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Thermodynamic properties of semiconductor compounds studied based on Debye-Waller factors

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Abstract: Thermodynamic properties of semiconductor compounds have been studied based on Debye-Waller factors (DWFs) described 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 the statistical moment method (SMM) and the empirical many-body Stillinger-Weber potentials. Numerical results for the MSDs of GaAs, GaP, InP, InSb, which have zinc-blende structure, are found to be in reasonable agreement with experiment and other theories. This paper shows that an elements value for MSD is dependent on the binary semiconductor compound within which it resides.

Keywords: thermodynamic properties; Debye-Waller factor; Stillinger-Weber potential; statistical moment method; semiconductor compounds

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1 Introduction

Thermal vibrations and disorder in X-ray Absorption Fine Structure (XAFS) and related spectroscopy methods give rise to Debye-Waller factors (DWFs) [1–6]. These, varying as $e^{-W(T)}$, dampen XAFS and related spectra with respect to increasing temperature T and wave number k (or energy). For XAFS spectroscopy, $W(T) \approx 2k^2\sigma^2(T)$ where $\sigma^2(T)$ is the mean square relative displacement (MSRD) of the bond between absorber and backscattering atoms. The 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 X-ray absorption or neutron diffraction, $u^2(T)$ refers to the mean square displacement (MSD) of a given atom. The MSRD and MSD are closely related as illustrated in this paper. 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 thermodynamic quantities from XAFS spectroscopy. Therefore, investigation of temperature dependence of DWF including MSD is of great interest.

Semiconductors are important materials in technological and electronic applications, the DWFs of which are the subject of many interesting papers [7–18]. For Si the MSRD has been studied by XAFS calculation [7] and by XAFS experiment [8–10]. For Ge, MSRD has been studied via calculation using the methods LDA, GGA and hGGA [11], and by using a similar approach to that of Lee & Gronze [12] for a variety of group IV, III-V and II-VI semiconductors [13]. The MSD 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 work presented in this paper is devoted to studying the thermodynamic properties of semiconductor compounds described by the MSDs. Their analytical expressions have been derived based on statistical moment method (SMM) [19–21] which 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 (ACEM) [2–6] and the anharmonic correlated Debye model (ACDM) [22] due to taking into account three-dimensional interatomic interaction, this theory uses the empirical many-body Stillinger-Weber potentials [23, 25] to describe the interatomic interaction. Numerical results for the MSD

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$u^2(T)$ of semiconductor compounds GaAs, GaP, InP, InSb which have zinc-blende type, are compared to those calculated using the other theories [13, 14] and to the experimental values [15, 16]. These comparisons show reasonable agreement to previous results. From these numerical results, some detailed thermodynamic properties of semiconductor compounds and their constituent elements have been discussed and some meaningful conclusions have been obtained.

2 Formalism

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

$$u^2(T) = \langle (R \cdot u_i)^2 \rangle = \langle (R \cdot u_0)^2 \rangle = \frac{\sigma^2(T) + C_R(T)}{2}, \tag{1}$$

where

$$\begin{aligned} \sigma^2 &= \langle [R \cdot (u_i - u_0)]^2 \rangle, \\ C_R &= -2 \langle (R \cdot u_i)(R \cdot u_0) \rangle, \end{aligned} \tag{2}$$

u_0 and u_i are the atomic displacements of the *zero*th and the *i*th sites from their equilibrium positions, R is the unit vector pointing from the *zero*th site towards the *i*th site, and the brackets <> 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 the 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

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

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

$$\begin{aligned} y &= \frac{1}{12}\left\{\sum_i \left[\left(\frac{\partial^4 \phi_i}{\partial u_{ix}^4}\right)_{eq} + 6\left(\frac{\partial^4 \phi_i}{\partial u_{ix}^2 \partial u_{iy}^2}\right)_{eq}\right]\right\}; \\ \alpha &= \left(\frac{\partial^3 \phi_i}{\partial u_{ix} \partial u_{iy} \partial u_{iz}}\right)_{eq}, \end{aligned} \tag{5}$$

