



# Advances in EXAFS studies of thermodynamic properties and anharmonic effects based on Debye-Waller factors. Applications to semiconductors

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## ABSTRACT

This paper presents the advances in EXAFS studies of the thermodynamic properties and anharmonic effects based on Debye-Waller factors presented in terms of cumulant expansion. The advances are succeeded based on the generalized anharmonic correlated Einstein model (GACEM) derived for all material structures including complex systems and separated for each structure by its anharmonic effective potential parameters contained in the derived analytical expressions of three first EXAFS cumulants and thermal coefficient. Many-body effects are accounted in the present one-dimensional model based on the first-shell near-neighbor contributions to the vibrations between absorber and backscatterer atoms. Morse potential is assumed to describe single-pair atomic interaction. The method created in this GACEM has the advantage of using it all considered quantities are provided based on only the calculation or measurement of second cumulants. The advanced studies are successfully applied to semiconductors. The results calculated using the present theory and those obtained by the created method for Ge and Si having diamond structure are found to be in good and reasonable agreement with experiment and with those of other theories.

## 1. Introduction

Thermal vibrations and disorder in extended X-ray absorption fine structure (EXAFS) give rise to Debye-Waller factors (DWFs) that damp EXAFS spectra with respect to increasing temperature  $T$  and wave number  $k$  (or energy). Anharmonicity in atomic interaction potential yields additional terms in DWF, which ignored can lead to non-negligible errors in structural and other parameters [1–14]. The formalism for including anharmonic effects in EXAFS is often based on cumulant expansion [1], where the even cumulants contribute to the amplitude, the odd ones to the phase of EXAFS spectra, and they account for the net thermal expansion (first cumulant), the mean square relative displacement (MSRD) (second cumulant) and the asymmetry of the pair distribution function (third cumulant). Consequently, the lack of the precise DWFs has been one of the largest limitations not only to accurate structural determinations but also to definitions of the thermodynamic properties and anharmonic effects from EXAFS data. Therefore, investigation of DWFs is of great interest.

Many efforts have been made to develop procedures for the

calculation and analysis of EXAFS cumulants for different material systems. Classical theories work very well at high-temperatures [2–6], but they are limited due to zero-point vibration. Quantum theories can be applied to both low- and high-temperatures [7–21,28–31]. Here, the effective single-particle potential [7], single-bond model [8] and full lattice dynamical approach [9] have been derived to include anharmonic contributions in EXAFS considerations. The correlated Einstein model is applied to study DWFs but these researches are mainly focusing on the calculation and analysis of the MSRDS (second cumulant) [10–12] and mean square displacement (MSD) [10]. Based on the cumulant expansion the anharmonic correlated Einstein model (ACEM) [13–15], anharmonic correlated Debye model (ACDM) [16], path integral calculation [17], force constant model [18], dynamic matrix calculation [19] and many theories have been derived for EXAFS cumulant studies. Especially, several works have dealt with semiconductors [19–31], the very important materials in technological and electronic applications. Here, the temperature-dependent MSRD or second cumulant has been studied by the generalized gradient approximation (GGA), half-GGA (hGGA) [19], local density

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approximation (LDA) [19,20], and by EXAFS experiment for Ge [22–27], as well as by EXAFS calculation for Si [21] and by using a similar approach to that of Lee & Gronze [28] for a variety of group IV, III-V and II-VI semiconductors [29]. The local dynamical behaviors of several semiconductors having diamond and zinc blende structures, affected by negative thermal expansion at low-temperatures, have been investigated by EXAFS [30]. The temperature-dependent MSRD of semiconductors having diamond structure and MSD of semiconductor compounds having zinc blende structure have been studied [31] using statistical moment method (SMM) and Stillinger-Weber potentials, where their thermodynamic properties have been in detail analyzed and discussed. All the above derived methods significantly contributed to studying EXAFS DWFs of the materials. Based on the ACDM a theory for evaluating the thermodynamic properties and anharmonic effects of materials of all structures including complex systems has been derived [32], but such development based on the ACEM is still not available.

