the suitability of the theory. Have presented with the results obtained by experiment and other theories.

According to the ACDM, the anharmonic effective potential has a form

$$U_{eff}(x) = U(x) + 2U\left(\frac{x}{2}\right) + 8U\left(-\frac{x}{4}\right) + 8U\left(\frac{x}{4}\right) \tag{4.1}$$

With Au crystal, the interactions between the atoms are hypothesized that can be described by the semi-experimental multi-particle interaction potential similar to the tight bonding model in the second order moment approximation;

$$U(r) = U^B(r) + U^R(r) \tag{4.2}$$

in the above expression;

$$U^B(r) = -\sqrt{\xi e^{-2q\left[(r/r_0)-1\right]}} \tag{4.3}$$

$$U^R(r) = Ae^{-p\left[(r/r_0-1)\right]}. \tag{4.4}$$

From the expression of the effective potential potential, we can determine

$$\omega_D = 2\sqrt{\frac{k_{eff}}{M}}; \theta_D = \frac{\hbar\omega_D}{k_B} \tag{4.5}$$

The cumulants in ACDM has form;

$$\sigma^{(1)} = \frac{3\hbar a k_3}{2\pi k_{eff}^2} \int_0^{\pi/a} \omega(q)\frac{1 + Z(q)}{1 - Z(q)}dq \tag{4.6}$$

$$\sigma^2 = -\frac{\hbar a}{2\pi k_{eff}} \int_0^{\pi/a} \omega(q)\frac{1 + Z(q)}{1 - Z(q)}dq \tag{4.7}$$

$$\sigma^{(3)} = \frac{3\hbar a^2 k_3}{4\pi^2 k_{eff}^3} \int_0^{\pi/a} dq_1 \int_{-\pi/a}^{\pi/a-q_1} F(q_1, q_2) dq_2$$

$$\sigma^{(4)} = \frac{9\hbar^3 a^3 k_4}{4\pi^3 k_{eff}^4} \int_0^{\pi/a} dq_1 \int_{-\pi/a}^{\pi/a-(q_1+q_2)} G(q_1, q_2, q_3) dq_3$$

The TB-SMA potential parameters determine the firt - principles calculations for gold bulk material are respectively $\xi = 1.8241eV$, $A = 0.2145eV$, $q = 4.3769$, $p = 108842$ và $r_0 = 28652$Å. Using these parameters, we derve the three force constants as follows $k_{eff} = 3.06eV/Å^2$, $k_3 = -1.58eV/Å^3$ and $k_4 = 1.49eV/Å^4$.

The thesis also considered the calculation of thermodynamic parameters for Pt crystals under the influence of pressure.

Using the dissertation's data to draw graphs to compare other theories and experimental values:
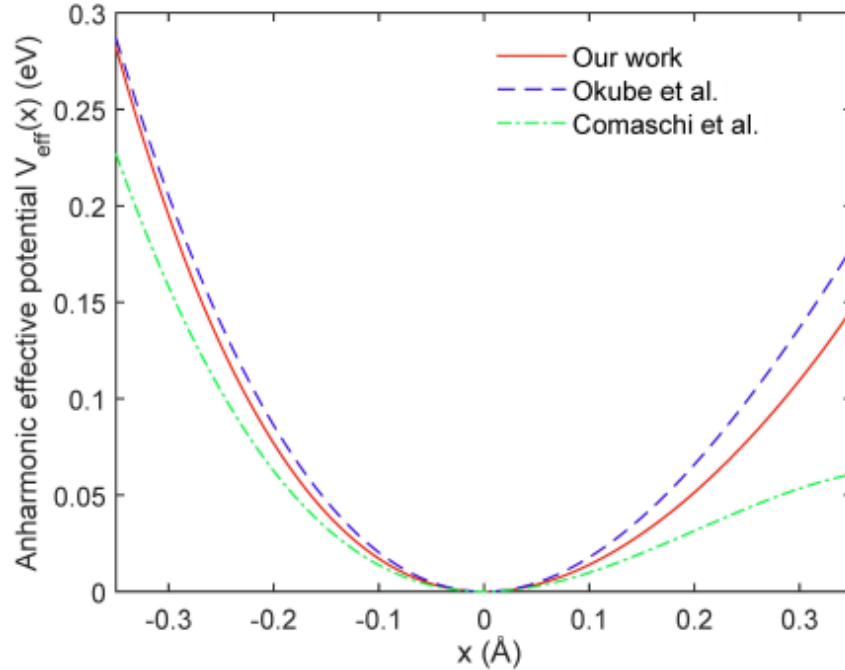

