

Quantum Statistical Approach to Debye-Waller Factor in EXAFS, EELS and ARXPS. III. Applicability of Debye and Einstein Approximation

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We investigate the availability of Debye and Einstein approximations to calculate Debye-Waller factors in EXAFS, EELS and ARXPS for one-dimensional models. These approximate results were compared with the *ab initio* results shown in the previous paper II. For monatomic chains the Debye model can give a good result even for third and fourth cumulants. In the case of diatomic chains, a mixed model where Debye (Einstein) approximation is used for acoustic (optical) mode give quite a good result for harmonic second order cumulant. This simple approximation, however, gives rather poor results for third and fourth order cumulants and also anharmonic correction to the second order cumulant. This result is due to the fact the phases of the eigenvectors of the dynamical matrix play an important role for the accurate estimation of those thermal factors.

[EXAFS, EELS, ARXPS, Debye-Waller factor, one-dimensional model, Debye approximation, Einstein approximation]

§1. Introduction

In recent years, it has become apparent that higher order terms of Debye-Waller factor, say third and fourth order cumulants in EXAFS, has interesting information about anharmonic pair potential of interatomic bonds within classical approximation.¹⁻³⁾ With the progress of experimental study for the higher order Debye-Waller factors, first principle calculation beyond harmonic approximation has been carried out⁴⁾ based on finite temperature Green's function perturbation theory and applied to one-dimensional systems.⁵⁾ On the other hand, *ab initio* calculation of Debye-Waller factors for two- and three-dimensional systems is so complicated that Debye or Einstein approximations are widely used for the acoustic and optical modes, respectively, to carry out the practical calculation. For example, Dalba *et al.*⁶⁾ studied the temperature dependence of the harmonic Debye-Waller factor for AgI by use of this approximation, and found that the experimental behavior is satisfactorily reproduced. This result is promising

for the interpretation of EXAFS Debye-Waller factors of complex crystalline compounds which have both optical and acoustic branches. From these successful results it is interesting to study whether the above simplified approximation gives still satisfactory results for anharmonic cumulants such as third and fourth order.

As recent progress in the study of EXAFS thermal factors, we can refer to the work by Frenkel and Rehr⁷⁾ where they clarify the relation between the thermal expansion coefficient and the anharmonic cumulants in EXAFS by use of elementary quantum statistical perturbation theory based on the Einstein model. This result is important for the EXAFS application, however, it is questionable whether the Einstein model can reasonably approximate those anharmonic cumulants.

Arvanitis *et al.*²⁾ obtained anharmonic pair potential between adsorbed O atom and substrate Cu atom by assuming the form,

$$V(r-r_0) = \frac{\alpha}{2} (r-r_0)^2 - \beta (r-r_0)^3, \quad (1.1)$$

and the Einstein approximation. This kind of study offers valuable information about pair interaction, however, the applicability of the Einstein approximation to the anharmonic cumulants does not have sound theoretical background.

Temperature effects on angle resolved UPS have been studied on the basis of the adiabatic approximation, where phonon effects are taken into account to the complex electron self-energy.⁸⁾ Calculations for the 3d-band region of Cu yield the vibration induced hole lifetime broadening and real energy shifts. This behavior is quite different from the high energy core spectra considered here.

In part I of this series of papers,⁴⁾ we have derived general expression for Debye-Waller factors in EXAFS, EELS and ARXPS using first principle quantum statistical approach in the framework of plane wave approximation where cubic and quartic anharmonicity are taken into account. From these formulas, we discuss high and low temperature behavior of these cumulants. Furthermore real space representation for them is given to compare it with the classical expression. In part II,⁵⁾ we have applied these formulas to one-dimensional Morse crystals. For diatomic chains we can separate out the contribution of optical phonons from that of acoustic phonons only for harmonic vibration approximation and its lowest order anharmonic correction. Our results show that optical phonons dominate the thermal factor in the low temperature region for the first shell atoms because of large relative motion, whereas both equally contributes to that factor in high temperature region. This result is quite different for second shell atoms; the contribution from acoustic phonons dominates the thermal factors. For higher order cumulants the phase factors of eigenvectors of the dynamical matrix play an important role because mixed contribution is to be taken into account which had not been discussed so far.