The purpose of this work is to advance the EXAFS studies of the thermodynamic properties and anharmonic effects based on DWFs presented in terms of cumulant expansion. The most advantageous developments in these studies are presented in Section 2. They are succeeded based on the generalized anharmonic correlated Einstein model (GACEM) derived based on quantum statistical theory with the purposes firstly for application to all material structures including complex systems, and secondly for creating a method using it all considered EXAFS quantities can be provided based on only the calculation (theoretical study) or measurement (experimental study) of second cumulants. All previously derived models for fcc [13,14], hcp [15] crystals are only the special cases of this GACEM. The model is separated for each material structure by its anharmonic effective potential parameters contained in the derived analytical expressions of three first EXAFS cumulants  $\sigma^{(1)}(T)$ ,  $\sigma^{(2)}(T)$ ,  $\sigma^{(3)}(T)$  and thermal expansion coefficient  $\alpha_T(T)$ . The GACEM is simplified by using the one-dimensional model with taking the many-body effects into account based on the first-shell near-neighbor contributions to the vibration between absorber and backscatterer atoms. Morse potential contained in the derived anharmonic effective potential is assumed to describe the single-pair atomic interaction. The advanced studies based on this GACEM are applied to semiconductors where their thermodynamic properties and anharmonic effects have been evaluated. In Section 3 the results calculated using the present theory and those obtained by using the created method, i.e., from the available theoretical [19–21] or experimental [22–24] second cumulants of Ge and Si having diamond structure are compared to experiment [22–27], and to those of the other theories [19–21,31], which show good and reasonable agreement. The cumulant ratios  $\sigma^{(1)}\sigma^{(2)}/\sigma^{(3)}$  and  $\alpha_T\text{Tr}\sigma^2/\sigma^{(3)}$  of Ge and Si have been calculated and compared to those of other crystal structures [2,6,10,14] to define them to be standards for cumulant studies of semiconductors. The conclusions are presented in Section 4.

## 2. Generalized anharmonic correlated Einstein model

### 2.1. Anharmonic effective potential

To determine EXAFS cumulants of a material it is necessary to specify its interatomic interaction potential and force constant [1–19]. Let us consider an anharmonic interatomic effective potential for the present GACEM expanded to the third order around its equilibrium

$$V_{\text{eff}}(x) = \frac{1}{2}k_{\text{eff}}x^2 + k_{3\text{eff}}x^3 + \dots, \quad x = r - r_0 \quad (2.1.1)$$

where  $k_{\text{eff}}$  is the effective local force constant,  $k_{3\text{eff}}$  is the cubic anharmonic effective parameter giving an asymmetry of the anharmonic effective potential,  $x$  is the deviation of the instantaneous bond length  $r$  between two immediate neighboring atoms from its equilibrium value  $r_0$ .

Note that the parameters  $k_{\text{eff}}$ ,  $k_{3\text{eff}}$  of this anharmonic effective

potential are different for different material structures in the present GACEM.

The anharmonic effective potential Eq. (2.1.1) in the present GACEM is defined based on an assumption in the center-of-mass frame of single bond pair of an absorber with a mass  $M_1$  and a backscatterer with a mass  $M_2$  as

$$V_{\text{eff}}(x) = V(x) + \sum_{i=1,2} \sum_{j \neq i} V\left(\frac{\mu}{M_i}x\hat{\mathbf{R}}_{12}\hat{\mathbf{R}}_{ij}\right), \quad \mu = \frac{M_1M_2}{M_1 + M_2}, \quad (2.1.2)$$

where  $M_i$  is  $i$ th atom mass,  $\hat{\mathbf{R}}$  is bond unit vector, the sum  $i$  is over absorber ( $i = 1$ ) and backscatterer ( $i = 2$ ), the sum  $j$  is over their first-shell near-neighbors excluding absorber and backscatterer themselves whose contributions are described by the term  $V(x)$ , the second term on the right describes the lattice contributions to the pair interaction, thanks to that the many-body effects are taken into account.

Hence, this effective potential is quite different from the single-bond (SB) [8] and single-pair (SP) [9] potentials which concern only each pair of immediate neighboring atoms, i.e., only  $V(x)$  without the second term in the right-hand side of Eq. (2.1.2).

A Morse potential is assumed to describe the single-pair atomic interaction expanded up to the third order around its minimum

$$V(x) = D(e^{-2\alpha x} - 2e^{-\alpha x}) = D(-1 + \alpha^2x^2 - \alpha^3x^3 + \dots), \quad (2.1.3)$$

where  $\alpha$  describes the width of the potential and  $D$  is the dissociation energy.

In order to describe different cases for different material structures in the present GACEM the anharmonic effective potential Eq. (2.1.2) is transformed into

$$V_{\text{eff}}(y) = D(S_2\alpha^2 + 3S_3\alpha^3a)y^2 + S_3D\alpha^3y^3, \quad y = x - a, \quad a = \langle x \rangle, \quad (2.1.4)$$

which contains  $S_2$  and  $S_3$  as the structural parameters defined based on the second term on right-hand side of Eq. (2.1.2) depending on the atomic distribution of each considered material structure.

Hence, comparing Eq. (2.1.4) to Eq. (2.1.1), the anharmonic effective potential parameters describing respectively the effective local force constant and cubic effective anharmonic parameter in the present GACEM have resulted as

$$k_{\text{eff}} = 2D(S_2\alpha^2 + 3S_3\alpha^3a) \cong 2DS_2\alpha^2, \quad k_{3\text{eff}} = S_3D\alpha^3, \quad (2.1.5)$$

which are different for different material structures based on the structural parameters  $S_2$  and  $S_3$ .