Figure 4.1: Anharmonic effective potential of gold

4.2 Calculate the cumulants and thermodynamic parameters for crystals with a cubic structure dependent on temperature and doping rate by ACEM, error and comparison.

4.2.1 Graph representing the thermodynamic parameters and parameters

Applying the expressions presented in section ref pt, we can calculate and plot the thermodynamic parameters of Cu-Ag doped crystal to evaluate the validity of the theory.
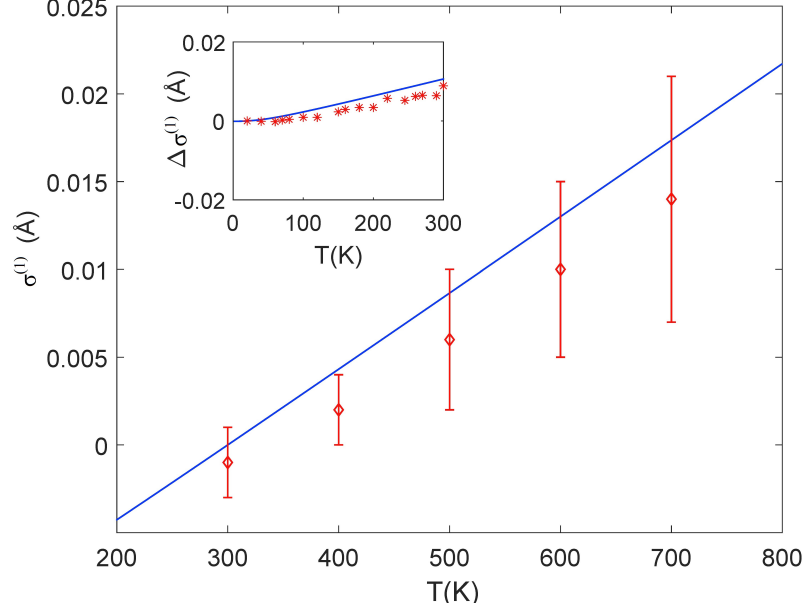
Figure 4.2: The temperature dependence of the first cumulant of gold. The solid line (—) is the thesis theory and experimental values of Newville

- *The firt cumulant*

$$\sigma^{(1)} = \frac{3\hbar}{40D_{12}\alpha_{12}}\sqrt{\frac{k_{eff}}{\mu_{12}}}\frac{\left(1 + exp\left(-\frac{\hbar}{k_BT}\left(\sqrt{\frac{k_{eff}}{\mu_{12}}}\right)\right)\right)}{\left(1 - exp\left(-\frac{\hbar}{k_BT}\left(\sqrt{\frac{k_{eff}}{\mu_{12}}}\right)\right)} \tag{4.8}$$

- *The second cumulant*

$$\sigma^{(2)} = \frac{\hbar}{10D_{12}\alpha_{12}}\sqrt{\frac{k_{eff}}{\mu_{12}}}\frac{\left(1 + exp\left(-\frac{\hbar}{k_BT}\left(\sqrt{\frac{k_{eff}}{\mu_{12}}}\right)\right)\right)}{\left(1 - exp\left(-\frac{\hbar}{k_BT}\left(\sqrt{\frac{k_{eff}}{\mu_{12}}}\right)\right)\right)} \tag{4.9}$$