In this work we study the widely used mixed model where we apply the Debye model for acoustic branches and the Einstein model for optical branches based on the method described in I⁴⁾ and II.⁵⁾ It is well known that this approximation works well for the description

of the EXAFS Debye-Waller factor in the harmonic approximation,^{6,9)} whereas the applicability of the model has not been clear for the anharmonic cumulants. This work clearly shows the strength and limitation of this simple model for the EXAFS, EELS and ARXPS thermal factor.

§2. Monatomic Chain

First we consider a one-dimensional monatomic chain in which the atoms are interacting by anharmonic Morse potential, and we take into account first 4 terms in the expansion of the potential as same as in the previous paper II,⁵⁾

$$\begin{aligned} V(x) &= D(e^{-2\alpha x} - 2e^{-\alpha x}) \\ &= -D + D\alpha^2 x^2 - D\alpha^3 x^3 + \frac{7}{12} D\alpha^4 x^4 \\ &\quad + \dots, \end{aligned} \quad (2.1)$$

where x is the scaled relative deviation defined by $x = (l - a)/a$, l is the instantaneous distance between n th and $n + 1$ th atoms and a is the equilibrium distance between these two atoms. The Morse parameter α describes the width of the potential and D measures the dissociation energy. In the case of monatomic chain, the dispersion relation $\omega(k)$ is simply shown¹⁰⁾

$$\omega(k) = 2 \sqrt{\frac{2D\alpha^2}{Ma^2}} \left| \sin\left(\frac{ka}{2}\right) \right|, \quad |ka| \leq \pi \quad (2.2)$$

where M is atomic mass. First we apply the Debye approximation to the dispersion relation, where $\omega(k)$ is approximated by linear dispersion

$$\omega(k)_I = \sqrt{\frac{2D\alpha^2}{M}} k. \quad (2.3)$$

In this Debye model the slope is the same as the one at small k in eq. (2.2). Let us call this model *Debye I*. The second order cumulant in the harmonic approximation M_{20} for the nearest neighbor correlation can be calculated with aid of the formula shown by eq. (3.19) in ref. 4. From now on we designate it as (I, 3.19). Figure 1 shows the temperature dependence of $\bar{M}_{20} [= M_{20}/(\hbar a/\pi\alpha\sqrt{2DM})]$. \bar{T}_m is the dimensionless temperature $\bar{T}_m = k_B T/\hbar\omega_m$

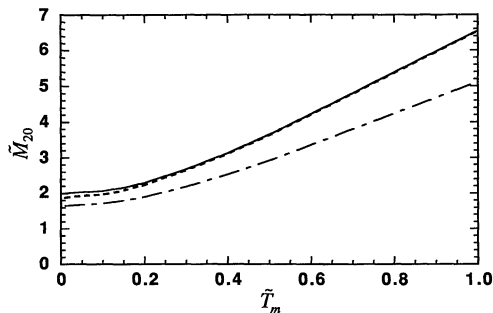


Fig. 1. Temperature dependence of harmonic EXAFS Debye-Waller factors. We show the scaled factors $\tilde{M}_{20} = M_{20}/(\hbar a/\pi\alpha\sqrt{2DM})$ as a function of $\tilde{T}_m = k_B T/\hbar\omega_m$ for the first shell atoms. Solid line represents the result for the *ab initio* calculation by use of the dispersion relation shown by eq. (2.2), dash-dotted line that for the *Debye I* (see eq. (2.3)) model and dashed line that for the *Debye II* model (see, eq. (2.4)).

where $\omega_m = \sqrt{8D\alpha^2/Ma^2}$; \tilde{T}_m is about 0.66 for Cu metal at room temperature.⁵⁾ The dispersion relation given by eq. (2.2) gives the result for M_{20} shown by the solid line (*ab initio*), whereas dash-dotted line indicates the result in the *Debye I* model. This Debye approximation gives the similar temperature dependence to the *ab initio* calculation, however, the disagreement is pronounced in the whole temperature region. Next we consider the best choice of the linear coefficient in the Debye approximation. We can obtain the best fit result within Debye approximation to the dispersion relation shown by eq. (2.2), when we use the relation

$$\omega(k)_{II} = 0.88k\sqrt{2D\alpha^2/M}. \quad (2.4)$$

We call this model *Debye II*. The dashed line in Fig. 1 shows the result for the *Debye II* model. In the high temperature region $\tilde{T}_m \geq 0.3$, the agreement with the *ab initio* result is excellent, but we find small disagreement in the low temperature region $\tilde{T}_m \leq 0.3$.