For further calculation of EXAFS cumulants using quantum thermodynamic perturbation theory in the present GACEM the anharmonic effective potential Eq. (2.1.4) is expressed in the sum of the harmonic contribution and a perturbation  $\delta V$  due to the weak anharmonicity in EXAFS as

$$V_{\text{eff}}(y) \cong \frac{1}{2}k_{\text{eff}}y^2 + \delta V(y), \quad (2.1.6)$$

where the perturbation term  $\delta V(y)$  has the following form

$$\delta V \cong (k_{\text{eff}} + 3k_{3\text{eff}}\alpha^2)ay + k_{3\text{eff}}y^3. \quad (2.1.7)$$

The above expressions for the anharmonic effective potential are quite different from those of the SB and SP potentials or called for both SP potentials, for which the local force constant and cubic anharmonic parameter taken from Eq. (2.1.3) are given by

$$k_{\text{SP}} = 2D\alpha^2, \quad k_{3\text{SP}} = -D\alpha^3. \quad (2.1.8)$$

### 2.2. XAFS cumulants and thermal expansion coefficient

Derivation of EXAFS cumulants in the present GACEM is based on quantum statistical theory [33] and the anharmonic effective potential derived in the previous Section 2.1. Now we consider the physical

quantity which is determined based on an averaging procedure using the canonical partition function  $Z$  and statistical density matrix  $\rho$ , e.g.,

$$\langle y^m \rangle = \frac{1}{Z} \text{Tr}(\rho y^m), \quad m = 1, 2, 3, \dots \quad (2.2.1)$$

Atomic vibrations are quantized in terms of phonons, and anharmonicity is the result of phonon-phonon interaction, that is why we express  $y$  in terms of the annihilation and creation operators,  $\hat{a}$  and  $\hat{a}^+$ , respectively

$$y \cong a_0(\hat{a} + \hat{a}^+), \quad a_0 = \sqrt{\frac{\hbar\omega_E}{2k_{\text{eff}}}}, \quad (2.2.2)$$

which have the following properties

$$[\hat{a}, \hat{a}^+] = 1, \quad \hat{a}^+|n\rangle = \sqrt{n+1}|n+1\rangle, \quad \hat{a}|n\rangle = \sqrt{n-1}|n-1\rangle, \\ \hat{a}^+\hat{a}|n\rangle = n|n\rangle, \quad (2.2.3)$$

as well as use the harmonic oscillator state  $|n\rangle$  as the eigenstate with the eigenvalue  $E_n = n\hbar\omega_E$  for  $n$  being the phonon number, ignoring the zero-point energy for convenience.

Based on the local force constant given by the first equation of Eq. (2.1.5), the correlated Einstein frequency  $\omega_E$  and temperature  $\theta_E$  in the present GACEM have resulted and given by

$$\omega_E = \sqrt{k_{\text{eff}}/\mu} = \sqrt{2DS_2\alpha^2/\mu}, \quad \theta_E = \hbar\omega_E/k_B, \quad (2.2.4)$$

where  $k_B$  is Boltzmann constant.

The canonical partition function in Eq. (2.2.1) can be expressed as

$$Z \cong Z_0 = \sum_n e^{-n\beta\hbar\omega_E} = \sum_{n=0}^{\infty} z^n = \frac{1}{1-z}, \quad z = \exp(-\theta_E/T). \quad (2.2.5)$$

Using the above results for the correlated atomic vibration and the procedure depicted by Eq. (2.2.1) - (2.2.5), as well as the first-order thermodynamic perturbation theory [33] the temperature-dependent EXAFS cumulants in the present GACEM have been derived.

Here, based on the procedure depicted by Eq. (2.2.1) we derived the even moment expressing the second cumulant or MSRD

$$\sigma^2(T) = \langle y^2 \rangle = \sum_n e^{-n\beta\hbar\omega_E} \langle n|y^2|n\rangle, \quad \beta = 1/k_B T, \quad (2.2.6)$$

and the odd moments expressing the first ( $m = 1$ ) and third ( $m = 3$ ) cumulants

$$\langle y^m \rangle = \frac{k_{\text{eff}}}{Z_0} \sum_{n,n'} \frac{e^{-\beta E_n} - e^{-\beta E_{n'}}}{E_n - E_{n'}} \langle n|\delta V(y)|n'\rangle \langle n'|y^m|n\rangle, \quad m = 1, 3, \quad (2.2.7)$$

where  $\delta V(y)$  is taken from Eq. (2.1.7) and the operations expressed by Eq. (2.2.2) - (2.2.3) have been applied to calculate the matrix elements given in Eq. (2.2.6) - (2.2.7).

