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High-order expanded XAFS Debye–Waller factors of HCP crystals based on classical anharmonic correlated Einstein model

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In this paper, high-order expanded anharmonic effective potential and Debye–Waller factors in X-ray absorption fine structure (XAFS) of hcp crystals have been studied based on classical anharmonic correlated Einstein model. Here XAFS Debye–Waller factors are presented in terms of cumulant expansion up to the fourth order and their analytical expressions have been derived based on classical statistical theory. They contain the parameters of a derived high-order anharmonic effective potential that takes into account all nearest neighbors of absorber and backscattering atoms, where Morse potential is assumed to describe interatomic interaction included in this derived anharmonic effective potential. The dependence of the derived cumulants on atomic vibrations is described by their proportionality to the correlated Einstein frequency. This model avoids full lattice dynamical calculations yet provides good agreement of numerical results for Zn and Cd with experiment at several temperatures.

Keywords: XAFS Debye–Waller factor; interatomic potential; classical correlated Einstein model; hcp crystals.

1. Introduction

Thermal vibrations and disorder in X-ray absorption fine structure (XAFS) give rise to Debye–Waller factors (DWFs) varying as $e^{-W(T)}$, which damp XAFS spectra with respect to increasing temperature T and wave number k (or energy).

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Anharmonicity in atomic interaction potential yields additional terms in DWF, which ignored can lead to non-negligible errors in structural parameters.[1–18] The formalism for including anharmonic effects in XAFS is often based on cumulant expansion,[1] where the even cumulants contribute to the amplitude, and the odd ones to the phase of XAFS. The accurate DWFs due to their exponential damping are crucial to quantitative treatment of XAFS spectra. Consequently, the lack of the precise DWFs has been one of the biggest limitations to accurate structural determinations (e.g. the coordination numbers and the atomic distances) from XAFS experiment. Therefore, investigation of DWF in XAFS is of great interest.

Many efforts have been made to develop procedures for calculation and analysis of XAFS and its parameters for different material systems using cumulant expansion approach,[2–18] where for small anharmonicities, it is sufficient to keep the third and fourth cumulant terms.[2] The anharmonic interatomic interaction potentials have also been intensively studied because they play an important role in the determination of the thermodynamic properties, anharmonic XAFS and its parameters of substances.[3–18] Several derived theories are limited to obtaining the second cumulant or mean square relative displacement (MSRD)[4–9] or to cumulant expansion up to the third order,[10–14] as well as to the second or three first orders of the interatomic interaction potentials involved in these studied cumulants and XAFS.[4–14] Such limitations are also there in studying the anharmonic XAFS and its parameters of Zn and Cd measured at HASYLAB (DESY, Germany) at 77 K and 300 K (Ref. 13) using the anharmonic correlated Einstein model[10] with cumulant expansion up to the third order. Anharmonic correlated Debye model[15] and full lattice dynamical theory[17] with cumulant expansion up to the fourth order have been derived, but they require many integrations over the first Brillouin zone and intensive full lattice calculations, respectively, to obtain the XAFS parameters. Classical theory is more simple and works very well at high-temperature.[3–5,16] It has been used for the calculation and analysis of DWFs included in high-temperature XAFS[3–5] and for interpreting the XAFS experimental results up to melting point,[16] where the anharmonic effects are important. Unfortunately, a classical analytical method for the calculation and analysis of high-order XAFS cumulants is not yet available.

The purpose of this work is to derive a classical anharmonic correlated Einstein model for studying the high-order expanded anharmonic effective potential and XAFS DWFs of hcp crystals, an interesting structure, that takes into account all nearest neighbors of absorber and backscattering atoms. The XAFS DWFs are presented in terms of cumulant expansion up to the fourth order instead of the lower ones.[4–14] In Sec. 2, the analytical expressions for the first $\sigma^{(1)}$, second σ^2, third $\sigma^{(3)}$, and fourth $\sigma^{(4)}$ XAFS cumulants have been derived based on classical statistical theory. The dependence of the obtained cumulants on atomic vibrations is described by their proportionality to the correlated Einstein frequency. The anharmonic effective potential has been developed further for hcp crystals with expansion up to the fourth order instead of the lower ones,[8–14] as well as of the single-pair[17] and single-bond model[18] potentials. The derived high-order XAFS cumulants contain the parameters of the high-order anharmonic effective potential to describe their direct relation. Morse potential is assumed to describe interatomic interaction included in the derived anharmonic effective potential. Numerical results for Zn and Cd (Sec. 3) are compared to the experimental values extracted from XAFS spectra measured at HASYLAB (DESY, Germany) at 77 K and 300 K (Ref. 13) to specify the temperatures at which they are found to be in good agreement. Moreover, based on this comparison we discuss the limitation of a classical theory for the first and second cunulants at low temperatures and the reduction of this limitation for the third and fourth cumulants. The cumulant ratio $\sigma^{(1)}\sigma^2/\sigma^{(3)}$ has been calculated to show its difference from that obtained from quantum theory.[10,13]