- *The third cumulant*

$$\sigma^{(3)} = \frac{3\hbar^2\frac{k_{eff}}{\mu_{12}}}{200D_{12}^2\alpha_{12}^3}\frac{\left(1 + 10exp\left(-\frac{\hbar}{k_BT}\left(\sqrt{\frac{k_{eff}}{\mu_{12}}}\right) + exp\left(-\frac{\hbar}{k_BT}\left(\sqrt{\frac{k_{eff}}{\mu_{12}}}\right)\right)\right.}{\left(1 - exp\left(-\frac{\hbar}{k_BT}\left(\sqrt{\frac{k_{eff}}{\mu_{12}}}\right)\right)\right)^2} \tag{4.10}$$

With patameters $D_{12} = 0.03376(eV)$, $\alpha_{12} = 1.3638(\text{Å})^{-1}$, $k_{eff} = 3.31397(eVA^{-2})$, $k_{3eff} = 1.0705(eVA^{-3})$, $\hbar = 6.5822 \times 10^{16}(eV.s)$, $k_B = 8.617 \times 10^5(eVA^{-1})$, and $\mu_{12} = 108 - 44.5n$. With the above parameters, we plot the graphs representing the thermodynamic parameters of Cu-Ag crystals.

4.3   Error and comparison

To evaluate the validity of the theory that the thesis gives, we have calculated and compared the values of coefficients thermodynamic parameters of some crystals through
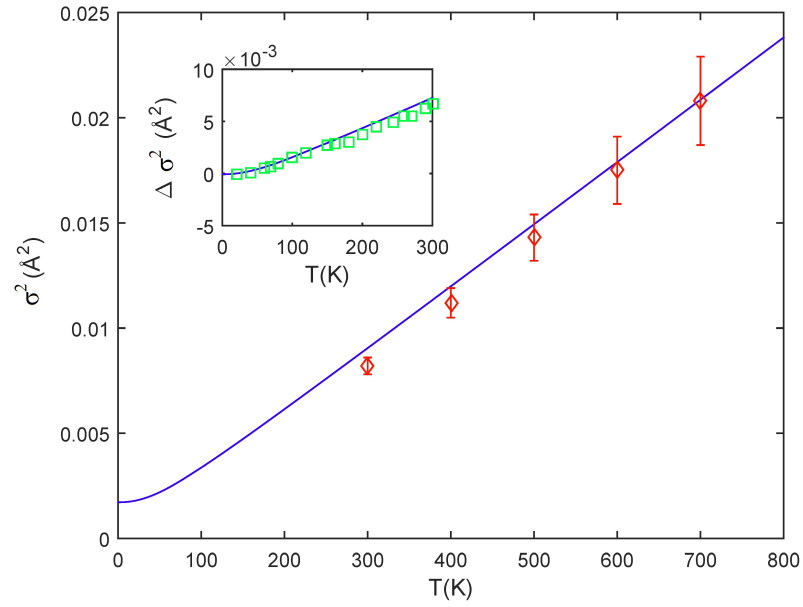
Figure 4.3: The temperature dependence of the second cumulant of gold compared with experimental values of Newville
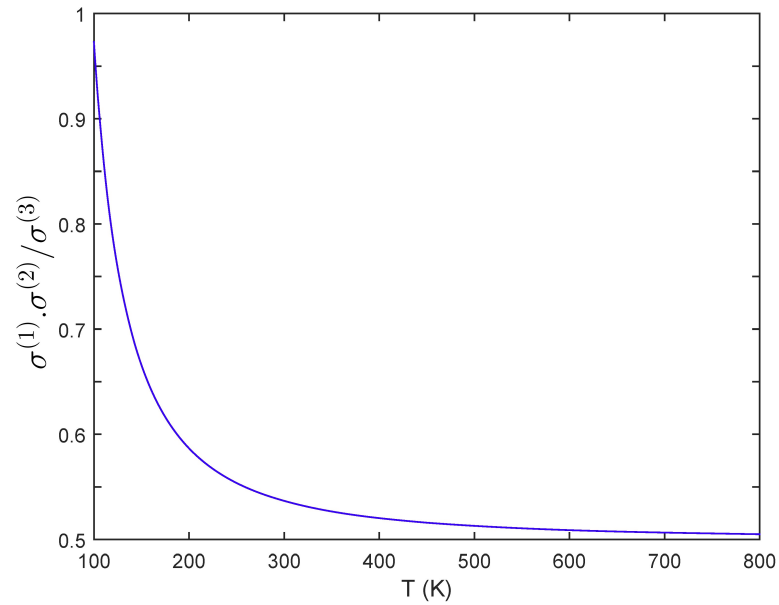