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

In the above expressions the atomic interaction potential ϕ_i plays an important role. For calculating DWF of semiconductors described by the MSD or MSRD, we use the empirical many-body Stillinger-Weber potential [23–25] shown for the atom i in the form

$$\phi_i = \sum_j \phi_{ij}(r_i, r_j) + \sum_{j,k} W_{ijk}(r_i, r_j, r_k). \tag{6}$$

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

$$\phi_{ij}(r_i, r_j) = \begin{cases} \varepsilon A \left[B\left(\frac{r_{ij}}{\sigma}\right)^{-4} - 1\right] \exp\left[\left(\frac{r_{ij}}{\sigma} - b\right)^{-1}\right], \\ \frac{r_{ij}}{\sigma} < b \\ 0, \ \ \frac{r_{ij}}{\sigma} \geq b \end{cases}, \tag{7}$$

where A, B are positive, σ has dimension of the length, r_{ij}s 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

$$\begin{aligned} W_{ijk}(r_i, r_j, r_k) &= \varepsilon\lambda \exp\left[\gamma\left(\frac{r_{ij}}{\sigma} - b\right)^{-1}\right. \\ &+ \left.\gamma\left(\frac{r_{ik}}{\sigma} - b\right)^{-1}\right]\left(\cos\theta_{ijk} + \frac{1}{3}\right)^2, \end{aligned} \tag{8}$$

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

The expressions derived in the previous section are now applied to numerical calculations for temperature-

Table 1: Stillinger-Weber potential parameters of GaAs, GaP, InSb, InP [24? , 25] ($b = 1.8$, $\gamma = 1.2$).

Semiconductor	ε (eV)	σ (Å)	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	1.4	2.4165	8.17499	0.754	26.83
InP	1.74	2.2046	7.90793	0.719	22.11

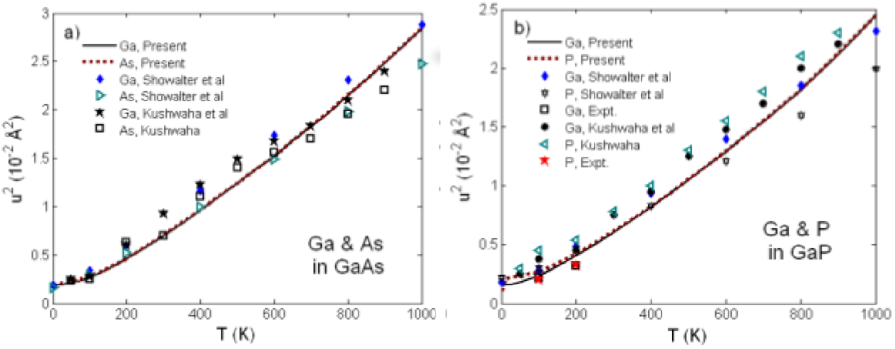

Figure 1: Temperature dependence of MSD $u^2(T)$ calculated using the presented theory for a) Ga and As in GaAs and b) Ga and P in GaP compared to those of M. Showalter *et al.* [13] deduced from generalized phonon densities of states and of M.S. Kushwaha [14] obtained by utilizing the eight-parameter bond-bending force model. Here, the results for GaP are compared to the experimental values at 100 K and 200 K [15, 16].