2. Formalism

To determine thermodynamic parameters of a crystal it is necessary to specify its interatomic potential and force constant.[10–18] Let us consider an anharmonic interatomic effective potential expanded up to the fourth order

$$V_{\text{eff}}(x) \approx \frac{1}{2}k_{\text{eff}}x^2 + k_{3\,\text{eff}}x^3 + k_{4\,\text{eff}}x^4, \quad x = r - r_0\,, \tag{1}$$

where k_{eff} is the effective local force constant, $k_{3\,\text{eff}}$ and $k_{4\,\text{eff}}$ are the effective parameters giving an asymmetry of the potential due to anharmonicity, x is the deviation of the instantaneous bond length r between the two atoms from its equilibrium value r_0.

The anharmonic effective potential Eq. (1) is defined based on an assumption in the center-of-mass frame of single-bond pair of absorber and backscatterer atom[10] and given by

$$\begin{aligned} V_{\text{eff}}(x) &= V(x) + \sum_{i=1,2}\sum_{j\neq i} V\left(\frac{\mu}{M_i}x\hat{\mathbf{R}}_{12}\cdot\hat{\mathbf{R}}_{ij}\right) \\ &= V(x) + 2V\left(-\frac{x}{2}\right) + 8V\left(-\frac{x}{4}\right) + 8V\left(\frac{x}{4}\right), \end{aligned} \tag{2}$$

where $\mu = M_1M_2/(M_1+M_2)$ is reduced mass of absorber with mass M_1 and backscatterer with mass M_2, and $\hat{\mathbf{R}}$ is unit vector, the sum i is over absorber ($i=1$) and backscatterer ($i=2$), and the sum j is over all near neighbors, excluding the absorber and backscatterer themselves, whose contributions are described by the term $V(x)$. Here, the first equation is valid for all crystal structures and the second one is for monatomic hcp crystals.

The above expression of the anharmonic interatomic effective potential is different from that of the single-pair[17] and single-bond model[18] potential, i.e. $V(x)$, which concerns only each pair of the immediate neighboring atoms without the remaining terms.

A Morse potential is assumed to describe interatomic interaction included in the anharmonic effective potential Eq. (2) and expanded up to the fourth order around its minimum

$$V(x) = D(e^{-2\alpha x} - 2e^{-\alpha x}) \cong D\left(-1 + \alpha^2 x^2 - \alpha^3 x^3 + \frac{7}{12}\alpha^4 x^4\right), \tag{3}$$

where α describes the width of the potential, and D is dissociation energy.

Applying this Morse potential Eq. (3) to Eq. (2) and comparing the results to Eq. (1), the anharmonic effective potential parameters k_{eff}, $k_{3\,\mathrm{eff}}$ and $k_{4\,\mathrm{eff}}$ in terms of Morse potential parameters are determined.

Atomic vibration is characterized by its vibration frequency. Using the obtained local effective force constant $k_{\mathrm{eff}} = 5D\alpha^2$, the correlated Einstein frequency ω_E and temperature θ_E have resulted as

$$\omega_E = \sqrt{\frac{5D\alpha^2}{\mu}}, \quad \theta_E = \frac{\hbar\omega_E}{k_{\mathrm{B}}}, \tag{4}$$

where k_{B} is Boltzmann constant, and for monatomic crystals the masses of all atoms are the same, i.e. $M_1 = M_2 = m$ being the atomic mass, so that the reduced mass $\mu = m/2$.