Consequently, the EXAFS cumulants have resulted for the first cumulant describing net thermal expansion or lattice disorder

$$\sigma^1(T) = a = \sigma_0^{(1)} \frac{1+z(T)}{1-z(T)} = \frac{\sigma_0^{(1)}}{\sigma_0^2} \sigma^2(T), \quad \sigma_0^{(1)} = -\frac{3k_{3\text{eff}}}{k_{\text{eff}}} \sigma_0^2 \quad (2.2.8)$$

for the second cumulant describing MSRD

$$\sigma^2(T) = \langle y^2 \rangle = \sigma_0^2 \frac{1+z(T)}{1-z(T)}, \quad \sigma_0^2 = \frac{\hbar\omega_E}{2k_{\text{eff}}}, \quad (2.2.9)$$

and for the third cumulant or mean cubic relative displacement (MCRD) describing the asymmetry of the pair distribution function

$$\sigma^3(T) = \langle y^3 \rangle = \sigma_0^{(3)} [3(\sigma^2(T)/\sigma_0^2)^2 - 2], \quad \sigma_0^{(3)} = -\frac{2k_{3\text{eff}}}{k_{\text{eff}}} (\sigma_0^2)^2. \quad (2.2.10)$$

Using the first cumulant given by Eq. (2.2.8), the analytical expression for the thermal expansion coefficient has been derived and

given by

$$\alpha_T(T) = \frac{1}{r} \frac{da}{dT} = \alpha_T^0 \frac{(\sigma^2(T))^2 - (\sigma_0^2)^2}{T^2}, \quad \alpha_T^0 = -\frac{3k_{3\text{eff}}}{k_B r}. \quad (2.2.11)$$

Here  $\sigma_0^{(1)}$ ,  $\sigma_0^2$ ,  $\sigma_0^{(3)}$  are zero-point energy contributions to the cumulants  $\sigma^{(1)}(T)$ ,  $\sigma^2(T)$ ,  $\sigma^{(3)}(T)$ , respectively, and  $\alpha_T^0$  is the constant value which the thermal expansion coefficient approaches at high-temperatures.

Hence, in the present derived GACEM all above analytical expressions for EXAFS quantities contain the anharmonic effective potential parameters so that their direct relationship has been defined. These expressions can be applied to all different material structures including fcc [13,14] and hcp [15], as well as semiconductors presented in this work as the special cases. They are separated for different structures based on the difference of the above mentioned anharmonic effective potential parameters ( $k_{\text{eff}}$ ,  $k_{3\text{eff}}$ ). Especially, the description of Eq. (2.2.8) - (2.2.11) in terms of second cumulant is useful not only for reducing the numerical calculations but also for creating a method for obtaining the remain theoretical or experimental EXAFS quantities of the considered material based on only the calculated (theoretical study) or measured (experimental study) second cumulants. This attempt will be examined for the case of semiconductors presented in Section 3.

### 2.3. Low- and high-temperature limits

It is useful to consider the low-temperature (LT) and high-temperature (HT) limits for the present GACEM. In the LT limit  $z \rightarrow 0$ , so that the terms with  $z^2$  and higher powers can be neglected, and in the HT limit it is approximated that  $z \cong 1 - \hbar\omega_E/k_B T$ . Using these approximations, the expressions for the cumulants given by Eqs. (2.2.8) - (2.2.10) and for the thermal expansion coefficient given by Eq. (2.2.11) have been transformed to those for the LT and HT limits which are written in Table 1.

Note that in the present GACEM (Table 1), at high-temperatures the first and second cumulants are linearly proportional to the temperature  $T$ , the third cumulant to  $T^2$ , and the thermal expansion coefficient approaches the constant value; at low-temperatures the cumulants contain zero-point energy contributions, a quantum effect, and the thermal expansion coefficient vanishes exponentially with  $\theta_E/T$ . Such properties have also been mentioned already for some material structures [7-9].

### 2.4. Application to semiconductors

In order to specify the GACEM for each material structure it is necessary to determine its anharmonic effective potential parameters containing the structural parameters  $S_2$  and  $S_3$ .

Based on the diamond structure, where each atom is bonded to four nearest neighbors, we calculated the structural parameters which have resulted as

$$S_2 = 7/6, \quad S_3 = -35/36 \quad (2.4.1)$$

Hence, from Eq. (2.1.5) the parameters of anharmonic effective potential describing respectively the effective local force constant and cubic anharmonic parameter for semiconductors are given by

**Table 1**

Expressions of the cumulants  $\sigma^{(1)}$ ,  $\sigma^2$ ,  $\sigma^{(3)}$  and thermal expansion  $\alpha_T$  in the LT ( $T \rightarrow 0$ ) and HT ( $T \rightarrow \infty$ ) limits.

Expressions	$T \rightarrow 0$	$T \rightarrow \infty$
$\sigma^{(1)}$	$\sigma_0^{(1)}(1+2z)$	$-3k_{3\text{eff}}k_B T/k_{\text{eff}}^2$
$\sigma^2$	$\sigma_0^2(1+2z)$	$k_B T/k_{\text{eff}}$
$\sigma^{(3)}$	$\sigma_0^{(3)}(1+12z)$	$-6k_{3\text{eff}}(k_B T)^2/k_{\text{eff}}^3$
$\alpha_T$	$\alpha_T^0 z(\ln z)^2(1+2z)$	$\alpha_T^0$

$$k_{eff} = 2D\alpha^2\left(\frac{7}{6} - \frac{105}{36}\alpha a\right) \cong \frac{7}{3}D\alpha^2, \quad k_{3eff} = -\frac{35}{36}D\alpha^3, \quad (2.4.2)$$

and the anharmonic effective potential for semiconductors has then resulted as

$$V_{eff}(x) \cong \frac{7}{6}D\alpha^2x^2 - \frac{35}{36}D\alpha^3x^3, \quad (2.4.3)$$

or in terms of parameter  $y$

$$V_{eff}(y) = D\left(\frac{7}{6}\alpha^2 - \frac{105}{36}\alpha^3a\right)y^2 - \frac{35}{36}D\alpha^3y^3. \quad (2.4.4)$$

