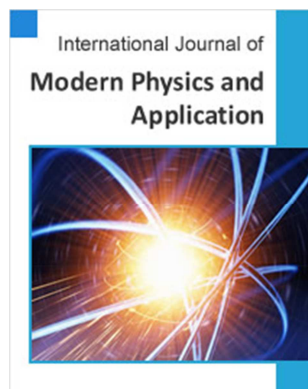




Keywords

Temperature Dependence,
Debye-Waller Factor,
Statistical Moment Method,
Stillinger-Weber Potential,
Semiconductor Compound

Received: March 16, 2016

Accepted: April 1, 2016

Published: September 29, 2016

Temperature Dependence of Debye-Waller Factors of Constituent Elements in Semiconductor Compounds

Nguyen Van Hung¹, Ha Dang Khoa²

¹Department of Physics, Hanoi University of Science. 334 Nguyen Trai, Thanh Xuan, Hanoi, Vietnam

²School of Engineering Physics, Hanoi University of Science and Technology, Hanoi, Vietnam

Email address

hungnv@vnu.edu.vn (N. V. Hung)

Citation

Nguyen Van Hung, Ha Dang Khoa. Temperature Dependence of Debye-Waller Factors of Constituent Elements in Semiconductor Compounds. *International Journal of Modern Physics and Application*. Vol. 3, No. 6, 2016, pp. 70-74.

Abstract

In this work, temperature dependence of Debye-Waller factors (DWFs) of constituent elements in semiconductor compounds have been studied. The DWFs are presented by the mean square displacement (MSD) which has close relation with the mean square relative displacement (MSRD). Their analytical expressions have been derived based on statistical moment method and empirical many-body Stillinger-Weber potentials. Numerical results for the MSDs of constituent elements in GaAs, GaP, InP, InSb having zinc-blende structure are found to be in reasonable agreement with experiment and with those of other theories. They show that the MSD describing thermodynamic properties of a semiconductor element becomes different when it is mixed with different other semiconductor elements to be compounds.

1. Introduction

Thermal vibrations and disorder in XAFS (X-ray Absorption Fine Structure) and related spectroscopies give rise to Debye-Waller factors (DWFs) [1-6] varying as $e^{-W(T)}$, which damp XAFS and related spectra with respect to increasing temperature T and wave number k (or energy). For XAFS spectroscopy, $W(T) \approx 2k^2\sigma^2(T)$ containing the mean square relative displacement (MSRD) $\sigma^2(T)$ of the bond between absorber and backscattering atoms. This XAFS DWF is analogous to that for X-ray and neutron diffraction or the Mössbauer effect, where $W(T) = (1/2)k^2u^2(T)$. The difference is that the XAFS DWF refers to correlated averages over relative displacements for the MSRD $\sigma^2(T)$, while that for X-ray absorption or neutron diffraction refers to the mean square displacement (MSD) $u^2(T)$ of a given atom. The MSRD and MSD have close relations illustrated in the next subsection. Due to their exponential damping, accurate DWFs are crucial to quantitative treatment of X-ray absorption 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) and to defining the thermodynamic quantities from XAFS experiment. Therefore, investigation of temperature dependence of DWF including MSD is of great interest.

Several works have dealt with semiconductors [7-18], the very important materials in technological and electronic applications. MSRD $\sigma^2(T)$ has been studied by XAFS calculation for Si [7], by XAFS experiment [8-10] and by calculation using the methods

LDA, GGA and hGGA [11] for Ge, or by using a similar approach to that of Lee & Gronze [12] for a variety of group IV, III-V and II-VI semiconductors [13]. MSD $u^2(T)$ for nine II-VI and III-V compound semiconductors having zinc-blende structure has been studied utilizing the eight-parameter bond-bending force model [14]. The MSD of some zinc-blende semiconductors have been measured at several temperatures [15, 16]. DWFs of several semiconductors have been studied by both XAFS and X-ray diffraction (XRD) methods [17]. Experimentally, the DWF can be measured using XRD [18] or neutron diffraction.