Within the classical limit and the assumption that the anharmonicity can be treated as a small perturbation, the temperature-dependent moments with using the anharmonic effective potentials given by Eqs. (1) and (2), about the mean $\langle x\rangle$, as determined by evaluating the thermal average

$$\begin{aligned}\langle(x - \langle x\rangle)^n\rangle &= \frac{\displaystyle\int_{-\infty}^{\infty} (x\langle x\rangle)^n \exp\left[-\frac{V_{\mathrm{eff}}(x)}{k_{\mathrm{B}}T}\right] dx}{\displaystyle\int_{-\infty}^{\infty} \exp\left[-\frac{V_{\mathrm{eff}}(x)}{k_{\mathrm{B}}T}\right] dx} \\ &\cong \frac{\displaystyle\int_{-\infty}^{\infty} (x - \langle x\rangle)^n \exp\left[-\frac{k_{\mathrm{eff}}x^2}{2k_{\mathrm{B}}T}\right]\left[\sum_{n=0}^{3}\frac{1}{n!}\left(\frac{k_{3\,\mathrm{eff}}x^3 - k_{4\,\mathrm{eff}}x^4}{k_{\mathrm{B}}T}\right)^n\right] dx}{\left(\dfrac{2\pi k_{\mathrm{B}}T}{k_{\mathrm{eff}}}\right)^{1/2}\left[1 + \dfrac{3(k_{\mathrm{B}}T)}{k_{\mathrm{eff}}^2}\left(\dfrac{5k_{3\,\mathrm{eff}}^2}{2k_{\mathrm{eff}}} - k_{4\,\mathrm{eff}}\right)\right]}\end{aligned} \tag{5}$$

to the lowest orders in T are given by

$$\langle x\rangle = \frac{3k_{\mathrm{B}}T}{20D\alpha}\left[1 + \frac{k_{\mathrm{B}}T}{25D\alpha}\left(\frac{133}{6}\alpha + 45\right)\right], \tag{6}$$

$$\langle(x - \langle x\rangle)^2\rangle = \frac{k_{\mathrm{B}}T}{5D\alpha^2}\left[1 + \frac{3k_{\mathrm{B}}T}{5D\alpha^3}\left(\frac{133}{48}\alpha^3 + \frac{15}{4}\right)\right], \tag{7}$$

$$\langle(x - \langle x\rangle)^3\rangle = \frac{3(k_{\mathrm{B}}T)^2}{50D^2\alpha^3}\left(1 + \frac{2637}{800}\frac{k_{\mathrm{B}}T}{D}\right), \tag{8}$$

$$\langle(x - \langle x\rangle)^4\rangle = \frac{3(k_{\mathrm{B}}T)^2}{25D^2\alpha^4}\left(1 + \frac{139}{300}\frac{k_{\mathrm{B}}T}{D}\right), \tag{9}$$

where the effective parameters $k_{\rm eff}$, $k_{3\,\rm eff}$ and $k_{4\,\rm eff}$ of the high-order anharmonic effective potential for hcp crystals contained in Eqs. (6)–(9) have been substituted by their values in terms of Morse potential parameters.

The truncation of the series in Eq. (5) serves as a convergence cut-off while including enough terms to accurately obtain the second lowest-order expressions for the moments. The respective expressions obtained from Eqs. (6)–(9) to lowest order in the temperature T are given by for the first cumulant or net thermal expansion

$$\sigma^{(1)} = \langle r - r_0 \rangle = \langle x \rangle = \frac{3}{4}\alpha\sigma^2 \,, \tag{10}$$

for the second cumulant or MSRD

$$\sigma^2 = \langle (r - r_0)^2 \rangle \cong \langle x^2 \rangle = \frac{k_{\rm B}T}{5D\alpha^2} = \frac{2k_{\rm B}T}{m\omega_E^2} \,, \tag{11}$$

for the third cumulant

$$\sigma^{(3)} = \langle (r - r_0)^3 \rangle \cong \langle x^3 \rangle - 3\sigma^{(1)}\sigma^2 = \frac{3}{2}\alpha(\sigma^2)^2 \tag{12}$$

and for the fourth cumulant

$$\sigma^{(4)} = \langle (r - r_0)^4 \rangle - 3(\sigma^2)^2 \cong \langle x^4 \rangle - 3(\sigma^2)^2 = \frac{137}{40}\alpha^2(\sigma^2)^3 \,, \tag{13}$$

as well as for the cumulant ratio

$$\frac{\sigma^{(1)}\sigma^2}{\sigma^{(3)}} = \frac{1}{2} \,, \tag{14}$$

where ω_E is calculated using the first equation of Eqs. (4).

