

## TEMPERATURE DEPENDENCE OF ANHARMONIC EXAFS OSCILLATION OF CRYSTALLINE SILICON

Tong Sy Tien<sup>1,\*</sup>, Le Viet Hoang<sup>2</sup>

<sup>1</sup> Department of Basic Sciences, University of Fire, 243 Khuat Duy Tien, Thanh Xuan, Hanoi, Vietnam

<sup>2</sup> Department of Physics, Hanoi University of Science, 334 Nguyen Trai, Thanh Xuan, Hanoi, Vietnam

\*E-mail: tongsytien@yahoo.com

### Article info

Received:

16/9/2020

Accepted:

10/12/2020

### Keywords:

EXAFS analysis; Debye-Waller factor; Anharmonic correlated Einstein model; Crystalline silicon.

### Abstract:

In this work, the anharmonic extended X-ray absorption fine structure (EXAFS) oscillation of crystalline silicon (c-Si) is presented in terms of the Debye-Waller factor using the cumulant expansion approach up to the fourth-order. The first four EXAFS cumulant has been calculated based on the classical anharmonic correlated Einstein (ACE) model and suitable analysis procedure, in which thermodynamic parameters are derived from the anharmonic effective potential obtained using the first shell near-neighbor contribution approach. The analysis of the temperature dependence of the EXAFS oscillation is performed via evaluating the influence of the cumulants on the amplitude reduction and the phase shift of the anharmonic EXAFS oscillation. The numerical results are found to be in good agreement with those obtained using the quantum ACE model and experiments at various temperatures. The obtained results are useful in analyzing the experimental EXAFS data of c-Si.

### 1. Introduction

The extended X-ray absorption fine structure (EXAFS) has been developed into a powerful technique and is widely used to determine many structural parameters and dynamic properties of materials [1]. However, the position of atoms is not stationary, and their interatomic distance always changes due to thermal vibrations that were detected by Beni & Platzman [2]. They cause anharmonic effects on crystal vibrations and smear out the EXAFS oscillations. The anharmonicity of the potential yields additional terms in the EXAFS oscillation, so if ignoring these terms, can lead to

non-negligible errors in the structural parameters. The use of the moments of the radial distribution function (or cumulants) to investigate local disorder of EXAFS spectra was introduced by Rehr [3] who showed that the Debye-Waller (DW) factor of EXAFS spectra has a natural cumulant expansion in powers of the photoelectron wavenumber. The connection between the DW factor and the EXAFS cumulants was described in detail in the cumulant expansion approach (*ratio* method) by Bunker [4]. The ratio method is particularly appealing because it summarizes the relevant structural and dynamic

information that is easily obtained from the experimental EXAFS spectra.

Recently, a classical anharmonic correlated Einstein (ACE) model [5] was developed based on the anharmonic effective (AE) potential [6] and the classical statistical theory [7]. This model has the advantage that the expressions of the first four EXAFS cumulants are obtained in explicit and simple forms, so it is very convenient for anharmonic EXAFS data analysis in the range of temperatures not too low. It has also been successfully applied to investigate the anharmonic EXAFS oscillation for diamond crystals by Tien *et al.* [8]. However, the temperature dependence of anharmonic EXAFS amplitude and phase has not been discussed in detail. Besides, it has been applied to successfully investigate crystalline germanium but has not yet been investigated crystalline silicon (c-Si). Therefore, the analysis of the temperature dependence of anharmonic EXAFS oscillation for c-Si will be a necessary addition to evaluate the effectiveness of the classical ACE model in the EXAFS technique.

## 2. Basic formulae of EXAFS function and anharmonic effective potential of c-Si

### 2.1. Basic formulae of EXAFS function

The EXAFS oscillation for a single coordination shell, including thermal disorders has the form:

$$\chi(k, T) = A(k, T) \sin \Phi(k, T), \quad (1)$$

where  $A(k, T)$  and  $\Phi(k, T)$  are the EXAFS amplitude and phase, respectively, and  $k$  is the photoelectron wavenumber, and  $T$  is the temperature.

