PHYSICAL REVIEW B VOLUME 2, NUMBER 4 15 AUGUST 1970

Lattice Dynamics of ZnTe: Phonon Dispersion, Multiphonon Infrared Spectrum, Mode Grüneisen Parameters, and Thermal Expansion*

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(Received 2 March 1970)

A four-parameter rigid-ion model utilizing an effective ionic charge is used for the determination of phonon dispersion, phonon density of states, and the Debye characteristic temperature of ZnTe. Structures in the infrared spectrum of ZnTe are assigned to multiphonon combinations of various critical-point phonon frequencies. Using the long-wavelength optic-mode phonon frequencies as well as the elastic constants and their respective pressure derivatives as input data, the mode Grüneisen parameters, the Grüneisen constant, and the coefficient of thermal expansion of ZnTe are calculated.

I. INTRODUCTION

Detailed phonon dispersion data on zinc-blende–type crystals exist only for GaAs and GaP and were obtained[1, 2] by neutron scattering. The shell model[3] which incorporates both core and shell interaction between the respective ions to account for the dipole character of the ions has been utilized for lattice dynamical calculations[1, 2] on these crystals. The shell model or its various ramifications usually requires a rather large number of unknown parameters and is useful where detailed dispersion data are available. It is not so useful in predicting phonon dispersion for crystals for which extensive phonon dispersion data are not available, as is the case with most zinc-blende crystals. If the critical-point (CP) phonons happen to be incorrectly assigned, as is sometimes the case using data on infrared-active multiphonon processes, a shell model may not be able to detect such an error. A good example is the shell-model calculations on ZnS by Kaplan and Sullivan.[4] In cases where the shell model has given good agreement with neutron-scattering data, e.g., GaAs, quite often the model has a large number of parameters associated with it, some of which may have no more physical significance than that of fitting constants in an interpolation formula.

Recently, a four-parameter rigid-ion model has been employed by us for the calculation of phonon dispersion in SiC[5] and ZnS.[6] The calculated dispersion curves for SiC agree remarkably well with those measured by Raman scattering of SiC polytypes.[7] For ZnS the results also agree reasonably well with the neutron-scattering data on acoustic branches[8] and very well for the optic branches measured by Raman scattering on polytypes.[6] In fact, the four-parameter rigid-ion model gives better results for ZnS than a simple shell model[8] when compared with experimental data.[8] The applicability of the four-parameter rigid-ion model to zinc-blende crystals has been discussed by Vetelino and Mitra[9] in terms of an invariance relation connecting the elastic constants C_{11}, C_{12}, and C_{44} and the long-wavelength longitudinal and transverse optic (LO and TO) mode frequencies. An empirical relation[10] connecting the ratio of the LO and the longitudinal acoustic (LA) zone-boundary phonon frequencies at the X CP to the mass ratios for the diatomic cubic crystals is also substantiated by this model.[9] It was also found that the temperature dependence of the Debye characteristic temperature of ZnS and GaAs was very well expressed[9] by this model.

The purpose of this paper is to apply this lattice dynamical model to ZnTe, which also crystallizes in the zinc-blende structure, in order to obtain the phonon dispersion, phonon density of states, and related thermal properties. With the aid of the dispersion curves a multiphonon assignment of the infrared spectrum of the crystal is performed in terms of CP phonons. Next, the volume dependence of normal-mode frequencies are obtained by determining the four model parameters as functions of crystal volume. The treatment to be presented here is unique in the sense that it utilizes recently measured[11] pressure dependence of long-wavelength LO and TO mode frequencies as input data and does not use a potential function. In any case, such a potential function is not known for the zinc-blende–type partially ionic crystals. Finally, the mode Grüneisen parameters, the Grüneisen constant, and the coefficient of thermal expansion are calculated. Earlier theoretical treatments[12] of the mode Grüneisen parameters and the thermal expansion of crystals, e.g., KBr and Si, have been accomplished by rather elaborate lattice dynamical models. In these treatments some of the model parameters have been obtained by *a priori* curve fittings of the data which the models purport to predict. Recently, we have adapted[13] a rigid-ion model to the determination of the mode Grüneisen parameters, Grüneisen constant, and thermal expansion of CsCl, CsBr, and CsI, and excellent agreement with experimental data was achieved for the thermal expansion coefficient. Data on the pressure dependence of the Brillouin-zone-center optic phonons[11] and the elastic constants[14] of ZnTe are now available, and the present model can thus now be tested for a zinc-blende-type crystal also. It will be shown that reasonable values of the coefficient of thermal expansion of ZnTe as a function of temperature can be obtained by using only the long-wavelength optic-phonon frequencies, elastic constants, and their pressure derivatives as input data. Certain limitations of the model will also be pointed out.