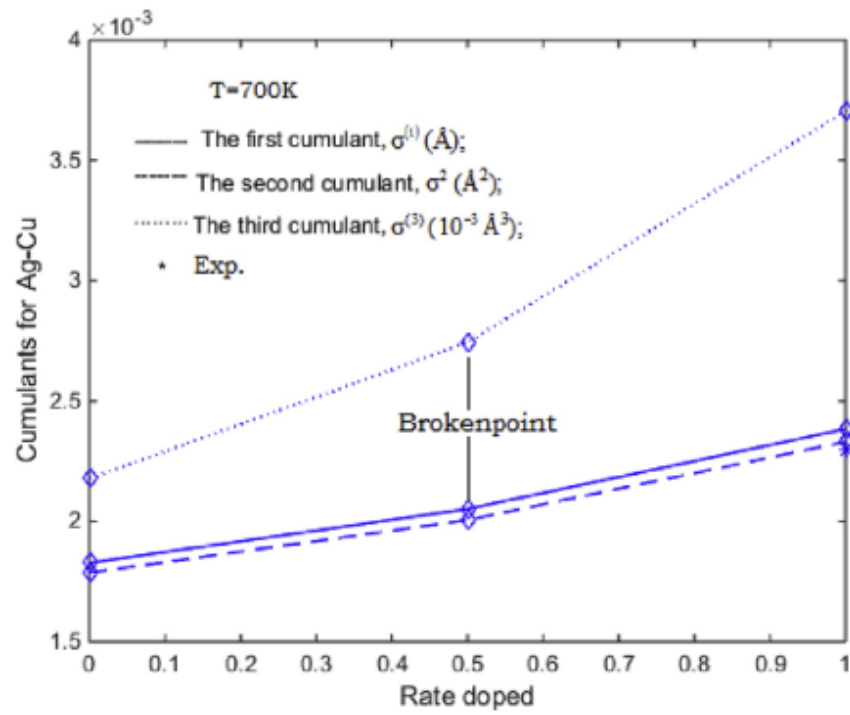Figure 4.4: Temperature dependence of cumulant rato $\sigma^{(}1).\sigma^{(}2)/\sigma^{(}3)$ of gold
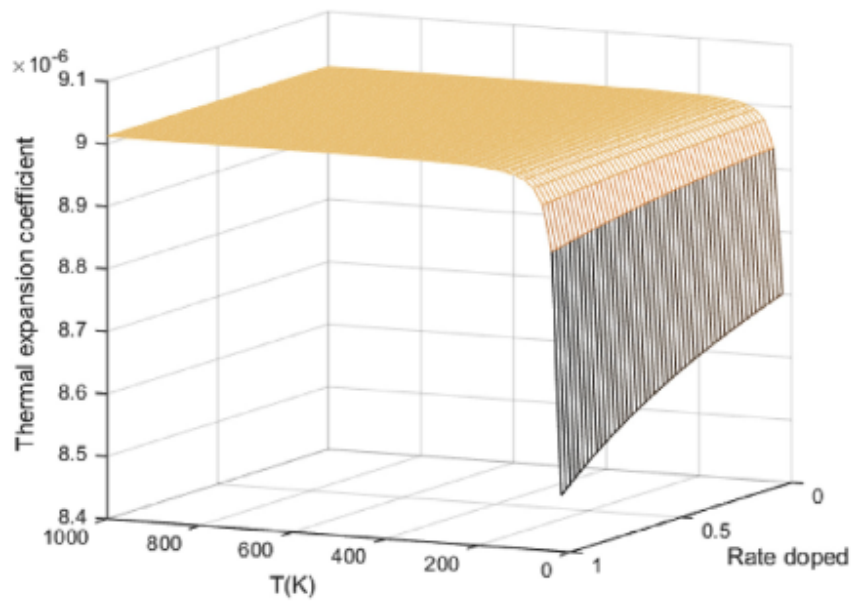
Figure 4.5: Dependence of cumulant ondoping ratio (DR)