The  $K$ -edge EXAFS oscillation for the distribution of identical atoms is described within the framework of single-scattering and plane-wave approximations. Following the approach proposed by Tien [9], the logarithm of amplitude ratio  $M(k, T_1, T_2) = \ln[A(k, T_2)/A(k, T_1)]$  and the linear phase difference  $\Delta\Phi(k, T_1, T_2) = \Phi(k, T_2) - \Phi(k, T_1)$  between temperatures  $T_2$  and  $T_1$  in the cumulant expansion approach up to the fourth-order, which are given as follows:

$$M(k, T_1, T_2) \approx -2k^2 \{ \sigma^2(T_2) - \sigma^2(T_1) \} + \frac{2k^4}{3} \{ \sigma^{(4)}(T_2) - \sigma^{(4)}(T_1) \}, \quad (2)$$

$$\Delta\Phi(k, T_1, T_2) \approx 2k \{ \sigma^{(1)}(T_2) - \sigma^{(1)}(T_1) \} - 4k \left\{ \frac{1}{r_0} + \frac{1}{\lambda} \right\} \{ \sigma^2(T_2) - \sigma^2(T_1) \} - \frac{4k^3}{3} \{ \sigma^{(3)}(T_2) - \sigma^{(3)}(T_1) \}. \quad (3)$$

where  $\sigma^{(n)}$  are  $n$  th-order cumulants and can be expressed in terms of the power moments of the true RD function  $\rho(T, r)$ .

### 2.2. Thermodynamic parameters and anharmonic effective potential of c-Si

To determine the thermodynamic parameters of a system, it is necessary to specify its AE potential and force constants [10]. One considers a monatomic system with an anharmonic effective potential (ignored the constant contribution) is extended up to the fourth-order:

$$V_{\text{eff}}(x) = \frac{1}{2} k_0 x^2 - k_3 x^3 + k_4 x^4, \quad (4)$$

where  $x = r - r_0$  is the deviation of the interatomic distance from the potential minimum position,  $k_0$  is the effective force constant,  $k_3$  and  $k_4$  are local force constants giving asymmetry of potential due to the inclusion of anharmonicity.

The Morse potential is assumed to describe the interatomic interaction model for the potential energy of a diatomic molecule. Applying the Morse potential to calculate the interaction energy between each pair of atoms in cubic metals was proposed by Girifalco and Weizer [11]. In the present study, we expand the Morse potential to the fourth-order:

$$V(x) = D(e^{-2\alpha x} - 2e^{-\alpha x}) \cong -D + D\alpha^2 x^2 - D\alpha^3 x^3 + \frac{7}{12}D\alpha^4 x^4. \quad (5)$$

where  $x$  is the same previously defined value,  $\alpha$  describes the width of the potential, and  $D$  is the dissociation energy.

In the relative vibrations of absorbing (A) and

$$V_{eff} = V(x) + \sum_{i=A,B} \sum_{j \neq A,B} V\left(\frac{\mu}{M_i} x \hat{R}_{AB} \hat{R}_{ij}\right), \quad (6)$$

where  $\mu = M_A M_B / (M_A + M_B)$  is the reduced mass of the absorber and backscatterer with masses  $M_A$  and  $M_B$ , respectively,  $\hat{R}$  is a unit

backscattering (B) atoms, including correlation effects and taking into account only the nearest-neighbor interactions, the AE potential [6] is given by

vector, the sum  $i$  is the over absorbers ( $i = A$ ) and backscatterers ( $i = B$ ), and the sum  $j$  is over the nearest neighbors.