The total MSRD is described as the sum of the harmonic term σ^2 and the anharmonic contribution σ_A^2 (Ref. 11) which in the present theory has the form

$$\sigma_{\rm tot}^2(T) = \sigma^2(T) + \sigma_A^2(T), \quad \sigma_A^2(T) = \beta(T)\sigma^2(T) \,, \tag{15}$$

where σ^2 is calculated using Eq. (11) and the anharmonic factor β is given by

$$\beta(T) = \frac{9\alpha^2}{8}\sigma^2\left[1 + \frac{3\alpha}{4R}\sigma^2\left(1 + \frac{3\alpha}{4R}\sigma^2\right)\right], \tag{16}$$

which is defined based on the second cumulant σ^2 and R is the first shell radius.

Hence, thanks to using the derived anharmonic effective potential of hcp crystals, all the obtained cumulants given by Eqs. (10)–(13) have been presented in very simple forms in terms of second cumulant or MSRD. It is useful not only for reducing the numerical calculations, but also for obtaining or predicting the other theoretical or experimental XAFS cumulants based on the calculated or measured second cumulant. Since the second cumulant σ^2 given by Eq. (11) is proportional to the temperature T, the first cumulant $\sigma^{(1)}$ is also linear with T, and the third and fourth cumulants vary as T^2 and T^3, respectively. Moreover, Eq. (11) shows inverse proportionality of this second cumulant σ^2 to the square of correlated Einstein frequency ω_E^2, so that from Eqs. (10)–(13), the cumulants $\sigma^{(1)}$, $\sigma^{(3)}$ and $\sigma^{(4)}$ are inversely proportional to ω_E^2, ω_E^4 and ω_E^6, respectively. The cumulant ratio $\sigma^{(1)}\sigma^2/\sigma^{(3)}$ is often considered as a standard for cumulant study. Its value of 1/2 given by Eq. (14) is valid for all temperatures, while such ratio resulted from quantum theory, approaches 1/2 only at high temperatures.[10,13]

3. Numerical Results and Discussions

For discussing the successes and efficiencies of our developments in this work, we apply the expressions derived in the previous section to numerical calculations of the anharmonic interatomic effective potentials and four first temperature-dependent XAFS cumulants of Zn and Cd using Morse potential parameters $D = 0.1698$ eV, $\alpha = 1.7054$ Å^{-1} for Zn and $D = 0.1675$ eV, $\alpha = 1.9069$ Å^{-1} for Cd which were obtained by generalizing the method for cubic crystals[19] to the one for hcp crystals, as well as their experimental values[13] $D = 0.1685$ eV, $\alpha = 1.700$ Å^{-1} for Zn and $D = 0.1653$ eV, $\alpha = 1.9053$ Å^{-1} for Cd.

Figure 1 illustrates good agreement of the anharmonic effective potentials of Zn and Cd expanded up to the fourth order, calculated using Eqs. (1)–(3), with experiment obtained from the measured Morse potential parameters.[13] They are significantly asymmetric compared to their harmonic terms due to including the anharmonic contributions given by $k_{3\,\mathrm{eff}}$ and $k_{4\,\mathrm{eff}}$. These calculated anharmonic effective potentials are used for the calculation and analysis of four first XAFS cumulants of Zn and Cd. Temperature dependence of the first cumulant or net thermal expansion $\sigma^{(1)}(T)$ calculated using Eq. (10) [Fig. 2(a)] and the second cumulant or MSRD $\sigma^2(T)$ calculated using Eq. (11), as well as the total MSRD $\sigma^2_{\mathrm{tot}}(T)$

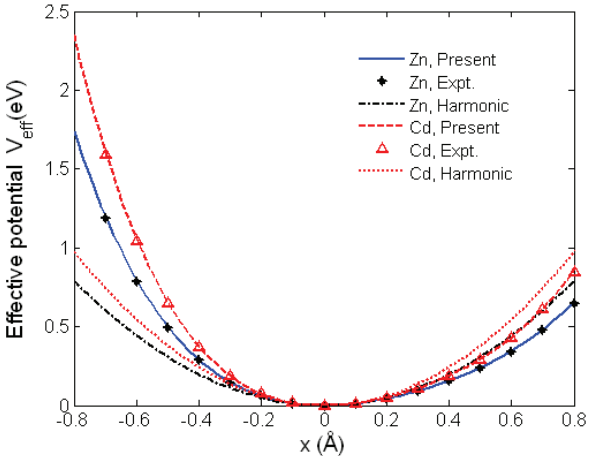

Fig. 1. (Color online) High-order anharmonic interatomic effective potentials of Zn and Cd calculated using the present theory compared to experiment obtained from the measured Morse potential parameters (Ref. 13) and to their calculated harmonic terms.