The present work is devoted to studying temperature dependence of the semiconductor constituent elements in their compounds described by the MSD and MSRD, another aspect of our previous one [22], as well as to adding comparison to experiment [15, 16]. Their analytical expressions have been derived based on statistical moment method (SMM) [19-22] that includes anharmonic effects. In this connection the MSRD, MSD and displacement correlation function (DCF) are in close relation. Based on the

success of the anharmonic correlated Einstein model [2-6] due to taking into account three-dimensional interatomic interaction, in this theory the empirical many-body Stillinger-Weber potentials [23-25] have been used for describing interatomic interaction. Numerical results for the semiconductor constituent elements in compounds GaAs, GaP, InP, InSb having zinc-blende type, are compared to those calculated using the other theories [13, 14] and to the experimental values [15, 16] which show reasonable agreement. From these numerical results, some detailed thermodynamic properties of the semiconductor constituent elements in compounds have been discussed and from that some meaningful conclusions have been obtained.

2. Formalism

The MSD function $u^2(T)$ having close relation with the MSRD $\sigma^2(T)$ and displacement correlation function $C_R(T)$ [21] and is given by

$$u^2(T) = \langle (\mathbf{R} \cdot \mathbf{u}_i)^2 \rangle = \langle (\mathbf{R} \cdot \mathbf{u}_0)^2 \rangle = \frac{\sigma^2(T) + C_R(T)}{2} \quad (1)$$

where

$$\sigma^2 = \langle [\mathbf{R} \cdot (\mathbf{u}_i - \mathbf{u}_0)]^2 \rangle, C_R = -2\langle (\mathbf{R} \cdot \mathbf{u}_i)(\mathbf{R} \cdot \mathbf{u}_0) \rangle \quad (2)$$

$\mathbf{u}_0$ and $\mathbf{u}_i$ are the atomic displacements of the *zeroth* and the *i*th sites from their equilibrium positions, $\mathbf{R}$ is the unit vector pointing from the *zeroth* site towards the *i*th site, and the brackets $\langle \rangle$ denote the thermal average.

Hence, using the MSRD $\sigma^2(T)$ and DCF $C_R(T)$ we can obtain the MSD $u^2(T)$, and inversely using $u^2(T)$ and $C_R(T)$ we can obtain the MSRD $\sigma^2(T)$.

In SMM, using the expressions of the second order moment [21] for the case of temperature dependence, the expression for the MSD has been derived and given by

$$\langle u_i^2 \rangle = \langle u_i \rangle^2 + \beta A_1 + \frac{\beta}{K} (Z - 1); Z = z \coth(z); z = \frac{\hbar\omega}{2\beta}, \beta = k_B T \quad (3)$$

$$A_1 = \frac{1}{K} \left[1 + \frac{2\gamma^2\beta^2}{K^4} \left(1 + \frac{Z}{2} \right) (Z + 1) \right]; K = k - \frac{\alpha^2}{3\gamma}, k = \frac{1}{2} \sum_i \left(\frac{\partial^2 \phi_i}{\partial u_{ix}^2} \right)_{eq} \equiv m\omega^2 \quad (4)$$

$$\gamma = \frac{1}{12} \left\{ \sum_i \left[\left(\frac{\partial^4 \phi_i}{\partial u_{ix}^4} \right)_{eq} + 6 \left(\frac{\partial^4 \phi_i}{\partial u_{ix}^2 \partial u_{iy}^2} \right)_{eq} \right] \right\}; \alpha = \left(\frac{\partial^3 \phi_i}{\partial u_{ix} \partial u_{iy} \partial u_{iz}} \right)_{eq} \quad (5)$$

where k_B is Boltzmann constant, m is atomic mass, and ω is atomic vibration frequency.