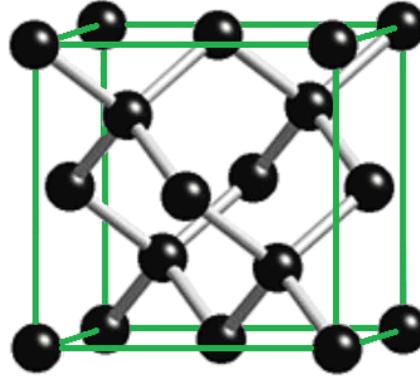


Fig. 1. Structural model of c-Si.

Applying Eqs. (5) and (6) to the structure of c-Si with a mass of atoms is  $M_A = M_B = m$ , as seen in Fig. 1, the AE potential is written as

$$V_{eff}(x) = \frac{7}{3}D\alpha^2 x^2 - \frac{35}{36}D\alpha^3 x^3 + \frac{1519}{2592}\alpha^4 x^4. \quad (7)$$

The local force constants  $k_0$ ,  $k_3$ , and  $k_4$  are deduced from Eq. (7) as follows:

$$\omega_E = \sqrt{\frac{k_{eff}}{\mu}} = \alpha \sqrt{\frac{10D}{m}}, \quad \theta_E = \frac{\hbar \omega_E}{k_B} = \frac{\hbar \alpha}{k_B} \sqrt{\frac{10D}{m}}, \quad (9)$$

where  $k_B$  is the Boltzmann constant,  $\hbar$  is the reduced Planck constant.

Consequently, the correlated Einstein frequency  $\omega_E$  and temperature  $\theta_E$ , and force constants

Comparing Eq. (4) with Eq. (7), we deduce the local force constants  $k_0$ ,  $k_3$ , and  $k_4$  as follows:

$$k_0 = \frac{7}{3}D\alpha^2, \quad k_3 = \frac{35}{36}D\alpha^3, \quad k_4 = \frac{1519}{2592}D\alpha^4. \quad (8)$$

The thermal vibration of atoms is characterized by the correlated Einstein frequency  $\omega_E$  and temperature  $\theta_E$ , which are calculated from the effective force constant  $k_0$  in the following forms:

$k_0, k_3$ , and  $k_4$  are expressed in terms of the Morse potential parameters via Eqs. (8) and (9).

### 3. Temperature dependence of EXAFS oscillation within the classical ACE model

The EXAFS cumulants are explicitly related to low-order moments of the distribution function.

$$\sigma^{(1)}; \frac{15k_B}{28D\alpha}T = \frac{5\alpha}{4}\sigma^2, \quad (10)$$

$$\sigma^{(2)}; \frac{3k_B}{7D\alpha^2}T = \frac{2k_B}{m\omega_E^2}T \equiv \sigma^2, \quad (11)$$

$$\sigma^{(3)}; \frac{45k_B^2}{98D^2\alpha^3}T^2 = \frac{5\alpha}{2}(\sigma^2)^2, \quad (12)$$

$$\sigma^{(4)}; \frac{687k_B^3}{686D^2\alpha^4}T^3 = \frac{229\alpha^2}{18}(\sigma^2)^3. \quad (13)$$

Substituting the anharmonic EXAFS cumulants from Eqs. (10)-(13) into Eqs. (2) and (3) to calculate the logarithm of amplitude ratio  $M(k, T_1, T_2)$  and the linear phase difference  $\Delta\Phi(k, T_1, T_2)$ , the results are obtained as

$$M(k, T_1, T_2) \approx -\frac{6k_B}{7D\alpha^2}k^2(T_2 - T_1) + \frac{229k_B^3}{343D^3\alpha^4}k^4(T_2^3 - T_1^3), \quad (14)$$

$$\Delta\Phi(k, T_1, T_2) \approx \frac{15k_B}{14D\alpha}k(T_2 - T_1) - \frac{12k_B}{7D\alpha^2}\left\{\frac{1}{r_0} + \frac{1}{\lambda}\right\}k(T_2 - T_1) - \frac{30k_B^2}{49D^2\alpha^3}k^3(T_2^2 - T_1^2). \quad (15)$$