Figure 4.6: Dependence of therma expansion coefficient on temperature and DR of Cu-Ag.
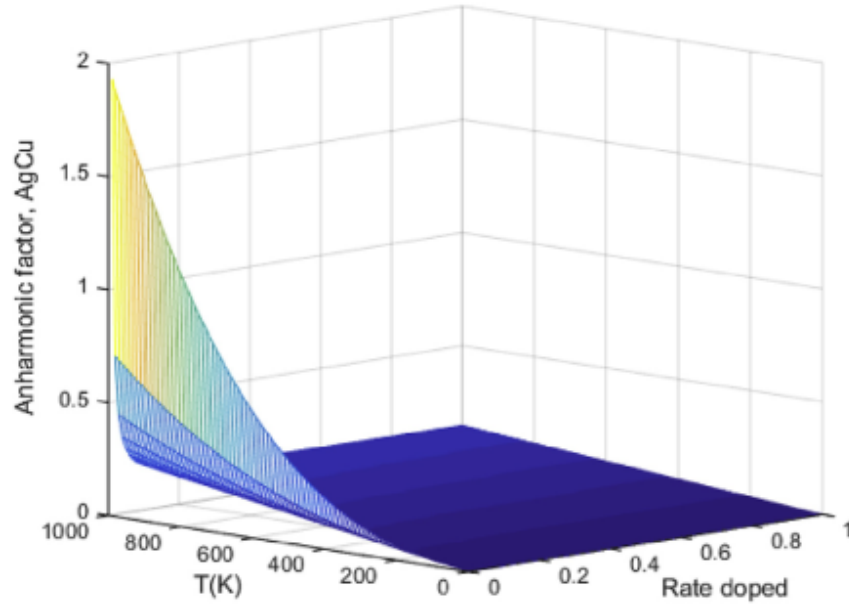
Figure 4.7: Dependence of anharmonic factor on temperature and DR of Cu-Ag.

the value table.

The thesis has calculated the relative error through the thermodynamic quantities according to the structural coefficients compared with the experimental values, for example the coefficient c_1 according to the formula:

$$\Delta c = \frac{|c_{calc.} - c_{expt.}|}{c_{calc.}},$$

"$calc.$" is the coefficient c calculate from our theory and "$expt$" is the measurement from the experiment.The results obtained according to the above formula are listed in Table (4.1).(θ_E) of Cu, (σ^2) of, or the third cumualnt ($\sigma^{(3)}$) of Cu, therma expansion coefficient (α_T) of W are the values measured from the experiment. The results obtained describe the high precision of the method of determining thermodynamic parameters through structural coefficients In particular the relative error of the quantities calculated by theoretical structural coefficients with measurements for fcc crystals just 1.2% for θ_E, with ω_D of Al it just2.5%,... The calculated data with very small error compared to the experiment confirmed that the use of ACEM in XAFS theory is appropriate.