Figure 2 shows the temperature dependence of the ratio $\tilde{M}_{21}/\tilde{M}_{20}$, $\tilde{M}_{21} = M_{21}/(7\hbar^2/2\pi^2DM)$; the solid line shows the result for the *ab initio* calculation, the dash-dotted line shows the one for the *Debye I* model and the dashed line that for the *Debye II* model. The denominator \tilde{M}_{20} in the ratio corresponds to the *ab initio* calculation and the effect of approximation is included only in M_{21} . We find

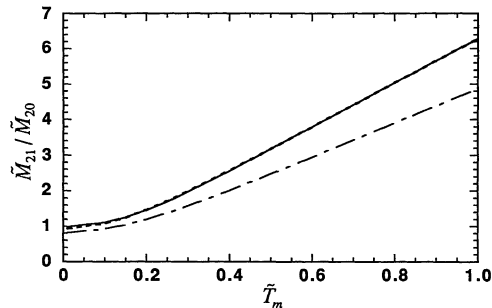


Fig. 2. Temperature dependence of the lowest order anharmonic correction to the second order cumulant $\tilde{M}_{21}/\tilde{M}_{20}$, where $\tilde{M}_{21} = M_{21}/(7\hbar^2/2\pi^2DM)$. The each line corresponds to the ones shown in Fig. 1.

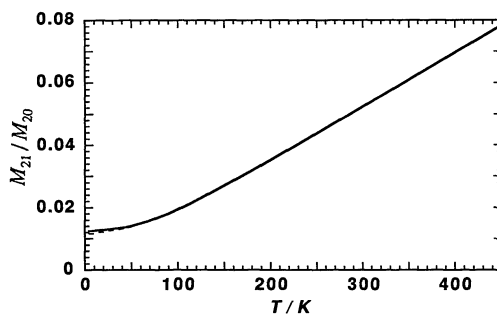


Fig. 3. The ratio M_{21}/M_{20} as a function of T , which is relative anharmonic correction to the harmonic EXAFS Debye-Waller factor for Cu metal; $D=0.84$ eV, $\alpha=4.531$ and $a=2.545$ Å.¹¹⁾ The dashed line represents the result for *Debye II* model and the solid line that for the *ab initio* result.

the similar result to that in Fig. 1. The *Debye II* model gives quite a good result, whereas the *Debye I* model gives a poor result for the anharmonic correction. Figure 3 shows temperature dependence of M_{21}/M_{20} for Cu metals as a function of T calculated by use of the *Debye II* model (dashed line): We employ the values of Morse parameters given by Yokoyama *et al.*¹¹⁾ The agreement with the *ab initio* result (solid line) is excellent.

The temperature dependence of the third order cumulant \tilde{M}_3 , $\tilde{M}_3 = M_3/3a\hbar^2(4\alpha\pi^2MD)^{-1}$, is shown in Fig. 4; the solid line represents the result for the *ab initio* calculation, the dash-dotted line that for the *Debye I* model, long-dashed line that for *Debye II* model when the factor is 0.88 which is the best fit parameter for the case of M_{20} and M_{21}/M_{20} ,

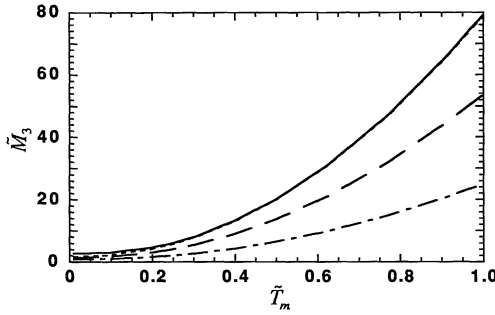


Fig. 4. Temperature dependence of $\tilde{M}_3 = M_3 / 3a\hbar^2(4\alpha\pi^2MD)^{-1}$. The solid and dash-dotted lines are the same as those used in Fig. 1, but the short-dashed line for the Debye model with linear coefficient 0.825 and the long-dashed line 0.88.