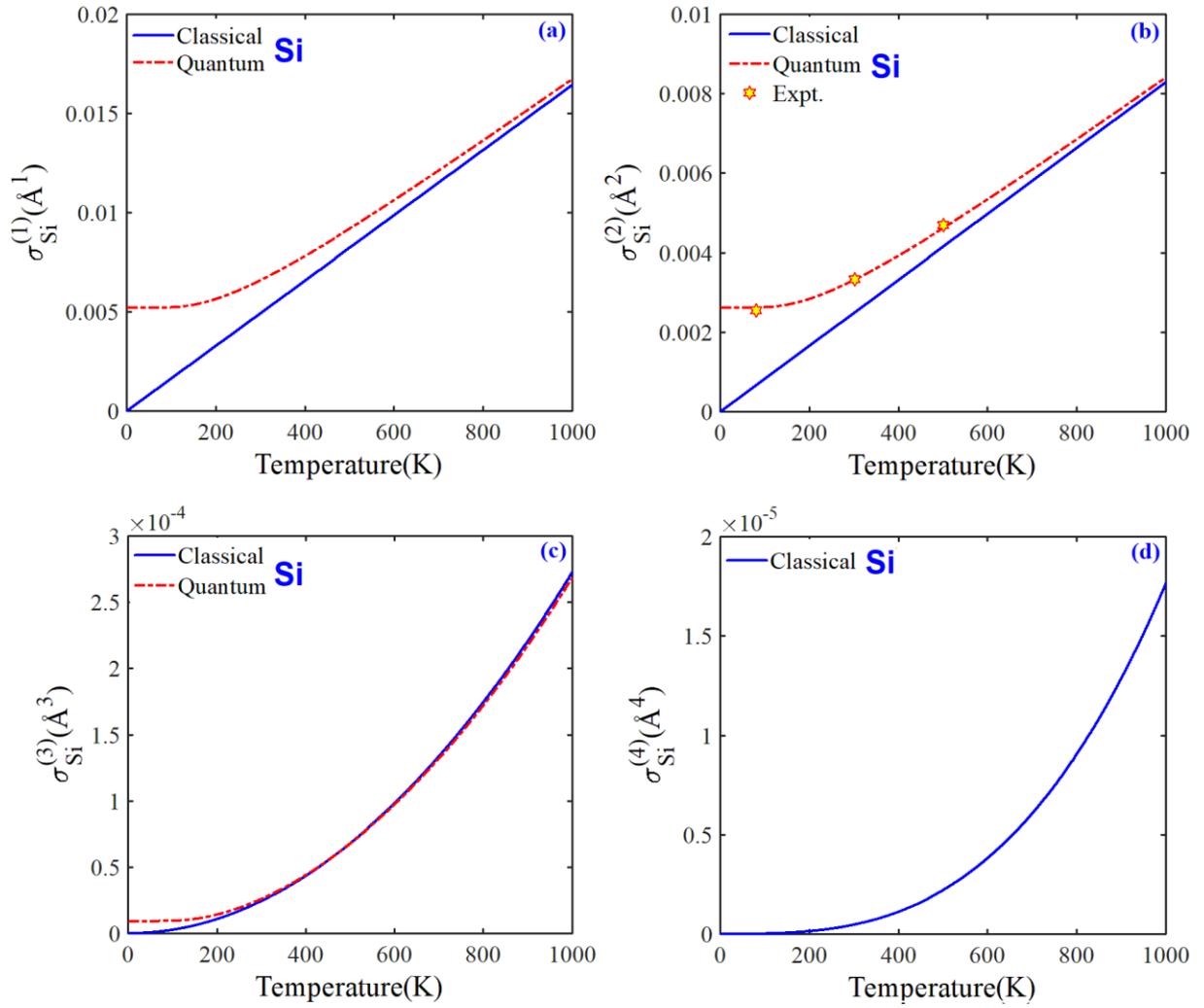
Thus, the EXAFS cumulants using the CACE model can be expressed in the explicit and simple forms of the mean-square relative displacement (MSRD)  $\sigma^2$  or temperature  $T$ . Consequently, the logarithm of amplitude ratio and the phase difference of the EXAFS oscillation is also expressed in simple forms of temperature via the EXAFS cumulants. These obtained results can describe the influence of anharmonic effects on the classical limit at high temperatures, and show that the cumulants are very useful for the quantitative treatment of the anharmonic EXAFS oscillation.