II. LATTICE DYNAMICS

The lattice dynamical model utilized for ZnTe incorporates a combination of the classical treatments by Kellermann[15] for the electrostatic part and by Smith[16] for the nonelectrostatic part. The necessary equations and the expressions for the coupling coefficients for the zinc-blende structure are summarized in a previous paper.[5] The nonelectrostatic part of the interaction includes first-neighbor central and noncentral interactions between the zinc and tellurium atoms and second-neighbor central interactions between like atoms. The electrostatic part represents the long-range Coulomb interactions. The four model parameters are the first-neighbor force constants α and β, the second-neighbor force constant μ (assumed equal for Zn-Zn and Te-Te interactions), and the total effective ionic charge Ze.

TABLE I. Long-wavelength optic-mode frequencies (Ref. 11), elastic constants (Ref. 14), and the model parameters at pressures of 1 atm and 3 kbar.

Quantity	1 atm	3 kbar
ω_{LO} (cm^{-1})	206	206.9
ω_{TO} (cm^{-1})	179	180.6
C_{11} (10^{11} dyn/cm^2)	7.114	7.262
C_{12} (10^{11} dyn/cm^2)	4.069	4.224
C_{44} (10^{11} dyn/cm^2)	3.132	3.146
α (10^3 dyn/cm)	22.6276	22.9510
β (10^3 dyn/cm)	21.6104	22.0172
μ (10^3 dyn/cm)	2.4928	2.5596
Z (dimensionless)	0.718	0.709

The four parameters are determined by relating them to the elastic constants and the LO and TO mode frequencies at the Brillouin-zone center, $\vec{k} \sim 0$. These relationships can be shown to be[5]

$$\begin{aligned} C_{11} &= (1/a)\,(\alpha + 8\mu + 0.251\, Z^2e^2/V_a)\ , \\ C_{12} &= (1/a)\,(2\beta - \alpha + 4\mu - 2.648\, Z^2e^2/V_a)\ , \\ C_{44} &= \frac{1}{a}\left[\alpha + 4\mu - 0.126\,\frac{Z^2e^2}{V_a} \times \frac{(2.519\, Z^2e^2/V_a - \beta)^2}{\alpha - \pi Z^2e^2/3V_a}\right]\ , \end{aligned} \tag{1}$$

$$\begin{aligned} \omega_{\mathrm{LO}}^2 &= \mu'\ (4\alpha + \tfrac{8}{3}\pi Z^2e^2/V_a)\ , \\ \omega_{\mathrm{TO}}^2 &= \mu'\,(4\alpha - \tfrac{4}{3}\pi Z^2e^2/V_a)\ , \end{aligned} \tag{2}$$

where a is the lattice constant, μ' is the reciprocal of the reduced mass, $V_a = \frac{1}{4}a^3$ is the unit cell volume, and Ze is the total effective ionic charge.

Since there are five equations with four unknowns, these equations were solved in the least-squared sense. It is interesting to point out that the resulting invariance relation[9] between C_{11}, C_{12}, C_{44}, ω_{TO}, and ω_{LO} when applied to ZnTe using recent data[11, 14] gives a value of 1.049 as compared to the expected value of unity. This is well within the realm of experimental error. The values of the force constants α, β, and μ and the charge number Z are summarized in Table I.

The phonon dispersion for ZnTe was calculated in various symmetry directions and is presented in Fig. 1. To date, no experimental data on phonon dispersion exist for ZnTe.

The frequency distribution function $g(\omega)$ was calculated for a mesh of 4096 points in the first Brillouin zone. Due to the symmetry properties of the Brillouin zone for the zinc-blende structure, one need consider the determination of the eigenfrequencies only at the nonequivalent points in the $\vec{k}$ space defined as

$$\vec{k} = [\,(\pi/8a)\,q_x, (\pi/8a)\,q_y, (\pi/8a)\,q_z]\ ,$$

where $16 \geq q_x \geq q_y \geq q_z \geq 0$

and $q_x + q_y + q_z \leq 24$.