Consequently, the analytical expressions for EXAFS cumulants and thermal expansion coefficient of diamond type semiconductors in the present GACEM have the same forms given by Eqs. (2.2.8) - (2.2.11) but the parameters  $k_{eff}$  and  $k_{3eff}$  in which are given by Eq. (2.4.2).

### 3. Numerical results and discussions

Now we apply the expressions derived in the previous sections to numerical calculations for temperature dependence of EXAFS cumulants and thermal expansion coefficient of diamond structure type semiconductors Si and Ge using their Morse potential parameters [34]  $D = 1.83$  eV,  $\alpha = 1.56 \text{ \AA}^{-1}$ ,  $r_0 = 2.34 \text{ \AA}$  for Si and  $D = 1.63$  eV,  $\alpha = 1.50 \text{ \AA}^{-1}$ ,  $r_0 = 2.44 \text{ \AA}$  for Ge. The calculated values of the local force constant  $k_s$ , anharmonic cubic parameter  $k_{3s}$ , correlated Einstein frequency  $\omega_{ES}$  and temperature  $\theta_{ES}$  for the anharmonic effective ( $S = eff$ ) potential are written in Table 2 which show their difference from those calculated using the single-pair ( $S = SP$ ) potential. They are used for the calculations and discussions of the considered EXAFS quantities of semiconductors. Since the derived expressions given by Eqs. (2.2.8) - (2.2.10) for the cumulants and by Eq. (2.2.11) for the thermal expansion coefficient are described in terms of second cumulant or MSRD, we also calculate the first, third cumulants and thermal expansion coefficient from the calculated (calc.) [19–21] or experimental (exp.) [22–24] MSRD taken from their related works [19–24] and compare the results with experiment [23,26,27]. The agreement of these calculated quantities with experiment confirms their validity as the values of the first, third cumulants and thermal expansion coefficient of the considered semiconductors which have not been calculated or measured in their related works [19–24].

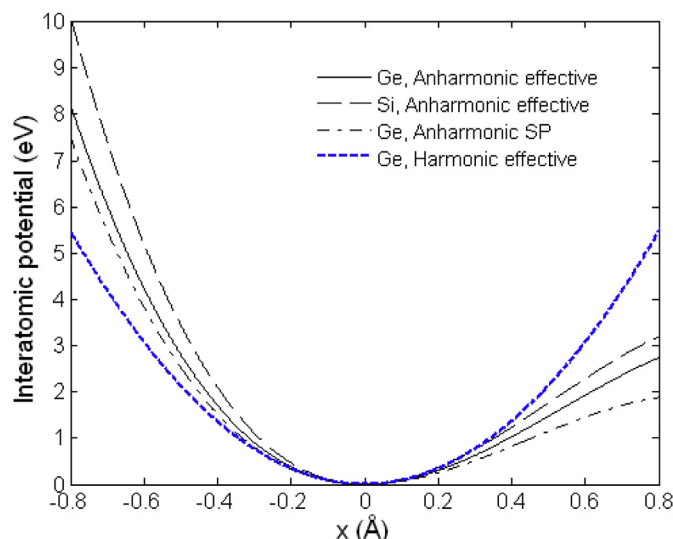
Fig. 1 illustrates the anharmonic intratomic effective potentials of Ge and Si calculated using the present theory. They are asymmetric due to the anharmonic contributions described by the third order parameter  $k_{3eff}$  of these potentials. Here, the anharmonic effective potential of Ge is compared to the anharmonic SP potential to show their difference and to its harmonic effective term to show the rate of its asymmetry due to anharmonicity. These anharmonic effective potentials of Ge and Si are used for calculating the considered EXAFS quantities.

Temperature dependence of second cumulant or MSRD  $\sigma^2(T)$  of Ge (Fig. 2a) calculated using the present theory agrees well with the experimental values of G. Dalba et al. (Expt.) [22], (Expt1) [23], and of A. E. Stern et al. [24], with the result of J. J. Rehr et al. [20] calculated using LDA, and of N. V. Hung et al. [31] calculated using the SMM and Stillinger-Weber potentials, as well as is found to be in reasonable

**Table 2**

Calculated values of  $k_s$ ,  $k_{3s}$ ,  $\omega_{ES}$ ,  $\theta_{ES}$  of semiconductors Si and Ge for effective ( $S = eff$ ) and single-pair ( $S = SP$ ) potentials using Morse potential parameters [34].