### 4. Numerical results and discussions

To discuss the effectiveness of the classical ACE model for the analysis of the EXAFS oscillation of c-Si in this work, we apply Eqs. (8)-

The analysis of the EXAFS spectra usually uses the first four EXAFS cumulants [10]. The expressions of the first four cumulants of diamond crystals within the classical ACE model are given as follows [8]:

(9) in Sec. 2 and Eqs. (10)-(15) in Sec. 3 to the numerical calculations. Firstly, we perform numerical calculations for the force constants of the AE potential, the thermodynamic parameters, and the temperature dependence of the first four EXAFS cumulants in the range from 0 K to 1000 K. Our results of the cumulants are compared with those obtained using the quantum ACE model [6] in the range from 0 K to 1000 K by Hung *et al.* [12] and experiment at 80 K, 300 K, and 500 K by Benfatto *et al.* [13]. Then, we analyze the logarithm of amplitude ratio and the phase difference of the anharmonic EXAFS oscillation with reference value at  $\theta_E$  in the wavenumber range from 0  $\text{\AA}^{-1}$  to 20  $\text{\AA}^{-1}$  at 700 K, 800 K, and 900K. Lastly, we evaluate and comment on the results obtained using the classical ACE model in this work.



**Fig. 2.** Temperature dependence of (a) the first, (b) second, (c) third, and (d) fourth EXAFS cumulants of c-Si obtained using the ACE model, the quantum ACE model [12], and the experiments [13].

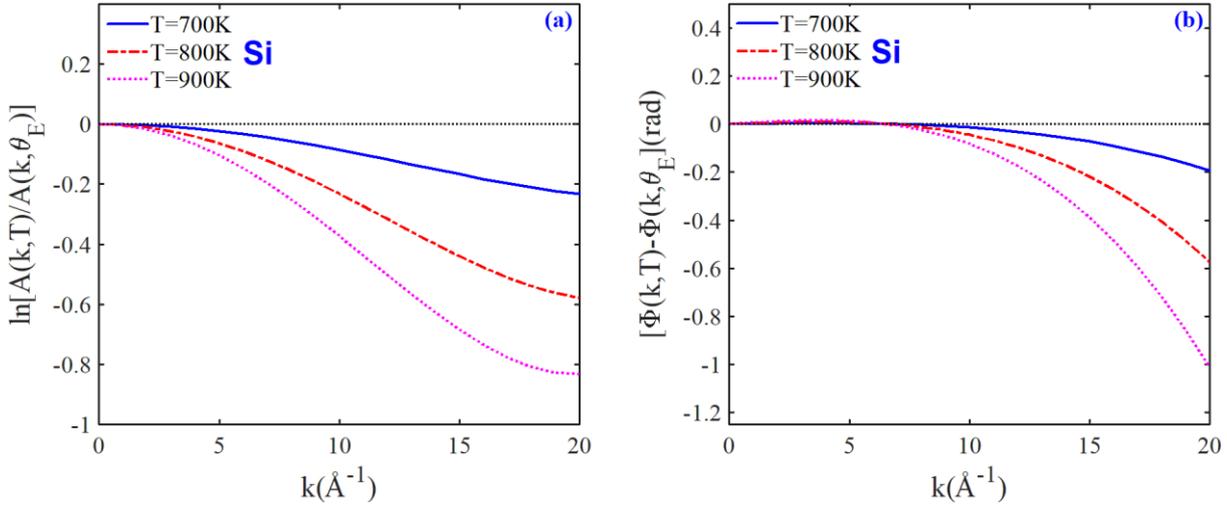
The force constants  $k_0$ ,  $k_3$ , and  $k_3$ , and the correlated Einstein frequency  $\omega_E$  and temperature  $\theta_E$  are calculated via Eqs. (8)-(9). Our obtained results are  $k_0 \approx 10.39 \text{ eV}\text{\AA}^{-2}$ ,  $k_3 \approx 6.75 \text{ eV}\text{\AA}^{-2}$ ,  $k_4 \approx 6.35 \text{ eV}\text{\AA}^{-2}$ ,  $\omega_E \approx 8.42 \times 10^{13} \text{ Hz}$ , and  $\theta_E \approx 643.49 \text{ K}$ , in which the use of the Morse potential parameters  $D = 1.83 \text{ eV}$  and  $\alpha = 1.56 \text{\AA}^{-1}$  in calculations were determined by Swalin (1961) [14].