This type of sampling gave a total of 24 576 frequencies from which a histogram of $g(\omega)$ was plotted. The frequency distribution function with a sampling width of $\Delta\omega = 0.2 \times 10^{13}$ sec^{-1} is presented in Fig. 2. The calculated variation of the Debye temperature with the temperature is shown in Fig. 3. So far no detailed specific heat measurement on ZnTe has been reported. A value of

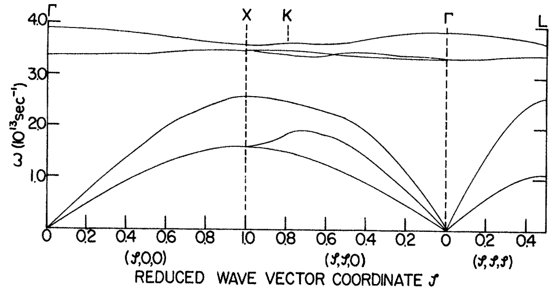

FIG. 1. Dispersion curves for ZnTe in the [100], [110], and [111] directions.

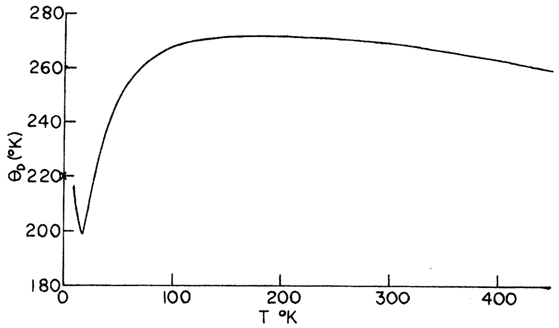

FIG. 3. Debye characteristic temperature of ZnTe as a function of temperature. The cross denotes Θ_D at 0 °K calculated from De Launay's tables (Ref. 18) using room-temperature elastic constants.

204 °K has been reported for the Debye temperature of ZnTe by Keleman *et al.*[17] and is within the range of values calculated by us. Using room-temperature elastic constants and De Launay's tables,[18] a value of 220 °K is obtained for the Debye temperature at 0 °K. The agreement with our calculated value is very good considering the fact that room-temperature elastic-constant values were used for the computation of Θ_D at 0 °K.

III. INFRARED-ACTIVE MULTIPHONON PROCESSES

The infrared absorption spectrum of ZnTe due to multiphonon processes has been reported by Nahory and Fan[19] and Narita, Harada, and Nagasaka.[20] The former authors note prominent absorption peaks in the two-phonon region. From an analysis of their spectrum they quote the following Brillouin-zone-boundary characteristic phonon frequencies: 178, 129, and 57 cm^{-1}. These compare extremely well with our calculated values of TO(L) = 182 cm^{-1}, LA(X) = 136 cm^{-1}, and TA(L) = 58 cm^{-1}. Narita *et al.*[20] have observed extensive multiphonon structures in the infrared spectrum extending to two- and three-phonon regions. In the absence of a lattice dynamical calculation for a guide, both Nahory and Fan and Narita *et al.* were unable to obtain specific CP frequencies from analyses of their spectra.

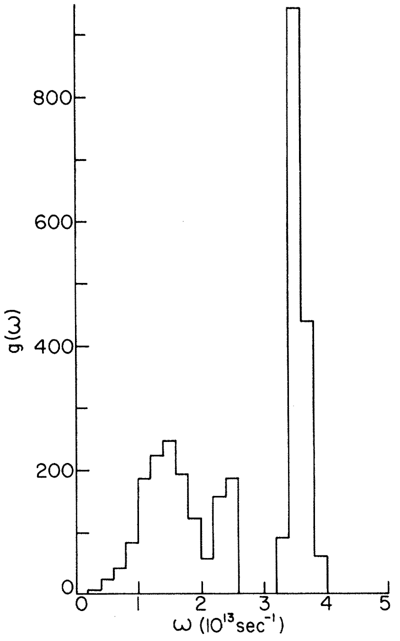

FIG. 2. Calculated phonon density of states $g(\omega)$ of ZnTe. Frequency interval used $\Delta\omega = 0.2 \times 10^{13}$ sec^{-1}, and units of $g(\omega)$ are arbitrary.

