

Compressibilities, Debye-Waller factors, and melting criteria for II-VI and III-V compound semiconductors

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We calculate the compressibilities and mean-square displacements (MSD) for nine II-VI and III-V compound semiconductors having zinc-blende structure utilizing a recently proposed eight-parameter bond-bending force model. A modified Brout sum rule was used to calculate the compressibilities. The calculated values of the MSD are also used to check the validity of the Lindemann's melting criteria. Present theoretical results are discussed in the light of available experimental and earlier theoretical results. It is concluded that consideration of the temperature dependence of input data used to calculate the model parameters and inclusion of anharmonic interactions may give further insight into the results.

I. INTRODUCTION

The sum rule [$\sum_i \omega_i^2(\vec{q}) = \text{const}$, where ω is the angular phonon frequency at the wave vector $\vec{q}$] for lattice vibrations was originally derived by Brout.¹ The rule was stated to be valid for the diatomic ionic crystals whose constituents interact only by two-body Coulomb forces between all ions and repulsive forces between nearest neighbors alone—and to be useful as a check on the numerical computation of phonon dispersion. Rosenstock^{2,3} has generalized the sum rule such that $\sum_i \omega_i^2(\vec{q}) = \text{const} + \sum_k \beta_k \psi^{(k)}(\vec{q})$, where the index k labels the k th force between atoms present in the crystal, $\psi^{(k)}(\vec{q})$ is an explicitly $\vec{q}$ -dependent contribution from that force to the sum on the left-hand side, and β_k is the constant related to that force. What makes this rule of interest is the fact that $\psi^{(k)}$ for many forces—indeed for most common forces—does in fact vanish so that these forces contribute only constant terms to the sum. The forces that contribute nothing but a constant term to $\sum_i \omega_i^2(\vec{q})$ were named³ “trace-constant” forces and those that contribute explicitly $\vec{q}$ -dependent $\psi^{(k)}(\vec{q})$ function “trace-variable” forces. It is important to note that all forces which act between (i) unlike atoms only, and (ii) which are electrostatic in nature (viz., Coulomb, dipole, quadrupole, . . . , 2^l pole¹) are all trace constant; the trace-variable forces are then those that are not electrostatic in nature and act between like atoms. It is thus obvious that trace-variable forces are rather obscure ones, for most of the forces are likely to be trace constant. If they are of long range, it means that they are likely to be electrostatic in nature, and if short range, because strongest ones, are likely to be between nearest neighbors, which are always unlike atoms. The sum rule, however, seems not only to be of intrinsic interest for theoreticians but it also provides a useful tool for the

experimentalists to analyze the measured phonon dispersion relations. The sum rule was rightly expected by Rosenstock² to be valid even for nonionic crystals,⁴ such as diamond⁵ and zinc-blende (ZB) crystals.⁶ In the present investigations we have made use of the modified Brout sum rule⁴ (Sec. II) to calculate the compressibilities of nine ZB compounds of our interest.

The intensity of scattered radiation from a crystal is observed to be varying with temperature according to e^{-W} , the famous Debye-Waller factor (DWF). The DWF is related to mean-square displacements (MSD) of the constituent atoms in a crystal. The MSD and their characteristic temperatures are found to be of utmost utility in determining the basic characteristics of the compound semiconductors, namely, width of the forbidden band, mobility of charge carriers, and temperature dependence of the energy gap.⁷ A number of useful physical properties, such as heat of formation, internal energy, specific heat, elastic constants, and linear expansion coefficients may also be determined from their quantitative relationships with the characteristic temperatures and MSD of the constituent atoms. Further a knowledge of root-mean-square displacements (RMSD) of the constituent ions in a crystal at temperatures nearer the melting point may also enable one to gain an insight into the melting process of the system. DWF, in addition, is also useful in interpreting the effect of the electron-phonon interaction on the temperature dependence of the energy gap.

The calculations of MSD for a number of crystals were performed by several workers in cubic metals,⁸⁻¹³ rare-gas solids,^{14,15} NaCl structure,¹⁶⁻²³ and CsCl structure.²⁴ In ZB crystals such calculations were carried out by Vetelino *et al.*²⁵ using a four-parameter rigid-ion model and by Talwar and Agrawal,²⁶ using a seven-parameter second-neighbor

ionic model. Both of the authors^{25,26} have compared their results with the available experimental data and have shown a reasonable agreement between the two. However, theoretical results of Vetelino *et al.*²⁵ seem to be physically more reliable, as discussed later on, than those of Talwar and Argawal.²⁶ The theoretical models are uncertain because they can be compared with data²⁷⁻³³ which exist for only a limited range and are in some cases questionable. An extensive calculation on DWF of ZB crystals, will thus serve a useful purpose in the interpretation of neutron and x-ray scattering and in Mössbauer effect.