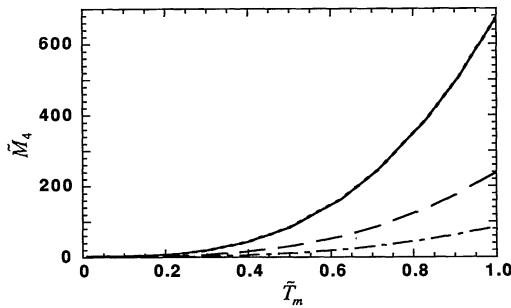


Fig. 5. Temperature dependence of $\tilde{M}_4 = M_4 / \{7a/2\alpha(\hbar/\pi\sqrt{2DM})^3\}$. The lines are the same as those used in Fig. 4, but in this case the linear factor for the Debye model is 0.773 for the short-dashed line.

and the dashed line that for the Debye model when the factor is 0.825. The deviation of the Debye I model from the *ab initio* result is larger than that for the case of M_{20} and $M_{21}/$

M_{20} and even Debye II model gives rather pronounced disagreement in the whole temperature region. The best fit linear coefficient 0.825 in Debye model is smaller than that for M_{20} ; We see that the best fit Debye model for harmonic cumulant does not necessarily give the best result for anharmonic cumulants.

The temperature dependence of the fourth order cumulant \tilde{M}_4 , $\tilde{M}_4 = M_4 / \{7a\hbar^3(2\alpha)^{-1}(\pi\sqrt{2DM})^{-3}\}$, is shown in Fig. 5; each line is the same as those shown in Fig. 4. In the case of fourth cumulant the deviation of Debye I model from the *ab initio* result is larger than that for M_3 and the best fit linear coefficient of the Debye model is 0.773 which is smaller than that for M_3 . The Debye II model gives rather poor result for M_4 , say that, the error is about 66% at $\tilde{T}_m = 0.6$ (room temperature in usual cases). From these results, we can see that the Debye model can be a good approximation for EXAFS Debye-Waller factor, however, the best choice of the linear coefficient is different for different order cumulant to get best fit with the corresponding *ab initio* result. In other words it is risky to analyse higher order cumulants by use of the best fit Debye approximation for the harmonic cumulant.

§3. Diatomic Chain

In this section we consider a diatomic chain in which atom A and B are arranged alternately with atomic masses M_A and M_B . In this case, $x = (2l - a)/a$ for the Morse potential in eq. (2.1) where l is the instantaneous distance between atom A and B and a is the lattice constant. The phonon dispersion relation is easily given by¹⁰⁾

$$\omega(k)_{\pm} = \frac{\gamma(M_A + M_B)}{M_A M_B} \left\{ 1 \pm \sqrt{1 - \frac{4M_A M_B \sin^2\left(\frac{ka}{2}\right)}{(M_A + M_B)^2}} \right\}, \quad (3.1)$$

where $\gamma = 8D\alpha^2/a^2$ and subscript + (-) refers to the optical (acoustic) mode. For the acoustic mode we can apply the Debye approximation as discussed in §2, where the mode $\omega(k)_-$ is approximated by the leading term in the small k region,

$$\omega(k)_- = \frac{2\sqrt{D\alpha^2}}{\sqrt{M_A + M_B}} k. \quad (3.2)$$

We call this model Debye I model. In contrast to acoustic modes optical modes show weak dispersion, so that we can approximate them

constant values independent on k .⁶⁾ However we have the problem to get the best fit for such *Einstein* frequencies. First we assume that ω_+ is set to be the value of ω_+ at $k=0$;

$$\omega_{\text{EI}} = \sqrt{2\gamma/\mu}, \quad (3.3)$$

where μ is the reduced mass. We call this model *Einstein I*. For practical purpose we can obtain the value of Einstein frequency ω_{EI} from vibrational spectroscopic technique like IR spectra or Raman scattering.⁶⁾