Form	fcc	bcc	$Cu(\theta_E)$	$Cu(\sigma^{(3)})$	Al (σ^2)	$W(\alpha_T)$
$T^0 K$				600	295	2.000
experimental measu-rements			$237K$	0.00013	0.0287	$6.4 \times 10^{-5} K^{-1}$
c_1	5	3.667	5.036	5.018	3.6287	3.632
Δc			0.012	0.006	0.025	0.01

Table 4.1:   Table of examples of relative error of structure parameters c_1

Form	Type	$D_{12}(eV)$ (LT)	$D_{12}(eV)$ (TN)	α_{12} (LT)	α_{12} (TN)
Cu	Cu-Cu	0.354	0.3429	1.3590	1.3588)
Ag	Ag-Ag	0.3253	0.3323	1.3667	1.3690
Al	Al-Al	0.2709	0.2703	1.1874	1.1646
Ni	Ni-Ni	0.4314	0.4205	1.1584	1.1502

Table 4.2: Morse potential parameters calculated according to theory (LT) and experimental data (TN)

Form	Type	$k_{eff}(eVA^{-2})$ (LT)	$k_{eff}(eVA^{-2})$ (TN)	ω_E $(10^{13}Hz)$	$\theta_E(K)$ (LT)	$\theta_E(K)$ (TN)
Cu	Cu-Cu	3.1655	3.4931	3.0889	236	232
Ag	Ag - Ag	3.1139	2.9797	3.3933	176	167)
CuAg	Cu-Ag	3.1423	-	2.6874	207	-

Table 4.3:   The values of the parameters of anharmonic effective, Einstein frequency and Einstein temperature

CONCLUSION

The thesis directly contributes to solving an important and topical problem of modern XAFS theory, namely:

1. The dissertation has built up general analytical expressions of thermodynamic parameters through structural coefficients with anharmonized contributions. The expressions obtained contain classical results at the high temperature limit and contain the zero energy contribution, a quantum effect at low temperatures. The coefficient of thermal expansion has the form of isothermal capacity heat, so it satisfies the basic theory of thermal expansion.

2. The thesis has built up the effective interaction potential representing the relationship between the pair interaction potential and the effective interaction potential of the system and the contribution of neighboring atoms. It is possible to provide structural coefficients through which it is possible to simplify the memorization of thermodynamic expressions and cumulants, and to infer the structure of materials knowing these coefficients.

3. The thesis has expanded the research to calculate the thermodynamic parameters and cumulants for the system with doped cubic structure. Describe the dependence of the thermodynamic parameters and the cumulants on the doping rate of the material. The discovery of structural anomalies for CuAg50 alloy opens up a new research direction for graduate students of this material.

4. The thesis has studied the dependence of thermodynamic parameters on temperature and the influence of pressure according to the Debye model with effective anharmonized correlation in the non-regulated XAFS spectrum. As pressure increases, the mean squared displacement, a characteristic quantity of the Debye-Waller coefficient decreases, resulting in a decrease in the thermodynamic parameters as well as the amplitude of the XAFS spectrum. This phenomenon has not been fully explained, hoping to open a new research direction on the influence of pressure on thermodynamic parameters.

5. The good agreement between the numerical results of the thesis and the experimental values confirmed the advantages and feasibility of the theory that the thesis considers.

LIST OF PUBLICATIONS

1. Nguyen Ba Duc, Vu Quang Tho, Nguyen Van Hung, Doan Quoc Khoa, Ho Khac Hieu, *Anharmonic effects of gold in extended X-ray absorption fine structure*, Vacuum, 145, 272-277, (2017), (ISI, IF: 2.515).

2. Nguyen Ba Duc, Vu Quang Tho, Tong Sy Tien, Doan Quoc Khoa, Ho Khac Hieu, *Pressure and temperature dependence of EXAFS Debye-Waller factor of Platinum*, Radiation Physics and Chemistry, 149, 61-64, (2018), (ISI, IF: 1.43).

3. Nguyen Ba Duc, Vu Quang Tho, *Dependence of cumulants and thermodynamic parameters on temperature and doping ratio in extended X-ray absorption fine structure spectra of cubic crystals*, Physica B 552, pp 1-5, (2019), (ISI, IF: 1.5).