Element, $S$	$k_s$ (N/m)	$k_{3s}$ (eV. $\text{\AA}^{-3}$ )	$\omega_{ES}$ ( $\times 10^{13}$ Hz)	$\theta_{ES}$ (K)
Si, $eff$	166.4911	-6.7545	8.4243	643.5014
Si, $SP$	142.7067	-6.9474	7.7994	595.7665
Ge, $eff$	137.1074	-5.3484	4.7556	363.2636
Ge, $SP$	117.5206	-5.5012	4.4028	336.3167



**Fig. 1.** Anharmonic intratomic effective potentials  $V_{eff}(x)$  of Ge and Si calculated using the present theory compared to the harmonic effective and anharmonic SP potentials of Ge.

agreement with the one of F. D. Vila et al. [19] calculated using the LDA. Temperature dependence of the first cumulant or net thermal expansion  $\sigma^{(1)}(T)$  of Ge (Fig. 3a) calculated using the present theory agrees well with the experimental values of G. Dalba et al. [26]. Such good agreement is also shown for the third cumulant  $\sigma^{(3)}(T)$  of Ge (Fig. 4a) calculated using the present theory with the EXAFS experimental values of G. Dalba et al. (Expt.) [23] and (Expt1.) [26], as well as of P. Fornasini et al. [27]. Temperature dependence of second cumulant (Fig. 2b), first cumulant (Fig. 3b) and third cumulant (Fig. 4b) of Si calculated using the present theory also agree well with the results of these cumulants calculated using the second cumulant or MSRD of M. Benfatto et al. [21] calculated using the structural correlation matrices at 80 K, 300 K and 500 K. Fig. 5a shows reasonable agreement of temperature dependence of thermal expansion coefficient  $\alpha_T(T)$  of Ge calculated using the present theory with the one calculated from the experimental (exp.) MSRD of G. Dalba et al. [22]. These calculated results approach the constant value at high temperatures, illustrating the behavior of  $\alpha_T(T)$  which was expressed in the other works for the other crystal structures [8,10,11]. Moreover, the results calculated using the present theory presented in Fig. 2 for the second cumulant, in Fig. 3 for the first cumulant, and in Fig. 4 for the third cumulant of Ge and Si agree with experiment better than those calculated using the SP potential. This limitation of SP potential can be attributed to neglecting the many-body effects or three-dimensional interaction and it can also be treated by including the many-body effect contributions as it was done in the present GACEM.

The cumulant ratios are often considered in the anharmonic EXAFS studies [2,6,10,13,14]. Fig. 5b illustrates temperature dependence of cumulant ratios  $\sigma^{(1)}\sigma^2/\sigma^{(3)}$  and  $\alpha_T\text{Tr}\sigma^2/\sigma^{(3)}$  calculated using the present theory for Ge. Here,  $\sigma^{(1)}\sigma^2/\sigma^{(3)}$  approach 3/2,  $\alpha_T\text{Tr}\sigma^2/\sigma^{(3)}$  vanishes at low-temperatures, and both they approach the classical value [2,6] of 1/2 at high-temperatures beginning from the Einstein temperature ( $\theta_E = 363.26$  K for Ge, Table 2) as for the other crystal structures [2,6,10,13,14]. Hence, they remain to be considered as the standards for studying EXAFS cumulants and thermal expansion coefficient of semiconductors calculated using the present theory.

### 4. Conclusions

This work has advanced the EXAFS studies of the thermodynamic properties and anharmonic effects accounting for the net thermal expansion, the MSRD, the asymmetry of the pair distribution function and