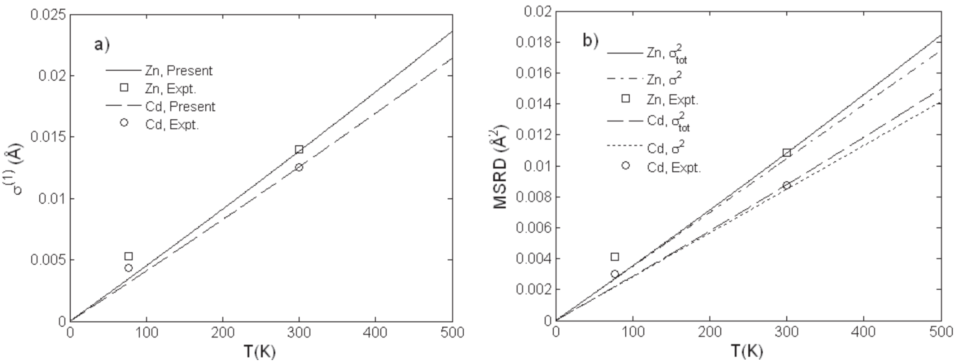

Fig. 2. Temperature dependence of (a) first cumulant $\sigma^{(1)}(T)$, and (b) second cumulant $\sigma^2(T)$ and total MSRD $\sigma^2_{\text{tot}}(T)$, calculated using the present theory for Zn and Cd compared to experiment at 77 K and 300 K (Ref. 13).

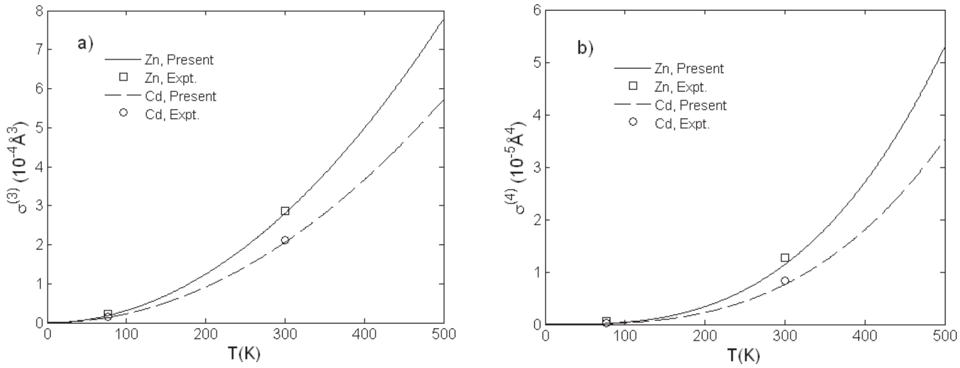

Fig. 3. Temperature dependence of (a) third cumulant $\sigma^{(3)}(T)$ and (b) fourth cumulant $\sigma^{(4)}(T)$, calculated using the present theory for Zn and Cd compared to the experimental values at 77 K and 300 K (Ref. 13).

calculated using Eq. (15) [Fig. 2(b)] of Zn and Cd agrees well with experiment at 300 K. The limitation here is unsatisfactory of the agreement of the calculated values of $\sigma^{(1)}(T)$, $\sigma^2(T)$ and $\sigma^2_{\text{tot}}(T)$ of Zn and Cd with experiment at 77 K. It is an evident limitation of any classical theory including the present one due to the absent of zero-point vibrations. The lowest temperature at which the classical limit can be applied to the first and second cumulants is about the correlated Einstein temperature θ_E,[10] i.e. $\theta_E = 205.61$ K for Zn, and $\theta_E = 174.14$ K for Cd calculated using Eq. (4). Unfortunately, this limitation is significantly reduced for the third and fourth cumulants. Temperature dependence of the third cumulant $\sigma^{(3)}(T)$ calculated using Eq. (12) [Fig. 3(a)] and the fourth cumulant $\sigma^{(4)}(T)$ calculated using Eq. (13) [Fig. 3(b)] for Zn and Cd agrees well with experiment not only at 300 K but also at 77 K. Hence, the present classical theory can be applied to the third and fourth cumulants of hcp crystals from the temperatures which are