The temperature dependence of (a) the first cumulant  $\sigma^{(1)}(T)$ , (b) the second cumulant

$\sigma^{(2)}(T)$ , (c) the third cumulant  $\sigma^{(3)}(T)$ , and (d) the fourth cumulant  $\sigma^{(4)}(T)$  of c-Si is calculated by Eqs. (9)-(12) and shown in Fig. 2. Our obtained results using the classical ACE model agree well with the results obtained using the quantum ACE model [12] (for the first three cumulants) and the experiments [13] (for the second cumulants) at high temperatures, especially for high-order cumulants. For example, at 500 K, the results obtained using the classical ACE model and quantum ACE model are  $\sigma^{(1)} \approx 8.1 \times 10^{-3} \text{\AA}$ ,  $\sigma^{(2)} \approx 4.1 \times 10^{-3} \text{\AA}^2$ ,  $\sigma^{(3)} \approx 6.7 \times 10^{-5} \text{\AA}^3$ , and  $\sigma^{(4)} \approx 2.2 \times 10^{-6} \text{\AA}^4$ , and  $\sigma^{(1)} \approx 9.2 \times 10^{-3} \text{\AA}$ ,  $\sigma^{(2)} \approx 4.7 \times 10^{-3} \text{\AA}^2$ , and  $\sigma^{(3)} \approx 6.8 \times 10^{-5} \text{\AA}^3$  [12], respectively, while the experimental value is  $\sigma^{(2)} \approx 4.3 \times 10^{-3} \text{\AA}^2$  at 500 K [13]. Our expressions of the first three EXAFS cumulants are the same as the corresponding expressions calculated by the quantum ACE model [12] in the

high-temperature limit. Moreover, our results of the EXAFS cumulants can agree with their experimental values at high temperatures although we have only experimental values of the second cumulant in comparisons. It is because the experimental values of other cumulants can all be deduced from the second cumulant [15].

Thus, the results of the temperature dependence of the first four EXAFS cumulants of c-Si are



**Fig. 3.** The (a) logarithm of amplitude ratio and (b) phase difference with reference value at  $\theta_E$  of c-Si obtained using the classical ACE model at various temperatures.

The (a) logarithm of amplitude ratio  $M(k,T) = \ln[A(k,T)/A(k,\theta_E)]$  and (b) phase difference  $\Delta\Phi(k,T) = \Phi(k,T) - \Phi(k,\theta_E)$  of c-Si at 700 K, 800 K, and 900 K are calculated by Eqs. (14)-(15) and shown in Fig. 3. It can be seen that the values of  $M(k,T)$  and  $\Delta\Phi(k,T)$  decrease with increasing temperature  $T$  and decrease with fast-increasing wavenumber  $k$ . For example, at  $T = 700$  K,  $T = 800$  K, and  $T = 900$  K, the approximate results of  $M(k,T)$  are  $-0.086$ ,  $-0.231$ , and  $-0.372$  at  $k = 10 \text{\AA}^{-1}$ , and  $-0.233$ ,  $-0.578$ , and  $-0.833$  at  $k = 20 \text{\AA}^{-1}$ , respectively, while the corresponding results of  $\Delta\Phi(k,T)$  are  $-0.014$ ,  $-0.043$ , and  $-0.080$  at  $k = 10 \text{\AA}^{-1}$ , and  $-0.192$ ,  $-0.573$ , and  $-1.012$  at  $k = 20 \text{\AA}^{-1}$ , respectively.