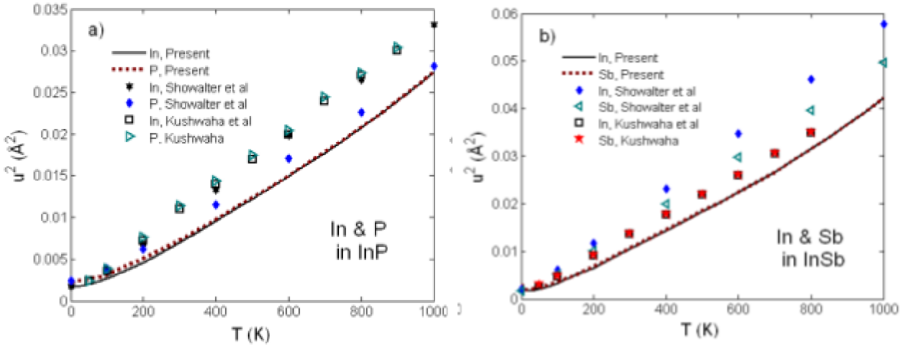

Figure 2: Temperature dependence of MSD $u^2(T)$ calculated using the presented theory for a) In and P in InP and b) In and Sb in InSb compared to those of M. Showalter *et al.* [13] deduced from generalized phonon densities of states and of M.S. Kushwaha [14] obtained by utilizing the eight-parameter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

dependent MSD $u^2(T)$ of semiconductors in binary compounds GaAs, GaP, InP, InSb which have zinc-blende structure. The Stillinger-Weber potential parameters of GaAs, GaP, InP, InSb [23–25] used in our calculations are written in Table 1.

Figure 1a illustrates temperature dependence of MSD $u^2(T)$ for Ga and for As in the binary semiconductor GaAs calculated using the presented theory. Both elements return similar values for MSD across the studied temperature range. The values are in reasonable agreement with those of M. Showalter *et al.* [13] and of M.S. Kushwaha [14] at several temperatures.

Figure 1b shows temperature dependence of MSD $u^2(T)$ for Ga and for P in the binary semiconductor GaP calculated using the presented theory. As before, the MSDs for both elements conicide and are 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 for P in InP (Figure 2a) calculated using the presented theory also coincide. They are found to be in reasonable agreement with the values of M. Showalter *et al.* [13] and of M.S. Kushwaha [14] at different temperatures.

Figure 2b illustrates temperature dependence of MSD $u^2(T)$ for In and for Sb in InSb calculated using the presented theory. The values also coincide 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.

Note that in the above figures, the temperature dependence of MSD $u^2(T)$ calculated using the presented 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 temperature-dependence of MSD $u^2(T)$ is confirmed by good agreement with the calculated results of M.S. Kushwaha [14], as well as by reasonable agreement with the calculated results of M. Showalter *et al.* [13] and of the experimental values of GaP at 100 K and 200 K [15, 16].

The following can be deduced from the results presented in this paper. At 1000 K the calculated value of MSD u^2 of Ga in GaAs is 0.0275 Å^2 which is the similar to the value for As in the same binary semiconductor (Figure 1a). However, the value of MSD u^2 of Ga in GaP is 0.024 Å^2, which is the same as the P in the binary semiconductor (Figure 1b). Similarly, the calculated value of MSD u^2 of In and P in InP is 0.0275 Å^2 (Figure 2a); but for In, and Sb, in InSb (Figure 2b) the value is 0.042 Å^2. Hence, from these results we can deduce that the MSD characterizing the thermodynamic properties of a semiconductor element is different depending on the other constituent semiconductor elements in the binary semiconductor compound. This value for MSD u^2 is similar for both elements in the semiconductor compound.

DWF described by MSD at high-temperatures due to anharmonic effects, included in the presented theory, differ 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 previously been shown using the ACEM and ACDM for the calculation of DWF and XAFS of Cu [2–5, 22].

4 Conclusions

In this work, the thermodynamic properties of semiconductor compounds have been studied based on Debye-Waller factors described by the MSD using the SMM. This methodology 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. The similarity and relation between the MSD and MSRD have also been discussed.

Temperature-dependent MSDs for semiconductor elements in compounds GaAs, GaP, InP, InSb having zinc-blend structure calculated using the presented theory at high-temperatures differ from the linear proportionality to the temperature due to anharmonic effects included in this theory and contain zero-point energy contributions at low-temperatures, a quantum effect.