Then, from Eqs. (1) - (5) the expression for the temperature-dependent MSRD has been determined and it has the form

$$\sigma^2(T) \approx \frac{4\gamma^2\beta^3}{K^5} \left(1 + \frac{Z}{2} \right) (Z + 1) + \frac{2\beta Z}{k} + 2\beta \frac{k - K}{kK} \quad (6)$$

At $T \rightarrow 0$ ($\coth z \rightarrow 1$) the zero-point contribution to DWF has resulted as

$$\sigma^2(0) \equiv \sigma_0^2 = \frac{\hbar\omega}{k} \quad (7)$$

In the above expressions the atomic interaction potential φ_i plays an important role. For calculating DWF as the second XAFS cumulant of semiconductors we use the empirical many-body Stillinger-Weber potential [23-25] described for the atom i in the form

$$\varphi_i = \sum_j \Phi_{ij}(r_i, r_j) + \sum_{j,k} W_{ijk}(r_i, r_j, r_k) \quad (8)$$

Hence, it is very important for Stillinger-Weber potential to define the two- and three-body terms. Here the two-body term is given by

$$\Phi_{ij}(r_i, r_j) = \begin{cases} \varepsilon A \left[B \left(\frac{r_{ij}}{\sigma} \right)^{-4} - 1 \right] \exp \left[\left(\frac{r_{ij}}{\sigma} - b \right)^{-1} \right], & \frac{r_{ij}}{\sigma} < b \\ 0, & \frac{r_{ij}}{\sigma} \geq b \end{cases} \quad (9)$$

where A, B are positive, σ has dimension of the length, r_{ij} is the bond between atom i and atom j , and ε the cohesive energy per bond, b is dimensionless parameter which represents the cutoff distance of the interaction.

The three-body term corresponds to the angle distortion energy and has the form

$$W_{ijk}(r_i, r_j, r_k) = \varepsilon \lambda \exp \left[\gamma \left(\frac{r_{ij}}{\sigma} - b \right)^{-1} + \gamma \left(\frac{r_{ik}}{\sigma} - b \right)^{-1} \right] \left(\cos \theta_{ijk} + \frac{1}{3} \right)^2 \quad (10)$$

where θ_{ijk} is the angle between the bonds ij and ik .

The parameters in the above equations should be determined so that some basic properties of the material are reproduced from the potentials [24]. They are determined from the cohesive energy, the equilibrium lattice constant, and the elastic properties. For a small distortion, the elastic properties of III-V compounds are well described by the Keating potentials [26] with parameters obtained by Martin [27]. The Keating potentials also consist of the two-body and three-body terms, and thus is easy to deduce the parameters in the Stillinger-Weber potentials from a comparison to the

Keating potentials.

3. Numerical Results and Discussions

Now we apply the expressions derived in the previous section to numerical calculations for temperature-dependent MSD $u^2(T)$ of the semiconductor constituent elements Ga, As, P, In, Sb in their compounds GaAs, GaP, InP, InSb having zinc-blende structure. The Stillinger-Weber potential parameters of GaAs, GaP, InP, InSb [23-25] used in our calculations are written in Table 1.

Table 1. Stillinger-Weber potential parameters of GaAs, GaP, InSb, InP [23-25] ($b = 1.8, \gamma = 1.2$).

Semiconductor	$\varepsilon(\text{eV})$	$\sigma(\text{\AA})$	A	B	λ
GaAs	1.63	2.1342	7.73502	0.696	30.25
GaP	1.78	2.0642	7.62333	0.681	29.57
InSb	1.40	2.4165	8.17499	0.754	26.83
InP	1.74	2.2046	7.90793	0.719	22.11

Figure 1 illustrates temperature dependence of MSD $u^2(T)$ for Ga and the one for As in GaAs calculated using the present theory. They coincide with one another and are found to be in reasonable agreement with those of M. Showalter et al [13] and of M. S. Kushwaha [14] at several temperatures. Figure 2 shows temperature dependence of MSD $u^2(T)$ for Ga and the one for P in GaP calculated using the present theory. They agree with one another and are found to be in reasonable agreement with those of M. Showalter et al [13]

and of M. S. Kushwaha [14] at different temperatures, as well as with the experimental values at 100 K and 200 K [15,16]. Temperature dependence of MSD $u^2(T)$ for In and the one for P in InP (Fig. 3) calculated using the present theory agree well with one another. They are found to be in reasonable agreement with those of M. Showalter et al [13] and of M. S. Kushwaha [14] at different temperatures. Figure 4 illustrates temperature dependence of MSD $u^2(T)$ for In and the one for Sb in InSb calculated using the present theory. They coincide

with one another and are found to be in reasonable agreement with those of M. Showalter et al [13] and of M. S. Kushwaha [14] at different temperatures.