The harmonic second order cumulant M_{20} is written by the sum⁴⁾

$$M_{20} = M_{20}^+ + M_{20}^-, \quad (3.4)$$

where $M_{20}^+(M_{20}^-)$ is that from optical (acoustic) mode, and they can be calculated by use of eqs. (II, 3.6) and (II, 3.8). For $\omega(k)_-$ we use the linear function of k shown by eq. (3.2), and for $\omega(k)_+$ we use the constant ω_{EI} given by eq. (3.3); M_{20}^+ is particularly simple as given by,

$$M_{20}^+ = \frac{\hbar\omega_{\text{EI}}}{4\gamma} \coth\left(\frac{\beta\hbar\omega_{\text{EI}}}{2}\right). \quad (3.5)$$

Figure 6 shows the temperature dependence of the harmonic cumulant \tilde{M}_{20} , $\tilde{M}_{20} = M_{20}/\hbar(\pi\sqrt{5\gamma\mu})^{-1}$, for this model, the combination of *Debye* and *Einstein* model with $M_A = 4M_B$. \tilde{T}_d is the dimensionless temperature for the dia-

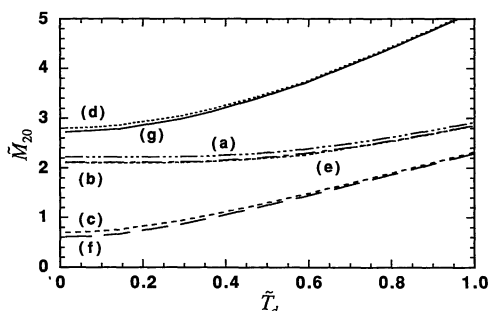


Fig. 6. Temperature dependence of the harmonic contribution to Debye-Waller factor $\tilde{M}_{20} = M_{20}/\hbar(\pi\sqrt{5\gamma\mu})^{-1}$ in diatomic chain with $M_A = 4M_B$. M_{20}^+ in (a) *Einstein I* model, (b) *Einstein I'* model (dotted line), M_{20}^- in (c) *Debye I* model, (d) Total contribution from the *Debye I* and *Einstein I'* model, (e) *ab initio* result of M_{20}^+ for the optical mode (dash-dotted line), (f) *ab initio* result of M_{20}^- for the acoustic mode and (g) *ab initio* result of M_{20} for the total contribution, $M_{20} = M_{20}^+ + M_{20}^-$.

atomic chain given by $\tilde{T}_d = 2k_B T/\hbar\omega_{\text{EI}}$. We also show the *ab initio* results both for acoustic (f) and optical modes (e) in the figure. The *Debye I* model gives quite a good result (c) to approximate acoustic modes, although we find small disagreement in the low temperature region. The *Einstein I* model for optical modes gives slightly larger M_{20}^+ (a) than the *ab initio* result (e) in the whole temperature range considered here. This is because the *Einstein* frequency ω_{EI} is always larger than $\omega(k)_+$. So that we choose a slightly different *Einstein* frequency as the average value of ω_+ 's at $k=0$ and $k=\pi/a$,

$$\omega_{\text{EI}} = (\sqrt{2\gamma/\mu} + \sqrt{\gamma/M_B})/2. \quad (3.6)$$

We call this model *Einstein I'*. The Debye-Waller factor M_{20}^+ calculated by use of the *Einstein I'* model for the optical modes (b) is also shown in Fig. 6, which shows better agreement with (e) than by *Einstein I* model. This result is easily understood because the *Einstein* frequency ω_{EI} properly approximates the whole spectra of $\omega_+(k)$ than ω_{EI} . So that we will adopt the *Einstein I'* model for the optical phonons from now on. The total contribution from these two branches (d) shows good agreement with *ab initio* result (g) as shown in this figure. Judging from this result, we can say that the Debye for acoustic mode and Einstein models for optical modes is a good approximation in the case of harmonic Debye-Waller factor in one-dimensional systems. This result is in agreement with the previous result by Dalba *et al.*⁶⁾ We should note that the *Debye I* model is a good approximation to the acoustic mode in diatomic chain, however the factor 0.88 should be multiplied to eq. (2.3) in order to obtain the best fit for monatomic chain as described in the previous section.