Moreover, in the temperature dependence, the value of  $\Delta\Phi(k,T)$  decreases faster than the value of  $M(k,T)$ . It is because high-order cumulants increase with temperature  $T$ , in which the third cumulant reduces the value of  $\Delta\Phi(k,T)$  and the fourth cumulant increases the value of  $M(k,T)$ , as seen Eqs. (14) and (15).

Thus, the results of the temperature dependence of anharmonic EXAFS oscillation of c-Si are obtained using the classical ACE model, which shows that the even-order cumulants contribute to the amplitude reduction, and the odd-order cumulants contribute primarily to the phase shift of the anharmonic EXAFS oscillation. Accurate calculation of the cumulants will allow us to accurately analyze the change of the anharmonic EXAFS oscillation, and from which one will determine the structural parameters from the experimental EXAFS data.

## 5 Conclusions

In this work, the classical ACE model has been used successfully in the analysis of the anharmonic EXAFS oscillation of c-Si. The EXAFS analysis is performed based on evaluating the contribution of terms of the Debye-Waller factor in the cumulant expansion approach up to the fourth-order. The results of the first four EXAFS cumulants are not only expressed in explicit and simple forms of the temperature  $T$  or MSR D but also satisfy all of their fundamental properties in temperature dependence. The analytical results show the role and meaning of the EXAFS cumulants for the amplitude reduction and the phase shift of the anharmonic EXAFS oscillation. The obtained results are very useful for analyzing the experimental data of the anharmonic EXAFS oscillation of c-Si.

The good agreement of our numerical results with those obtained using the quantum ACD model and the experiments at various temperatures show the effectiveness of the classical ACE model for calculating and analyzing the anharmonic EXAFS oscillation of c-Si. The obtained results can be applied to the analysis of the anharmonic EXAFS oscillation of c-Si starting from about the correlated Einstein temperature to just before the melting point.

## Acknowledgments

The authors are thankful to Professor Nguyen Ba Duc for helpful discussions and comments.