Since Narita *et al.* give an extensive table of observed peak frequencies (at 300 °K), we have used their data to obtain a multiphonon assignment. Selection rules for such electric dipole-active combination spectrum have been worked out by Birman.[21] Due regard has also been given to the expected strengths of absorption, viz., relatively stronger peaks are assigned to two-phonon processes, whereas weaker ones to three-phonon processes.[22] In the final selection of CP phonons to reproduce the observed infrared peaks within the limits of experimental error (2–3 cm^{-1}), we have been guided by the selection rules and the calculated frequencies from the present lattice dynamical model as approximate values. An assignment of the observed peak frequencies is given in Table II. The CP phonons obtained from this analysis are compared in Table III with the values from calculations of Sec. II. Considering the simplicity of the model used for the lattice dynamics, the agreement should indeed be regarded as good. The largest difference has been noted for TA(X), which is not surprising since it has been noted[6, 9] before that for GaAs, GaP, and ZnS, for which neutron-scattering data exist, the present rigid-ion model tends to overestimate this mode frequency.

Two other points are worth noting: (i) Frequencies are measured much more accurately by in-

TABLE II. Two- and three-phonon infrared-active combinations in ZnTe.

Absorption peak position (cm^{-1})[a]	Assignment	Calculated position (cm^{-1})[b]
253	LO (L) + TA (L);	252
	LO (X) + TA (X)	252
282	2 LA (L)	282
289	2TA (L) + TO (X)	291
302	TO (X) + LA (X)	303
313	TO (L) + LA (L)	313
332	LO (L) + LA (L)	335
351	2 TO (X)	350
359	2 LO (X)	360
374	TO (X) + TA (X) + LA (X)	375
380	TA (L) + LO (L) + LA (X)	380
387	2 LO (L)	388
403	TO (L) + TA (L) + TO (X)	405
410	TO (L) + TA (L) + LO (X)	410
414	2 TO (L) + TA (X)	416
423	2 TO (X) + TA (X)	422
435	TA (L) + LO (L) + LO (X)	432
	2 LO (X) + TA (X)	432
444	TO (L) + LA (L) + LA (X)	441
458	2 LA (L) + TO (Γ)	461
465	LO (L) + LA (L) + LA (X)	463
476	2 TO (X) + LA (X)	478

[a] Experimental data from Ref. 20.

[b] The CP phonon frequencies used are listed in Table

frared spectroscopy than by neutron scattering. However, to obtain correct CP phonon frequencies from the former measurements, it is essential to perform a correct analysis. In the absence of either neutron data or lattice dynamical calculations, it is not unusual to assign the CP phonons wrongly.[23, 24] However, when neutron-scattering data are available, a correct analysis of the infrared and/or Raman spectra is straightforward and yields correct values of CP phonons with an accuracy unobtainable by the neutron method alone, as recently demonstrated for diamond.[25] (ii) When neutron-scattering data for a crystal are not available, correct values of CP phonons may still be derived from optical data provided a reasonably approximate lattice dynamical calculation is available. The requirement is, however, that the lattice dynamical calculation does not require some CP phonons as input data for obtaining model parameters, but is able to predict approximate phonon dispersion from other well-established physical properties. The model presented here thus seems eminently suitable for this purpose. A model that requires many CP phonon frequencies for the determination of model parameters, among other limitations, may predict erroneous phonon dispersion when no neutron-scattering data are available. An earlier shell-model calculation[4] of this sort for ZnS is a classic example.

It was mentioned before that the present model is applicable to a crystal for which (i) an invariance relation connecting the elastic constants and the long-wavelength phonon frequencies holds good and (ii) $\mathrm{LO}(X)/\mathrm{LA}(X) = (m_1/m_2)^{1/2}$, where m_1 and m_2 ($m_1 > m_2$) are the two ionic masses. It was noted before that for ZnTe the criterion (i) is obeyed very well. Using the experimental (infrared) values of LO(X) and LA(X) from Table III, it is seen that $\mathrm{LO}(X)/\mathrm{LA}(X) = 1.406$, whereas $(m_1/m_2)^{1/2} = 1.397$. Thus the present model is indeed applicable to ZnTe, at least as far as the LO, TO, and LA branches are concerned.