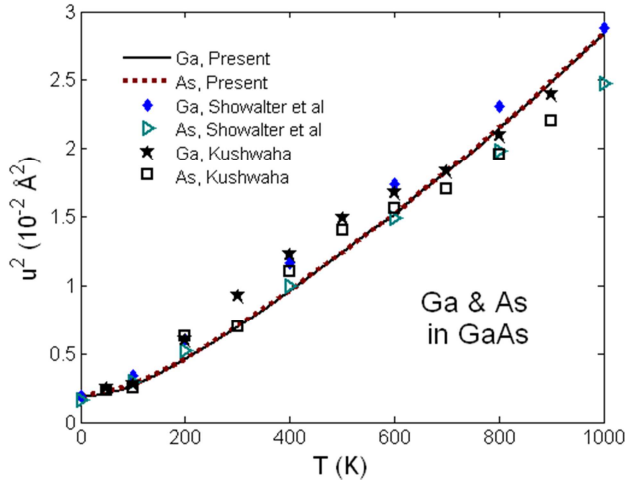


Fig. 1. Temperature dependence of MSD $u^2(T)$ calculated using the present theory for Ga and As in GaAs compared to those of M. Showalter et al [13] deduced from generalized phonon densities of states and of M. S. Kushwaha [14] obtained by utilizing the eight-parameter bond-bending force model.

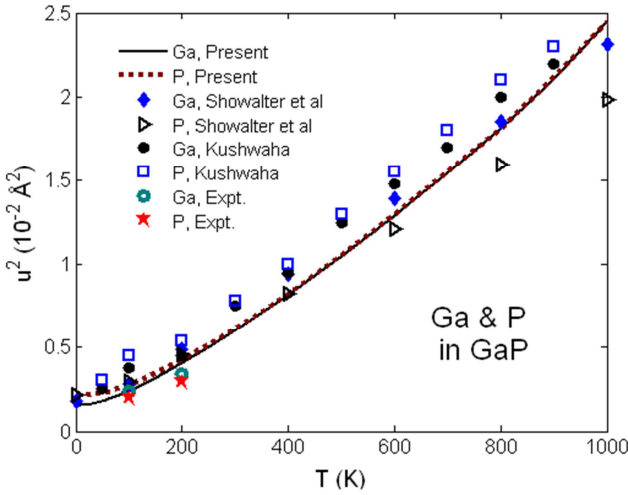


Fig. 2. Temperature dependence of MSD $u^2(T)$ calculated using the present theory for Ga and P in GaP compared to those of M. Showalter et al [13] deduced from generalized phonon densities of states and of M. S. Kushwaha [14] obtained by utilizing the eight-parameter bond-bending force model, as well as to the experimental values at 100 K and 200 K [15, 16].

Note that in the above figures the results of temperature dependence of MSD $u^2(T)$ calculated using the present theory are compared to those of M. Showalter et al [13] deduced from generalized phonon densities of states, and of M. S. Kushwaha [14] obtained by utilizing the eight-parameter bond-bending force model. Moreover, the agreement of our calculated temperature-dependent MSD $u^2(T)$ of Ga with the one of As in GaAs (Fig. 1), of Ga with the one of P in GaP (Fig. 2), of In with the one of P in InP (Fig. 3), and of In with the one of Sb in InSb (Fig. 4) is confirmed by good equality of the respective quantities in the calculated results of M. S. Kushwaha [14] and of the experimental values of GaP at 100 K and 200 K [15, 16], as well as by reasonable agreement of

these respective quantities in the calculated results of M. Showalter et al [13].