The lowest anharmonic correction to the second order cumulant \tilde{M}_{21} , $\tilde{M}_{21} = M_{21}/(14\alpha^2\hbar^2/5\pi a^2\gamma\mu)$, can be separately calculated for optical and acoustic mode as shown by eq. (II, 3.29), as far as we use the accurate dispersion relation given by eq. (3.1). However, the cross term \hat{K} given by eq. (II, 3.27) cannot necessarily vanish for the approximate dispersion relations used here. Figure 7 [A] shows the results for $\tilde{M}_{21}/\tilde{M}_{20}$ by use of the *Debye I* + *Einstein I'* mixed approximation for the first shell, [B]

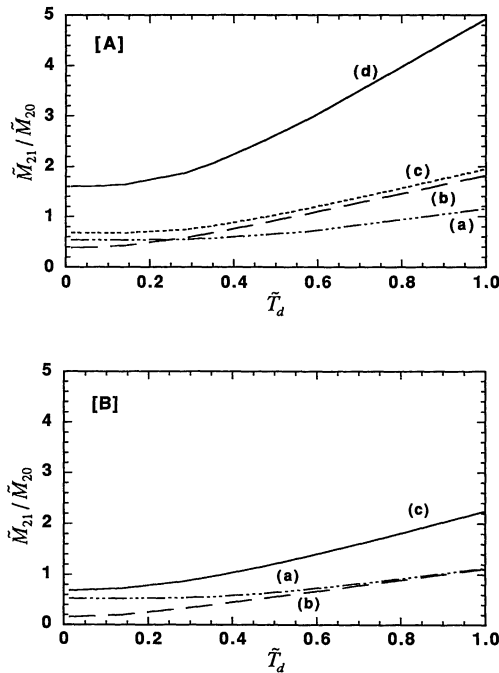


Fig. 7. [A]; Temperature dependence of the ratio $\tilde{M}_{21}/\tilde{M}_{20}$ for the first shell in the diatomic model chains with $M_A=4M_B$, where $\tilde{M}_{21}=M_{21}/(14\hbar^2\alpha^2/5\pi a^2\gamma\mu)$. (a) The contribution from optical phonons approximated by *Einstein I'* model, (b) the acoustic contribution approximated by *Debye I* model, (c) cross term from *Einstein I'* and *Debye I*, and (d) total contribution from (a), (b), and (c). [B]; *ab initio* result⁵⁾ for $\tilde{M}_{21}/\tilde{M}_{20}$. (a) optical mode, (b) acoustic mode, and (c) total contribution.

the *ab initio* results shown in the paper II for the comparison. We find that the *Einstein I'* model gives a good result which is in good agreement with the *ab initio* result for optical modes. In contrast to this result the *Debye I* model gives a rather poor result for the contribution from acoustic modes. We can improve the result by using the larger linear coefficient of the Debye model. A more serious problem comes from the approximation introduced here, since the cross term \hat{K} in eq. (II, 3.27) significantly contributes to the anharmonic correction $\tilde{M}_{21}/\tilde{M}_{20}$ as shown in this figure; it is larger than those contributions from acoustic and optical modes. Because of this cross contribution the mixed model gives poor result for the total anharmonic correction $\tilde{M}_{21}/\tilde{M}_{20}$. We see that the phase difference between acoustic and optical modes plays an important

role in the cross term as far as we use some approximate phonon dispersion relation. For the present simple model, we can easily obtain the exact dispersion relation and neglect the cross term because of subtle cancellation. However, it is difficult to calculate such phase factors accurately for general complicated systems. Figure 8 shows the temperature dependence of the ratio M_{21}/M_{20} , relative anharmonic correction to the second order cumulant, as a function of T for a model diatomic chain with the parameters $D=0.8$ eV, $\alpha=4.5$, $a=4.0$ Å, $M_A=64$, and $M_B=16$. The anharmonic correction in the second order cumulant is about 20% for the approximate calculation, although that for *ab initio* result is about 10% at room temperature.