In the previous papers,³⁴⁻³⁶ hereafter referred to as I, II, and III, a new eight-parameter bond-bending force model (BBFM) for phonons in ZB crystals was proposed with its successful application on lattice dynamical studies of a number of compounds. The details of BBFM, with the merits of its physical significance discussed in full, have been given in Papers I and II of this series. The same BBFM has been employed here to calculate the eigenfrequencies and eigenvectors utilized in the present computation. Explicit calculations of compressibilities, using modified Brout sum rule⁴ and DWF have been made for ZnS, ZnSe, ZnTe, CdTe, GaP, GaAs, GaSb, InP, and InSb. Also, the sum of the root-mean-square displacements (RMSD) of the constituent atoms is compared to their nearest-neighbor distance (NNI) at the melting point. For the numerical values of the model parameters a reader is referred to I (ZnSe, InSb), II (ZnTe, CdTe, GaP, and InP), and III (ZnS, GaAs, and GaSb) papers of this series.

II. THEORY

A. Brout sum rule

By assuming Coulombic attractive forces and repulsive forces between nearest neighbors, Brout¹ had established the following relation:

$$\sum_{i=1}^6 \omega_i^2(\vec{q}) = \frac{18r_0}{\mu\chi}, \quad (1)$$

in the lattices of tetrahedral symmetry, where $\omega_i(\vec{q})$ is the angular phonon frequency of the i th mode for a given wave vector $\vec{q}$, $\mu [=m_1m_2/(m_1+m_2)]$ is the reduced mass, r_0 is the interionic distance, and χ is the coefficient of compressibility. The relation was originally derived for highly ionic NaCl-type crystals and its application to II-VI and III-V compounds was regarded rather unexpected. Subsequently Rosenstock,^{2,3} has shown that as far as the constancy of the sum of squares of characteristic phonon frequencies over the entire Brillouin zone (especially zone center and zone boundary) is concerned, the relation is applicable to a wide variety of crystals including diamond and ZB crystals.

The relation (1) was thus modified⁴ for crystals with diamond and ZB structure as follows:

$$\sum_{i=1}^6 \omega_i^2(\vec{q}) = \frac{16\sqrt{3}r_0}{\mu\chi}. \quad (2)$$

This relation (2) has been utilized in the present calculations of the compressibilities of nine ZB compounds of our interest.

B. Debye-Waller factors

The DWF, which in Mössbauer effect describes the temperature dependence of the recoilless transitions, can be expressed as

$$D = e^{-W_k(T)}, \quad (3)$$

where

$$W_k(T) = \frac{8\pi^2}{3} \left(\frac{\sin\theta}{\lambda} \right)^2 \langle u^2 \rangle_k, \quad (4)$$

where λ is the wavelength of the incident radiation and (2θ) is the corresponding angle. $(\langle u^2 \rangle_k)$ is the MSD of the k th particle and can be expressed in terms of the eigenfrequencies and eigenvectors of the phonon states of the crystal lattice as³⁷

$$\langle u^2 \rangle_k = \frac{\hbar}{Nm_k} \sum_{\vec{q}} \sum_j \frac{|e(k|\vec{q},j)|^2}{\omega_j(\vec{q})} [n(\omega_j(\vec{q})) + 0.5], \quad (5)$$

where $\omega_j(\vec{q})$ is the eigenfrequency of the j th branch at wave vector $\vec{q}$ and $e(k|\vec{q},j)$ is the corresponding eigenvector of the dynamical matrix such that they satisfy the following orthonormality and closure conditions

$$\begin{aligned} \sum_{k,\alpha} e_{\alpha}^*(k|\vec{q},j) e_{\alpha}(k|\vec{q},j') &= \delta_{jj'}, \\ \sum_j e_{\beta}^*(k'|\vec{q},j) e_{\alpha}(k|\vec{q},j) &= \delta_{\alpha\beta} \delta_{kk'}. \end{aligned} \quad (6)$$

The quantity $n(\omega_j(\vec{q}))$ is the phonon occupation number defined as

$$n(\omega_j(\vec{q})) = (e^{\hbar\omega_j(\vec{q})/k_B T} - 1)^{-1}, \quad (7)$$

where $\hbar$ is Planck's constant, k_B is Boltzmann's constant, and T is the absolute temperature. The sum over $\vec{q}$ in Eq. (5) is performed over all the N $\vec{q}$ points in the first Brillouin zone.

The first Brillouin zone is divided into a mesh of 1000 wave-vector points. But, owing to the symmetry of the zone, one need only consider the determination of the eigenfrequencies and eigenvectors at the nonequivalent points in $\vec{q}$ space, defined as

$$\vec{q} = \frac{\pi}{10a} (q_x, q_y, q_z),$$

TABLE III. Root-mean-square displacements (in 10^{-8} cm) of III-V compounds.