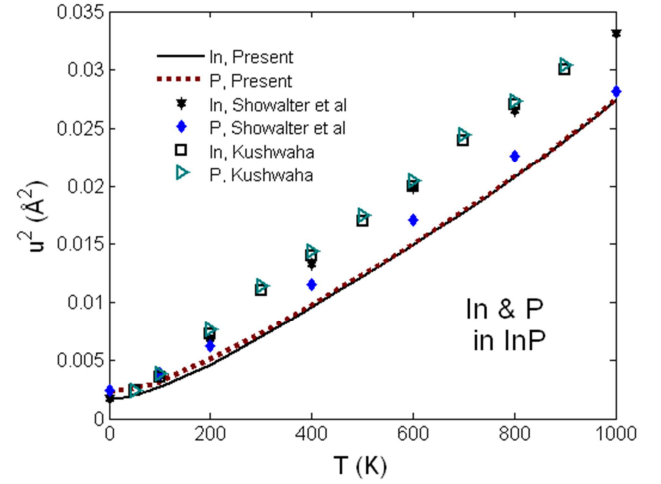


Fig. 3. Temperature dependence of MSD $u^2(T)$ calculated using the present theory for In and P in InP compared to those of M. Showalter et al [13] deduced from generalized phonon densities of states and of M. S. Kushwaha [14] obtained by utilizing the eight-parameter bond-bending force model.

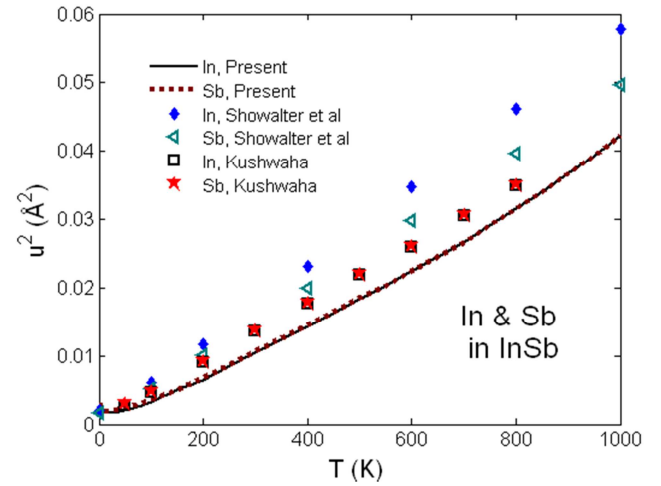


Fig. 4. Temperature dependence of MSD $u^2(T)$ calculated using the present theory for In and Sb in InSb compared to those of M. Showalter et al [13] deduced from generalized phonon densities of states and of M. S. Kushwaha [14] obtained by utilizing the eight-parameter bond-bending force model.

It is seen from the above figures that the following calculated results can be useful for some detailed discussions: At 1000 K the calculated value of MSD u^2 of Ga in GaAs is $0.0275 \text{ \AA}^2$ equaling the one of As (Figure 1a); but also this value of the same Ga in GaP is $0.024 \text{ \AA}^2$ equaling the one of P (Fig. 1). Similarly, the calculated value of MSD u^2 of In in InP is $0.0275 \text{ \AA}^2$ (Fig. 3) equaling the one of P; but also this value of the same In in InSb (Fig. 4) is $0.042 \text{ \AA}^2$ equaling the one of Sb. Hence, from these results we can deduce that the MSD characterizing the thermodynamic properties of a semiconductor element becomes different when it is mixed with different other constituent semiconductor elements to be compounds. This value is about equal to the one of the other constituent semiconductor elements after they are mixed with one another to be compounds.

It is shown that our calculated results of DWF described by MSD at high-temperatures due to anharmonic effects included in the present theory are a little different from the linear proportionality to the temperature obtained by the harmonic theory [28], and contain zero-point contributions at low-temperatures, a quantum effect. Such effects have also been already mentioned in the case using the ACEM [2-5] for the calculation of DWF and XAFS of Cu.

4. Conclusions

In this work, thermodynamic properties of semiconductor constituent elements in compounds have been studied based on Debye-Waller factors described by the MSD and MSRD using SMM that includes anharmonic effects. Here the Stillinger-Weber potential consisting of two-body and three-body terms is used to take into account three-dimensional atomic interaction.

Temperature-dependent MSDs of semiconductor constituent elements in GaAs, GaP, InP, InSb having zinc-blend structure calculated using the present theory at high-temperatures are a little different from the linear proportionality to the temperature due to anharmonic effects included in our theory and contain zero-point energy contributions at low-temperatures, a quantum effect.

It is deduced from the present theory that the MSD characterizing thermodynamic properties of one semiconductor element becomes different when this element is mixed with different other semiconductor elements to be compounds and is about equal to the one of the other constituent semiconductor elements.