It is deduced from the presented theory that the MSD characterizing the thermodynamic properties of one semiconductor element is dependent on the binary semiconductor compound within which it resides.

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 presented method in the calculation and analysis of the thermodynamic properties of semiconductor compounds based on their Debye-Waller factors.

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References

[1] E.D. Crozier, J.J. Rehr, R. Ingalls, In: X-ray Absorption: Principles, Applications, Techniques of EXAFS, SEXAFS and XANES (Wiley,

New York, 1988) Chap. 9, p. 373

[2] N.V. Hung, J.J. Rehr, Phys. Rev. B 56, 43 (1997)

[3] N.V. Hung, N.B. Duc, R.R. Frahm, J. Phys. Soc. Jpn. 72, 1254 (2003)

[4] M. Daniel, D.M. Pease, N. Van Hung, J.I. Budnick, Phys. Rev. B 69, 134414 (2004)

[5] N.V. Hung, P. Fornasini, J. Phys. Soc. Jpn. 76, 084601 (2007)

[6] N.V. Hung, T.S. Tien, N.B. Duc, D.Q. Vuong, Mod. Phys. Lett. B 28, 1450174 (2014)

[7] M. Benfatto, C.R. Natoli, A. Filipponi, Phys. Rev. B 40, 9626 (1989)

[8] G. Dalba, P. Fornasini, D. Diop, M. Grazioli, F. Rocca, J. Non-Crys. Sol. 164, 159 (1993)

[9] A.E. Stern, B.A. Bunker, S. M. Heald, Phys. Rev. B 21, 5521 (1980)

[10] A. Yoshiasa, T. Nagai, O. Ohtaka, O. Kamishima, O. Shimomur, J. Synchrot. Rad. 6, 43 (1999)

[11] F.D. Vila, J.J. Rehr, H.H. Rossner, H.J. Krappe, Phys. Rev. B 76, 014301 (2007)

[12] C. Lee, X. Gronze, Phys. Rev. B 51, 8610 (1995)

[13] M. Schowalter, A. Rosenauer, J.T. Titantah, D. Lamoen, Acta Cryst. A 65, 5 (2009)

[14] M.S. Kushwaha, Phys. Rev. B 24, 2115 (1981)

[15] V.V. Risov, N.N. Sirota, Chemical bonds in semiconductors, N.N. Sirota (Ed.) (Consutants Bureau, New York, 1967) 143

[16] K.S. Liang, G.S. Guenzer, A.I. Bienenstock, Bull. Am. Phys. Soc. 15, 1637 (1970)

[17] A. Yoshiasa, K. Koto, H. Maeda, T. Ishi, Jpn. J. Appl. Phys. 36, 781 (1997)

[18] J. Stahn, M. Joehler, U. Pietsch, Acta Cryst. B 54, 231 (1998)

[19] N. Tang, V.V. Hung, Phys. Stat. Sol. B 149, 511 (1988)

[20] K. Masuda-Jindo, V.V. Hung, P.D. Tam, Phys. Rev. B 67, 094301 (2003)

[21] N.V. Hung, V.V. Hung, H.K. Hieu, R.R. Frahm, Physica B 406, 456 (2011)

[22] N.V. Hung, N.B. Trung, B. Kirchner, Physica B 406, 456 (2011)

[23] F.H. Stillinger, T.A. Weber, Phys. Rev. B 31, 5262 (1985)

[24] M. Ichimura, Physica Stat. Sol. (a) 153, 431 (1996)

[25] S. Erkoc, Phys. Rep. 278, 79 (1997)

[26] P.N. Keating, Phys. Rev. 145, 637 (1966)

[27] R.M. Martin, Phys. Rev. B 1, 4005 (1970)

[28] J.M. Ziman, Principles of the Theory of Solids, Second ed. (Cambridge University Press, London, 1972)