## REFERENCES

- [1] F.W. Lytle, D.E. Sayers, E.A. Stern, Extended x-ray-absorption fine-structure technique. II. Experimental practice and selected results, *Phys. Rev. B* 11 (1975) 4825-4835.
- [2] G. Beni and P.M. Platzman, Temperature and polarization dependence of extended x-ray absorption fine-structure spectra, *Phys. Rev. B* 14 (4) (1976) 1514-1518.
- [3] J.J. Rehr and R.C. Albers, Theoretical approaches to x-ray absorption fine structure, *Rev. Mod. Phys.* 72 (3) (2000) 621-654.
- [4] G. Bunker, Applications of the ratio method of EXAFS analysis to disordered systems, *Nucl. Instrum. Methods* 207 (1983) 437-444.
- [5] N.V. Hung, T.S. Tien, N.B. Duc, D.Q. Vuong, High-order expanded XAFS Debye-Waller factors of HCP crystals based on classical anharmonic correlated Einstein model, *Mod. Phys. Lett. B* 28 (21) (2014) 1450174.
- [6] N.V. Hung and J.J. Rehr, Anharmonic correlated Einstein-model Debye-Waller factors, *Phys. Rev. B* 56 (1) (1997) 43-46.
- [7] E.A. Stern, P. Livins, Z. Zhang, Thermal vibration and melting from a local perspective, *Phys. Rev. B* 43 (11) (1991) 8850-8860.
- [8] T.S. Tien, N.V. Hung, N.T. Tuan, N.V. Nam, N.Q. An, N.T.M. Thuy, V.T.K. Lien, N.V. Nghia, High-order EXAFS cumulants of diamond crystals based on a classical anharmonic correlated Einstein model, *J. Phys. Chem. Solids* 134 (2019) 307-312.
- [9] T.S. Tien, Advances in studies of the temperature dependence of the EXAFS amplitude and phase of FCC crystals, *J. Phys. D: Appl. Phys.* 53 (2020) 315303.
- [10] T. Yokoyama, K. Kobayashi, T. Ohta, A. Ugawa, Anharmonic interatomic potentials of diatomic and linear triatomic molecules studied by extended x-ray-absorption fine structure, *Phys. Rev. B* 53 (10) (1996) 6111-6122.
- [11] L.A. Girifalco and V.G. Weizer, Application of the Morse potential function to cubic metals, *Phys. Rev.* 114 (3) (1959) 687-690.
- [12] V.V. Hung and H.K. Hieu, Study the Temperature Dependence of EXAFS Cumulants of Si and Ge by the Anharmonic Correlated Einstein Model, *Commun. Phys.* 21 (1) (2011) 25-34.
- [13] M. Benfatto, C.R. Natoli, A. Filipponi, Thermal and structural damping of the multiple-scattering contributions to the x-ray-absorption coefficient, *Phys. Rev. B* 40 (14) (1989), 9626-9635.
- [14] R.A.Swalin, Theoretical calculations of the enthalpies and entropies of diffusion and vacancy formation in semiconductors, *J. Phys. Chem. Solids* 18 (4) (1961) 290-296.
- [15] N.V. Hung, C.S. Thang, N.B. Duc, D.Q. Vuong, T.S. Tien, Temperature dependence of theoretical and experimental Debye-Waller factors, thermal expansion and XAFS of metallic Zinc, *Physica B* 521 (2017)198-203.

## SỰ PHỤ THUỘC VÀO NHIỆT ĐỘ CỦA DAO ĐỘNG EXAFS PHÍ ĐIỀU HÒA CỦA TINH THỂ SILIC

Tổng Sỹ Tiến, Lê Việt Hoàng

---

### Thông tin bài viết

---

Ngày nhận bài:

16/9/2020

Ngày duyệt đăng:

10/12/2020

---

### Từ khóa:

*Phân tích EXAFS; Hệ số Debye-Waller; Mô hình Einstein tương quan phi điều hòa; Tinh thể silic.*

---

### Tóm tắt

---

Trong công việc này, dao động của phổ cấu trúc tinh thể mở rộng (EXAFS) phi điều hòa của tinh thể silic đã được biểu diễn qua các số hạng của hệ số Debye-Waller bằng phương pháp khai triển cumulant đến bậc bốn. Bốn EXAFS cumulant đầu tiên đã được tính toán dựa trên mô hình Einstein tương quan phi điều hòa (ACE) cổ điển và qui trình phân tích phù hợp, trong đó các tham số nhiệt động được rút ra từ hàm thế hiệu dụng phi điều hòa thu được bằng cách tiếp cận các đóng góp lân cận của lớp nguyên tử đầu tiên. Việc phân tích sự phụ thuộc vào nhiệt độ của dao động EXAFS được thực hiện thông qua việc đánh giá ảnh hưởng của các cumulant vào sự giảm biên độ và sự dịch pha. Các kết quả tính số được tìm thấy trùng hợp tốt với các kết quả thu được bằng mô hình ACE lượng tử và thực nghiệm ở các nhiệt độ khác nhau. Các kết quả thu được là rất hữu ích đối trong việc phân tích các dữ liệu EXAFS thực nghiệm của c-Si.

---