For the third and fourth order cumulants, some cross terms are more important than the contribution from optical phonons in the *ab initio* calculation;⁵⁾ *O-O-A* (*O*=optical, *A*=acoustic) cross term is dominant in the third order cumulant. Figure 9 compares the approximate temperature dependence of the third order cumulant M_3 for the *Debye I*+*Einstein I'* model shown in [A] with the *ab initio* result shown in [B].⁵⁾ From eq. (II, 3.17) we can easily obtain the *O-O-O* contribution to M_3 by use of Einstein approximation;

$$M_3^E = C_3^E \left\{ \frac{3}{2} \coth^2 \left(\frac{\beta \hbar \omega_{EI}}{2} \right) - 1 \right\}, \quad (3.7)$$

where

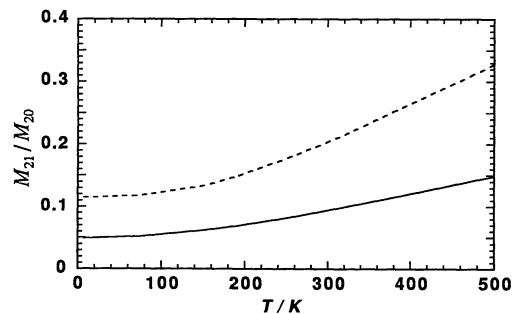


Fig. 8. The ratio M_{21}/M_{20} as a function of T , which is relative anharmonic correction to the harmonic EX-AFS Debye-Waller factor for a model of one-dimensional crystal; $D=0.84$ eV, $\alpha=4.5$ and $a=4.0$ Å, $M_A=64$ and $M_B=16$. The dashed line represents the result for the mixed model of *Debye I*+*Einstein I'* and the solid line that for *ab initio* result.⁵⁾

$$C_3^E = \frac{1}{\omega_{EI}^4} \left(\frac{16\alpha\gamma}{a\hbar} \right) \left(\frac{\hbar}{2N} \right)^3 \sum_{k_1 k_2 k_3} N \Delta(k_1 + k_2 + k_3) \times |h(k_1)|^2 |h(k_2)|^2 |h(k_3)|^2 \sin^2 [\theta(k_1) + \theta(k_2) + \theta(k_3)]. \quad (3.8)$$

The expression M_3^E is the same as that given by Arvanitis *et al.*,²⁾ however the prefactor C_3^E is quite different from their factor. In our treatment the phase of the eigenvectors of the dynamical matrix is explicitly taken into account. The contributions from $O-O-O$ (all optical) and $A-A-A$ (all acoustic) terms are slightly different from the *ab initio* result, but the agreement is satisfactory. However, this simple approximation gives rather poor result for the cross terms $O-O-A$ and $O-A-A$ in comparison with that for $O-O-O$ and $A-A-A$

terms, as shown by Fig. 9. For $O-O-A$ cross term, the ratio (*ab initio*)/(mixed model) is about 1.5, and for $O-A-A$ about 0.05. These large errors are introduced through inaccuracy of phase factors as shown by eq. (II, 3.17).

The result for the fourth order cumulant is shown in Fig. 10; The approximate result shown in [A] is compared with the *ab initio* result shown in [B].⁵⁾ In this case $A-A-A-A$ and $O-O-A-A$ give rather good result, however, other terms give rise to large errors; the approximate total contribution shown by the solid line (f) is about 3.5 times of the corre-