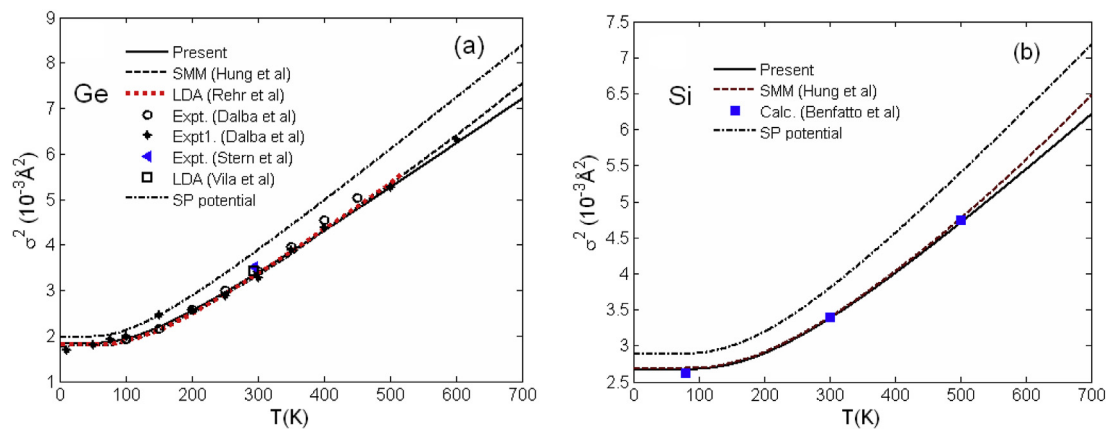


Fig. 2. Temperature dependence of second cumulant or MSR D  $\sigma^2(T)$  calculated using the present theory for (a) Ge compared to the experimental EXAFS values of G. Dalba et al. (Expt.) [22], (Expt1.) [23] and of E. A. Stern et al. [24], as well as to those of F. D. Vila et al. [19] and of J. J. Rehr et al. [20] calculated using LDA, and of N. V. Hung et al. [31] calculated using SMM and Stillinger-Weber potential, and (b) Si compared to the EXAFS calculated values of M. Benfatto et al. [21], and to that of N. V. Hung et al. [31] calculated using SMM and Stillinger-Weber potential. Both the results for Ge and Si are compared to those calculated using the SP potential.

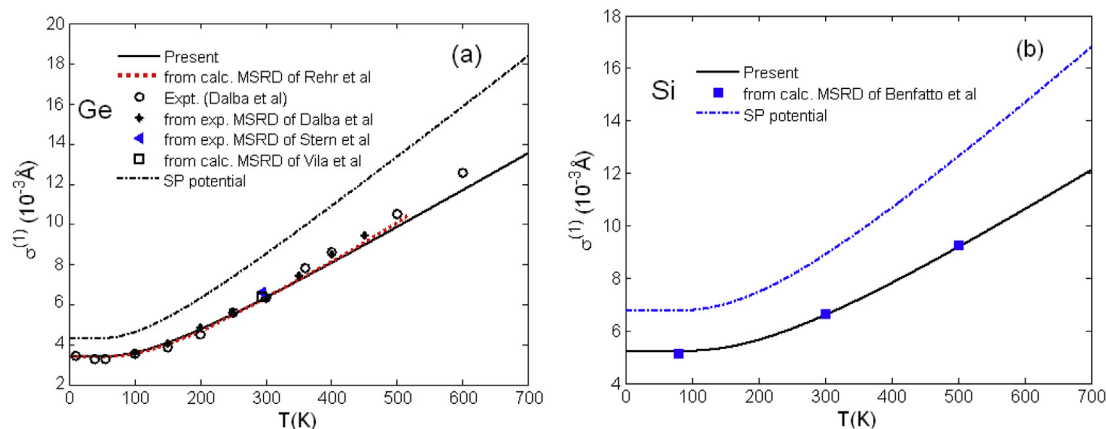


Fig. 3. Temperature dependence of first cumulant  $\sigma^{(1)}(T)$  calculated using the present theory for (a) Ge compared to the experimental values of G. Dalba et al. [26], and to those calculated from the experimental (exp.) MSR D of G. Dalba et al. [22], of E. A. Stern et al. [24], as well as from the calculated (calc.) MSR D of F. D. Vila et al. [19], and of J. J. Rehr et al. [20] calculated using LDA, and (b) Si compared to that calculated from the calculated (calc.) MSR Ds of M. Benfatto et al. [21]. Both the results for Ge and Si are compared to those calculated using the SP potential.

Note that the first and third cumulants of Ge have not been measured by G. Dalba et al. [22] and by E. A. Stern et al. [24], as well as have not been calculated by F. D. Vila et al. [19], and J. J. Rehr et al. [20]. But using the present theory, as well as its measured [22,24] and calculated [19,20] second cumulants or MSR Ds, they have been obtained and presented in Fig. 3a for the first cumulant and in Fig. 4a for the third cumulant. It is interesting that these calculated experimental and theoretical quantities agree well with the measured values of G. Dalba et al. [26] for the first cumulant (Fig. 3a), as well as of G. Dalba et al. [23,26], and of P. Fornasini et al. [27] for the third cumulant (Fig. 4a). Consequently, their agreements confirm not only the validity of the above obtained quantities but also the possibility of getting the other EXAFS parameters if the second cumulants are calculated or measured. This actually also confirms the validity of the above created method which has been used in the present studies.

the thermal expansion coefficient of materials of all structures including complex systems based on Debye-Waller factors presented in terms of cumulant expansion.

The advances are succeeded based on the GACEM derived for all material structures separated for each structure by its anharmonic effective potential parameters ( $k_{eff}$ ,  $k_{3eff}$ ) contained in the derived analytical expressions of the considered quantities.

The derived GACEM is simplified by using the one-dimensional model with taking the many-body effects into account based on including the first-shell near-neighbor contributions to the vibrations between absorber and backscatterer atoms.

The method created in this GACEM using which all theoretical and experimental EXAFS quantities are provided based on only the calculation (theoretical study) or measurement (experimental study) of second cumulants is useful not only for reducing the numerical calculations or measurements but also for creating a simple way of obtaining the considered quantities.