The Brout sum[26] as defined by $\sum_{i=1}^{6} \omega_i^2$ is a constant with respect to $\vec{k}$ only if the near-neighbor forces are operative. Its deviation from a constancy is thus a measure of second-neighbor interactions.[27] For most cubic crystals, however, the deviation has been found to be small (within 20%).[28] A variation of about 15% is noted for ZnTe as one goes from Γ to X to L CP.

IV. MODE GRÜNEISEN PARAMETERS AND COEFFICIENT OF THERMAL EXPANSION

We now intend to calculate the pressure dependence of the phonon dispersion at constant temperature. This can be readily done by determining the four model parameters as functions of pressure. The pressure dependence of both the elastic constants and the Brillouin-zone-center optic-phonon frequencies is not simultaneously available for many crystals. ZnTe is one of the few crystals for which all these quantities have recently been experimentally obtained.[11, 14] The three force constants and the effective ionic charge are calculated at a higher pressure using Eqs. (1) and (2) along

TABLE III. Critical-point phonon frequencies (cm^{-1}) of ZnTe. Comparison between values obtained from infrared data (Table II) and present lattice dynamical calculation.

	Γ (0,0,0)		X (0,0,1)		$L(\frac{1}{2},\frac{1}{2},\frac{1}{2})$	
Phonon branch	Raman[a]	lattice dynamics	Infrared	lattice dynamics	Infrared	lattice dynamics
LO	206	206	180	190	194	195
TO	179	179	175	185	172	182
LA			128	136	141	138
TA			72	84	58	58

[a] Data from Ref. 11 used as input.

with measured values of the long-wavelength optic-phonon frequencies and the elastic constants at that pressure. For example, the model parameters at a pressure of 3 kbar are given in Table I. With these parameters the phonon dispersion of ZnTe is next obtained as a function of pressure.

The Grüneisen parameter for the phonon frequency of the ith branch at a point $\vec{k}$ in the first Brillouin zone can be related to the bulk modulus and the pressure dependence of the phonon frequencies as

$$\gamma_i(\vec{k}) = [B/\omega_i(\vec{k})][\Delta\omega_i(\vec{k})/\Delta P]_T \ . \tag{3}$$

It is now possible to obtain the variation of the Grüneisen parameter with the wave vector. Figure 4 presents the variation of γ_i in the [100], [110], and [111] directions for ZnTe.

A number of significant points are to be noted with regard to Fig. 4. These are (i) for ZnTe, which is a partially ionic crystal with an effective ionic charge of $0.718e$ instead of the total formal charge of $2e$, the Grüneisen parameter for the long-wavelength TO mode is only about 1.52, which is significantly smaller than a value of about 3 usually obtained for a primarily ionic crystal like an alkali halide. On the other hand, γ_{LO} at $\vec{k}\sim 0$ is about 0.76, a value only slightly larger than that for an ionic crystal[29] like NaF. The long wavelength γ_{TO} thus appears to depend strongly on the effective ionic charge, a reference to which has been made earlier.[11] (ii) At the X CP the present model predicts $\gamma_{\text{LA}} = \gamma_{\text{LO}}$ which is a consequence of the fact that according to this model LO(X) and LA(X) are related only by the ionic masses. Since a large number of zinc-blende–type crystals appear to follow this criterion,[30] it is to be expected that γ_{LA} and γ_{LO} at X CP should be nearly equal for these crystals. (iii) The present model predicts negative values of γ_{TA} for most of the first Brillouin zone. A negative γ_{TA} at the zone boundary in zinc-blende and diamondlike materials is associated with an anomalous negative volume coefficient of thermal expansion.[31] Negative γ_{TA} may also indicate a decrease in stiffness of the lattice to a particular mode under compression, preceding a first-order transition.[32] For a number of zinc-blende crystals, including ZnTe, a negative thermal expansion coefficient has indeed been noted at low temperatures.[33] It may also be noted that the zinc-blende crystals do undergo a first-order pressure-induced phase transition to the NaCl structure. More recently we have measured $\gamma_{\text{TA}}(L)$ and in some cases $\gamma_{\text{TA}}(X)$ by pressure dependence of the Raman spectrum of polytypes or of multiphonon processes, and negative γ_{TA} values have been obtained[11, 34] for a number of zinc-blende- or wurtzite-type crystals. The present model thus, at least qualitatively, can explain this phenomenon. It is also interesting to note that when this model is applied to the CsCl structure, only positive γ_{TA}'s are obtained.[13] Incidentally, for the CsCl-type crystals no anomalous negative thermal expansion coefficient has been observed. Negative γ_{TA} is thus a peculiar property of the diamond- and zinc-blende–type structures, and this fact is not obscured by this model.