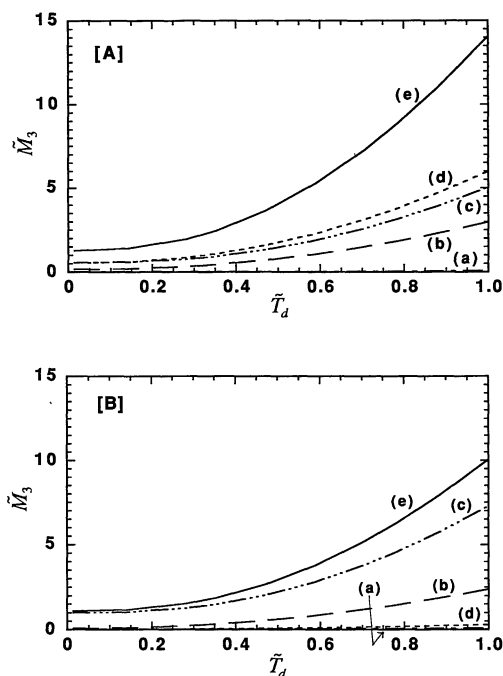


Fig. 9. Temperature dependence of the dimensionless third order cumulant $\tilde{M}_3 = M_3 / (32\alpha\hbar^2 / 5a\pi^2\gamma\mu)$ for a first shell atom in the diatomic model chain considered in Fig. 6. [A]: The result by use of the mixed model, (a) the contribution from optical phonons, (b) that from acoustic phonons, (c) that from $O-O-A$ cross term, (d) that from $O-A-A$ cross term, and (e) total contribution from (a), (b), (c) and (d). [B]: *ab initio* result⁵⁾ for third order cumulant for (a) optical mode, (b) acoustic mode, (c) the $O-O-A$ cross term, (d) the $O-A-A$ cross term, and (e) total contribution.

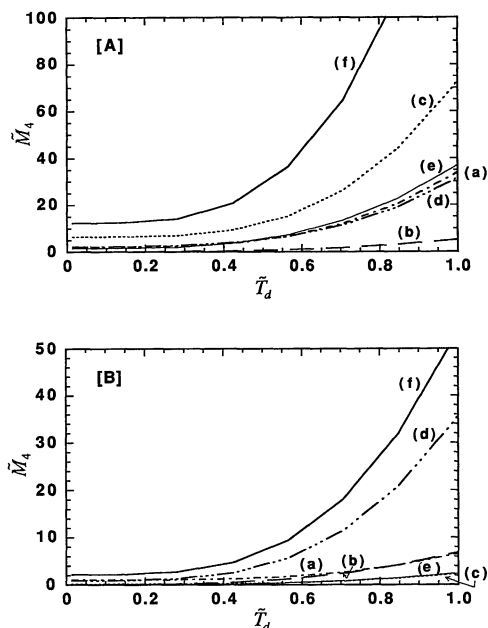


Fig. 10. Temperature dependence of the dimensionless fourth order cumulant $\tilde{M}_4 = M_4 / \{56\alpha^2 / a^2 (\hbar / \pi \sqrt{5\gamma\mu})^3\}$ for a first shell atom in the diatomic model chain considered in Fig. 6. [A]: The result by use of the mixed model, (a) the contribution from optical phonons, (b) that from acoustic phonons, (c) that from $O-O-O-A$ cross term, (d) that from $O-O-A-A$ cross term, (e) that from $O-A-A-A$ cross term, and (f) total contribution from (a), (b), (c), (d) and (e). [B]: *ab initio* result⁵⁾ for fourth order cumulant each of (a)–(f) corresponds to that in [A].

sponding *ab initio* result at $\tilde{T}_d=0.6$. This large error is much pronounced in comparison with the one in M_3 . In the *ab initio* result the $O-O-A$ contribution is the most important, whereas the $O-O-O-A$ contribution is the most important in this simple approximation. For these higher order cumulants the simple mixed model is not reliable even for qualitative discussion. These results also implies that the delicate phase factors are not correctly taken into account by those simple approximation and give rise to serious problems for higher order cumulants.

§4. Conclusion

The widely used Debye model gives satisfactory results for the description of the EXAFS thermal factors in monatomic chains where we have only acoustic modes. However the best fit linear coefficient of that model for the harmonic Debye-Waller factor gives rise to substantial errors for the anharmonic cumulants, though the results are qualitatively reliable.

In contrast to monatomic chains, the mixed model considered here for diatomic chains gives quantitatively reliable results for the description of the harmonic EXAFS Debye-Waller factors, however, they have a serious problem for the description of the anharmonic cumulants. The difficulty is due to the phase problem of the eigenvectors of the dynamical matrix which play an important role in those anharmonic cumulants. In conclusion it is risky for us to apply such a simplified model to the calculation of anharmonic cumulants. For the quantitative calculation of the anharmonic cumulants we have to apply *ab initio* calculation, otherwise we have to devise a new more

sophisticated technique than the simple mixed model.

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