The advanced studies are successfully applied to semiconductors

where their three first EXAFS cumulants and thermal coefficient describing their thermodynamic properties and anharmonic effects have been evaluated. They approach classical limits at high-temperatures and contain zero-point energy contributions at low-temperatures, a quantum effect. The cumulant ratios  $\sigma^{(1)}\sigma^2/\sigma^{(3)}$  and  $\alpha_T Tr\sigma^2/\sigma^{(3)}$  express the same properties as those for the other crystal structures so that they remain to be considered as the standards for EXAFS cumulant studies of semiconductors.

The good and reasonable agreement of the results calculated using the present theory and of those obtained by using the created method with experiment and with those of other theories for Si and Ge having diamond structure illustrates the simplicity, advantage and efficiency of the present theory and the created method in the theoretical and experimental EXAFS studies of the thermodynamic properties and anharmonic effects of materials having any structure including semiconductors.

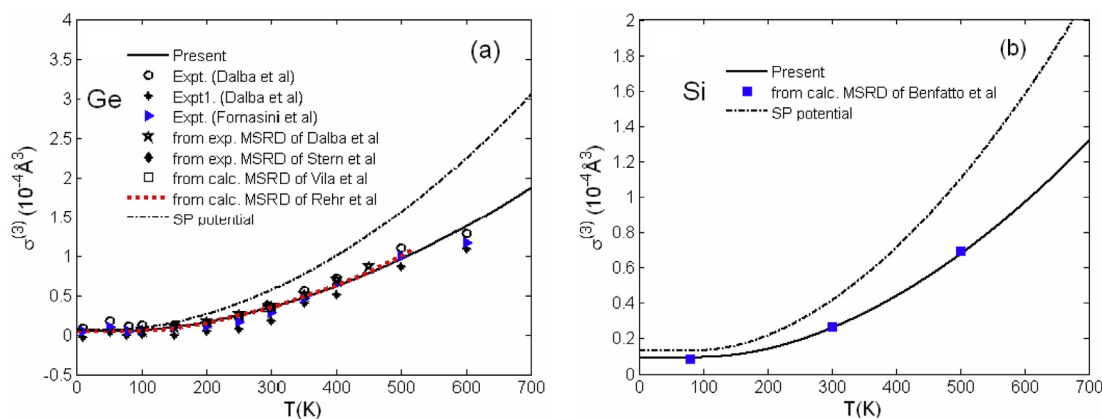


Fig. 4. Temperature dependence of third cumulant  $\sigma^{(3)}(T)$  calculated using the present theory for (a) Ge compared to the EXAFS experimental values of G. Dalba et al. (Expt.) [23], (Expt1.) [26] and of P. Fornasini et al. [27], as well as to those calculated from the experimental (exp.) MSRD of Dalba et al. [23], of E. Stern et al. [24] and from the calculated (calc.) MSRD of F. D. Vila et al. [19], and of J. J. Rehr et al. [20] calculated using LDA, and (b) Si compared to that calculated from the calculated (calc.) MSRD of M. Benfatto et al. [21]. Both the results for Ge and Si are compared to those calculated using the SP potential.

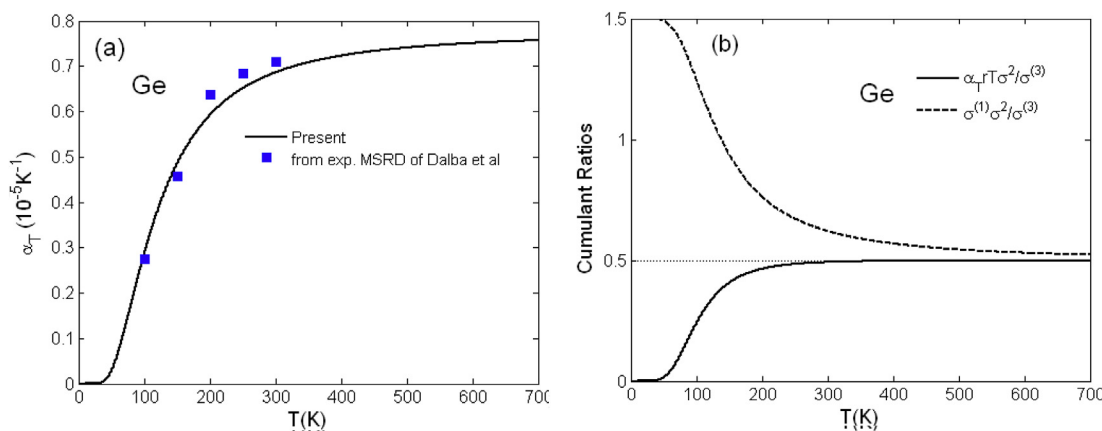


Fig. 5. Temperature dependence of (a) thermal expansion coefficient  $\alpha_T(T)$  and (b) cumulant ratios  $\sigma^{(1)}\sigma^2/\sigma^{(3)}$ ,  $\alpha_T T \sigma^2/\sigma^{(3)}$  of Ge calculated using the present theory compared to that calculated from the experimental (exp.) MSRD of Dalba et al. [22] for  $\alpha_T(T)$ .

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