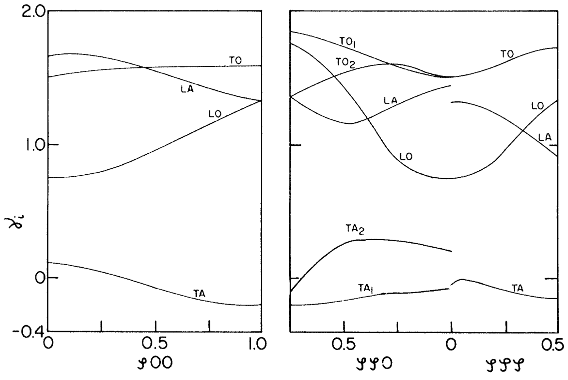

FIG. 4. Grüneisen parameters as functions of the wave vector.

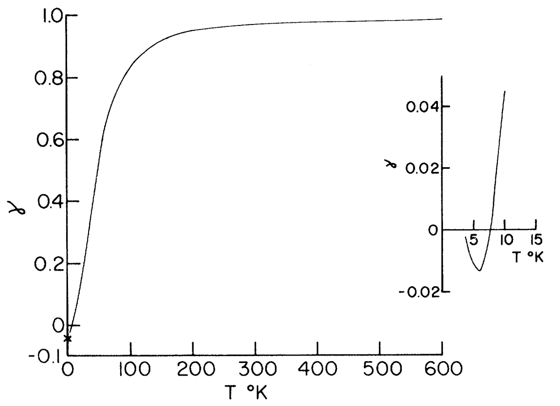

FIG. 5. Temperature dependence of Grüneisen constant. The cross indicates γ at 0 °K calculated from the formula given in Ref. 36.

In the quasiharmonic approximation[35] of lattice dynamics the mode Grüneisen parameters are regarded as temperature independent. But the Grüneisen constant defined as

$$\gamma(T) = \textstyle\sum_i C_i \gamma_i / \sum_i C_i \ , \tag{4}$$

where C_i is the Einstein specific heat function, may be temperature dependent. The temperature variation of the Grüneisen constant is presented in Fig. 5. The low-temperature limit of the Grüneisen constant, indicated by a cross in the figure, was calculated using the relationship given by Daniels.[36]

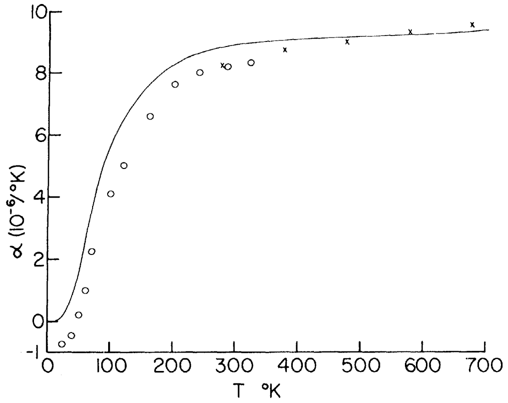

FIG. 6. Temperature dependence of the coefficient of linear thermal expansion of ZnTe. Line indicates calculated values; circles (Ref. 33) and crosses (Ref. 37) indicate experimental values.

The coefficient of linear thermal expansion is given by

$$\alpha(T)=\gamma(T)C_v(T)/3BV_a \ , \qquad (5)$$

where $C_v(T)$ is the specific heat at constant volume which was calculated using the present lattice dynamical model. The calculated temperature dependence of the coefficient of linear thermal expansion of ZnTe is compared to the available experimental data[33, 37] in Fig. 6.

It is interesting to point out that this four-parameter model, utilizing only the pressure derivatives of the elastic constants and the zone-center LO and TO mode frequencies, predicts a reasonable comparison with experiment for this quantity. It also predicts a slight negative value of the coefficient at low temperatures, a property peculiar to zinc-blende compounds. This negative coefficient can be attributed to the negative value of the Grüneisen constant. This property was first predicted theoretically by Blackman.[38] Later, multiparameter shell-model calculations for Ge and Si for which extensive neutron-scattering data exist were done by Bienenstock[39] and Dolling and Cowley.[12]

Primarily the negative Grüneisen parameter for the low-lying TA modes causes the negative value of $\gamma(T)$ at low temperatures. It is remarkable that our model, which is not expected to predict good agreement for the TA modes,[9] shows qualitative agreement with experiments for ZnTe. Work is now in progress with the purpose of obtaining more reasonable values of ω_{TA} and γ_{TA}, which in turn will give a more negative value for the Grüneisen constant, providing better agreement for $\alpha(T)$.