Reasonable agreement of our calculated results with experiment and with those obtained from the other theories for GaAs, GaP, InP, InSb denotes the efficiency of the present method in the calculation and analysis of the thermodynamic properties of semiconductor in compounds based on their Debye-Waller factors.

Acknowledgements

The authors thank Prof. J. J. Rehr and Prof. P. Fornasini for useful comments.

References

- [1] E. D. Crozier, J. J. Rehr, R. Ingalls, "X-ray Absorption: Principles, Applications, Techniques of EXAFS, SEXAFS and XANES", Wiley, New York, 1988, Chap. 9, p. 373.
- [2] N. V. Hung and J. J. Rehr, Phys. Rev. B 56 (1997) 43.
- [3] N. V. Hung, N. B. Duc, R. R. Frahm, J. Phys. Soc. Jpn. 72 (2003) 1254.
- [4] M. Daniel, D. M. Pease, N. Van Hung, J. I. Budnick, Phys. Rev. B 69 (2004) 134414.
- [5] N. V. Hung and P. Fornasini, J. Phys. Soc. Jpn. 76 (2007) 084601.
- [6] N. V. Hung, T. S. Tien, N. B. Duc, D. Q. Vuong, Mod. Phys. Lett. B 28 (2014) 1450174.
- [7] M. Benfatto, C. R. Natoli, and A. Filipponi, "Thermal and Structural Damping of the, Phys. Rev. B 40 (1989) 9626.
- [8] G. Dalba, P. Fornasini, D. Diop, M. Grazioli, F. Rocca, J. Non-Crys. Sol. 164 (1993) 159.
- [9] A. E. Stern, B. A. Bunker, and S. M. Heald, Phys. Rev. B 21 (1980) 5521.
- [10] A. Yoshiasa, T. Nagai, O. Ohtaka, O. Kamishima, and O. Shimomur, J. Synchrotr. Rad. 6 (1999) 43.
- [11] F. D. Vila, J. J. Rehr, H. H. Rossner, and H. J. Krappe, Phys. Rev. B 76 (2007) 014301.
- [12] C. Lee and X. Gronze, Phys. Rev. B 51 (1995) 8610.
- [13] M. Schowalter, A. Rosenauer, J. T. Titantah, and D. Lamoen, Acta Cryst. A 65 (2009) 5.
- [14] M. S. Kushwaha, Phys. Rev. B 24 (1981) 2115.
- [15] V. V. Risov and N. N. Sirota, "Chemical bonds in semiconductors", edited by N. N. Sirota (Consultants Bureau, New York, 1967) p. 143.
- [16] K. S. Liang, G. S. Guenzer, and A. I. Benenstock, Bull. Am. Phys. Soc. 15, 1637 (1970).
- [17] A. Yoshiasa, K. Koto, H. Maeda, and T. Ishi, Jpn. J. Appl. Phys. 36 (1997) 781.
- [18] J. Stahn, M. Joehler, and U. Pietsch, Acta Cryst. B 54 (1998) 231.
- [19] N. Tang and V. V. Hung, Phys. Stat. Sol. B 149 (1988) 511.
- [20] K. Masuda-Jindo, V. V. Hung, and P. D. Tam, Phys. Rev. B 67 (2003) 094301.
- [21] N. V. Hung, V. V. Hung, H. K. Hieu, and R. R. Frahm, Physica B 406 (2011) 456.
- [22] N. V. Hung, C. S. Thang, N. C. Toan, and H. K. Hieu, VAC. 101 63 (2014) 63.
- [23] F. H. Stillinger and T. A. Weber, Phys. Rev. B 31 (1985) 5262.
- [24] M. Ichimura, Physica Stat. Sol. (a) 153 (1996) 431.
- [25] S. Erkoc, Phys. Reports 278 (1997) 79.
- [26] P. N. Keating, Phys. Rev. 145 (1966) 637.
- [27] R. M. Martin, Phys. Rev. B 1 (1970) 4005.
- [28] J. M. Ziman, "Principles of the Theory of Solids", second edition by Cambridge University Press, London, 1972.