T (K)	GaP		GaAs		GaSb		InP		InSb	
	$\langle u^2 \rangle^{1/2}_{\text{Ga}}$	$\langle u^2 \rangle^{1/2}_{\text{P}}$	$\langle u^2 \rangle^{1/2}_{\text{Ga}}$	$\langle u^2 \rangle^{1/2}_{\text{As}}$	$\langle u^2 \rangle^{1/2}_{\text{Ga}}$	$\langle u^2 \rangle^{1/2}_{\text{Sb}}$	$\langle u^2 \rangle^{1/2}_{\text{In}}$	$\langle u^2 \rangle^{1/2}_{\text{P}}$	$\langle u^2 \rangle^{1/2}_{\text{In}}$	$\langle u^2 \rangle^{1/2}_{\text{Sb}}$
50	0.0674	0.0749	0.0770	0.0743	0.0607	0.0605	0.0626	0.0627	0.0667	0.0666
100	0.0899	0.0999	0.0828	0.0798	0.0819	0.0818	0.0843	0.0844	0.0933	0.0932
200	0.076 ^a	0.063 ^a	0.1151	0.1110	0.1142	0.1140	0.1174	0.1175	0.1314	0.1312
300	0.0997	0.1024								
400	0.1068 ^a	0.088 ^a								
500	0.1216	0.1249	0.1404	0.1355	0.1395	0.1392	0.1433	0.1434	0.1608	0.1606
600	0.1401	0.1438	0.1620	0.1562	0.1609	0.1606	0.1653	0.1656	0.1856	0.1854
700	0.1566	0.1608	0.1740	0.1679	0.1798	0.1794	0.1847	0.1849	0.2075	0.2073
800	0.1714	0.1761	0.1770	0.1707	0.1969	0.1965	0.2023	0.2024	0.2273	0.2270
900	0.1851	0.1902	0.1911	0.1843	0.2127	0.2123	0.2185	0.2187	0.2455	0.2452
1511	0.2033	0.2033	0.2043	0.1971	0.2273	0.2269	0.2335	0.2337	0.2625	0.2621
979	0.2156	0.2156	0.2166	0.2090	0.2411	0.2406	0.2447	0.2479	...	...
1232	...	...	0.2807	0.2797	...	...	...	...	...	...
803	...	...	...	...	0.2516	0.2510	0.2899	0.2900	0.2631	0.2626

^aExperimental values from Refs. 27 and 33.

exist. GaP is the only compound where we were able to compare our results at 100 and 200 K. Earlier such calculations of MSD were performed by Vetelino *et al.*²⁵ and Talwar and Agrawal.²⁶ We have, therefore, checked our results by comparing the same with those of the previous authors.^{25,26} The comparison thus reveals that our theoretical results are in closer resemblance with those of Vetelino *et al.*²⁵ than those of Talwar and Agrawal²⁶ at most of the temperatures. Further, our results depict a fact that at any particular temperature (save at the melting point) the value of the MSD is greater for lighter atoms. This criterion is also reflected from the results of Vetelino *et al.*²⁵ but fails to hold for those of Talwar and Agrawal.²⁶ Also the comparison of their^{25,26} theoretical results with the experimental ones reveals that results of Vetelino *et al.*²⁵ are in better agreement than those of Talwar and Agrawal.²⁶ It should be mentioned here that we have not specifically studied the contribution of acoustic and optical modes for the heavy and lighter atoms, as was done by Vetelino *et al.*²⁵ They²⁵ have shown that the relative contribution from the acoustic phonons predominates in the heavy atom, while the relative contribution from the optical phonons predominates for lighter atoms.

C. Lindemann's melting criteria

It was originally hypothesized by Lindemann³⁸ in 1910 that a material attains its melting temperature when RMSD of the atomic vibration reaches a critical fraction of the nearest-neighbor distance (NND). The ratio of RMSD to NND was presumed to be the same for all crystalline solids. It was later shown in various cubic metals³⁹ and alkali halides⁴⁰ that this ratio is indeed not constant, but in fact depends upon the crystal structure and the location of the constituent atoms in the periodic table. The present investigations show that this ratio (RMSD divided by NND), the so-called Lindemann parameter, is almost constant for II-VI and III-V compounds of our interest (see Table IV). It is observed that this ratio is greater for II-VI compounds than that for III-V compounds.

We may, therefore, conclude that the eight-parameter BBFM is reasonably consistent with the modified Brout sum rule,⁴ temperature dependence of MSD, and the melting criteria as proposed by Lindemann³⁸ for II-VI and III-V compounds having ZB structure. We hope, however, that consideration of the temperature dependence of the input data (i.e., lattice constants, elastic constants, and phonon frequencies) and anharmonic effects being more predominant at higher temperatures, should achieve better agreement with the experiment.

The investigation of thermodynamical properties

TABLE IV. Validity of Lindemann's melting criteria where A and B refer to the constituents of the compound AB .

Compounds	MP (K)	RMSD $(\langle u^2 \rangle^{1/2} A + \langle u^2 \rangle^{1/2} B)$	NND	Ratio of RMSD to NND
II-VI ZnS	1923	0.7257	2.350	0.308
ZnSe	1373	0.7249	2.454	0.295
ZnTe	1511	0.7389	2.628	0.281
CdTe	1371	0.8402	2.776	0.302
III-V GaP ^a	1623	...	2.360	...
GaAs	1511	0.5604	2.440	0.229
GaSb	979	0.5026	2.649	0.189
InP	1232	0.5799	2.541	0.228
InSb	803	0.5257	2.793	0.188

^aThe melting point (MP) of GaP was not available when the computation was performed.

(e.g., Gruneisen parameter, thermal expansion, etc.) are in progress and shall be reported in the subsequent papers of this series.

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