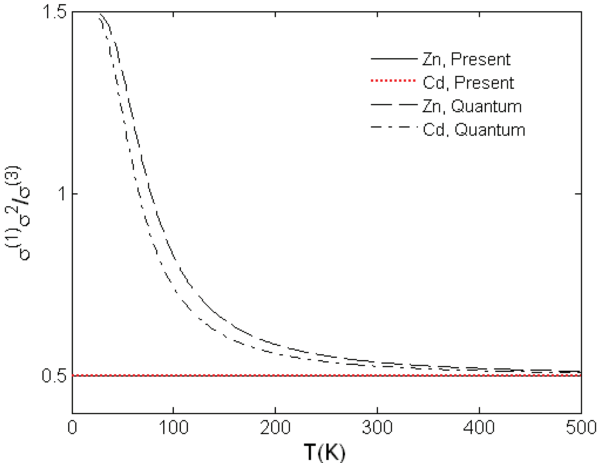

Fig. 4. (Color online) Temperature dependence of cumulant ratio $\sigma^{(1)}\sigma^2/\sigma^{(3)}$ of Zn and Cd calculated using the present theory compared to that obtained from quantum statistical theory (Ref. 13).

much lower than their Einstein temperatures. The reason of the above conclusions is attributed to the absent of zero-point vibrations, which are non-negligible for the first and second cumulants, and negligibly small for the third and fourth cumulants. Despite such limitation to the first and second cumulants, the present theory is suited for describing anharmonic effects in XAFS using cumulant expansion, because anharmonicity appears apparently from about room temperature.[3–15] The cumulant ratio $\sigma^{(1)}\sigma^2/\sigma^{(3)}$ is often considered as a standard for cumulant study.[10,13] Figure 4 illustrates the equality to 1/2 of $\sigma^{(1)}\sigma^2/\sigma^{(3)}$ for Zn and Cd calculated using Eq. (14) for all temperatures, while this ratio obtained from quantum theory approaches 1/2 only at high temperatures.[13]

Note that the experimental values of the first, second, third and fourth cumulants of Zn and Cd at 77 K and 300 K compared to our calculated results presented in the above figures have been extracted from XAFS spectra measured at HASYLAB (DESY, Germany) by a fitting procedure.[13] Moreover, the above numerical results for Zn and Cd have confirmed the proportionality of the first and second cumulants to the temperature T, the third and fourth cumulants to T^2 and T^3, respectively.

4. Conclusion

Although our model is one-dimensional, the three-dimensional interactions have been taken into account by a simple way based on using the derived anharmonic effective potential which includes all nearest neighbor interactions of absorber and backscattering atoms. Here Morse potential is used for describing interatomic interaction included in the derived anharmonic effective potential.

Thanks to using this derived high-order anharmonic effective potential, the analytical expressions of four first XAFS cumulants of hcp crystals derived in this classical anharmonic correlated Einstein model can be presented in very simple forms in terms of second cumulant or MSRD. They are suitable not only for reducing the numerical calculations, but also for obtaining or predicting the first, third and fourth cumulants based on the calculated or measured second cumulant, as well as for showing the proportionality of the first and second cumulants to the temperature T, and of the third and fourth cumulants to T^2 and T^3, respectively.

The cumulant ratio $\sigma^{(1)}\sigma^2/\sigma^{(3)} = 1/2$ obtained in this classical model is valid for all temperatures, which is different from that obtained from quantum theory, where this ratio approaches the constant value of 1/2 only at high temperatures.

The present classical theory can be applied to high-temperatures up to melting point starting from about the Einstein temperature for the first and second cumulants, and from a very low temperature for the third and fourth cumulants of hcp crystals. The reason of these conclusions is attributed to the absent of zero-point vibrations, which are non-negligible for the first and second cumulants and negligibly small for the third and fourth cumulants. Moreover, despite such limitation to the first and second cumulants, the present theory is suited for describing anharmonic effects in XAFS using cumulant expansion, because anharmonicity in XAFS appears apparently from about room temperature.

The good agreement of our calculated results for Zn and Cd with experiment at 300 K for the first and second cumulants and at 77 K and 300 K for the third and fourth cumulants illustrates the efficiencies of our developments in this work for the calculation and analysis of the anharmonic interatomic potentials and high-order XAFS cumulants by a simple measures.

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