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[*] Work supported in part by the U.S. Air Force In-House Laboratory Independent Research Fund under Contract No. AF19(628)-6042.

[1] J. L. T. Waugh and G. Dolling, Phys. Rev. 132, 2410 (1963).

[2] J. L. Yarnell, J. L. Warren, R. G. Wenzel, and P. J. Dean, in Proceedings of the Conference on Inelastic Neutron Scattering, Copenhagen, Denmark, 1968 (unpublished).

[3] W. Cochran, Proc. Roy. Soc. (London) A253, 260 (1959); R. A. Cowley, *ibid.* A268, 121 (1962).

[4] H. Kaplan and J. J. Sullivan, Phys. Rev. 130, 120 (1963).

[5] J. F. Vetelino and S. S. Mitra, Phys. Rev. 178, 1349 (1969).

[6] J. F. Vetelino, S. S. Mitra, O. Brafman, and T. C. Damen, Solid State Commun. 7, 1809 (1969).

[7] D. W. Feldman, J. H. Parker, Jr., W. J. Choyke, and L. Patrick, Phys. Rev. 170, 698 (1968); 173, 787 (1968).

[8] L. A. Feldkamp, G. Venkataraman, and J. S. King, Solid State Commun. 7, 1571 (1969).

[9] J. F. Vetelino and S. S. Mitra, Solid State Commun. 7, 1181 (1969).

[10] R. W. Keyes, J. Chem. Phys. 37, 72 (1962); S. S. Mitra, Phys. Rev. 132, 986 (1963).

[11] S. S. Mitra, O. Brafman, W. B. Daniels, and R. K. Crawford, Phys. Rev. 186, 942 (1969).

[12] E. R. Cowley and R. A. Cowley, Proc. Roy. Soc. (London) A287, 259 (1965); G. Dolling and R. A. Cowley, Proc. Phys. Soc. (London) 88, 403 (1966).

[13] J. F. Vetelino, S. S. Mitra, and K. V. Namjoshi, Phys. Rev. (to be published).

[14] B. H. Lee, Bull. Am. Phys. Soc. 14, 834 (1969).

[15] E. W. Kellermann, Phil. Trans. Roy. Soc. London A238, 513 (1940); Proc. Roy. Soc. (London) A178, 17 (1941).

[16] H. M. J. Smith, Phil. Trans. Roy. Soc. London A241, 105 (1948).

[17] F. Keleman, E. Cruceanu, and D. Niculescu, Phys. Status Solidi 11, 865 (1965).

[18] J. De Launay, J. Chem. Phys. 22, 1676 (1954).

[19] R. E. Nahory and H. Y. Fan, Phys. Rev. 156, 825 (1967).

[20] S. Narita, H. Harada, and K. Nagasaka, J. Phys. Soc. Japan 22, 1176 (1967).

[21] J. L. Birman, Phys. Rev. 131, 1489 (1963).

[22] See, for example, S. S. Mitra, in *Optical Properties of Solids*, edited by S. Nudelman and S. S. Mitra (Plenum, New York, 1969), pp. 333–452.

[23] T. Deutsch, in *Proceedings of the International Conference on Semiconductors, Exeter*, 1962 (The Institute of Physics and the Physical Society, London, 1962), p. 505.

[24] For example, four different and conflicting CP analyses of optical spectra of CdTe have been reported, viz., A. Mitsuishi, U.S.-Japan Cooperative Seminar on

Far Infrared Spectroscopy, Columbus, Ohio, 1965 (unpublished); G. A. Slack, F. S. Ham, and R. M. Chrenko, Phys. Rev. 152, 376 (1966); G. L. Bottger and A. L. Geddes, J. Chem. Phys. 47, 4858 (1967); O. M. Stafsudd, F. A. Haak, and K. Radisavljevic, J. Opt. Soc. Am. 57, 1475 (1967).

[25] S. A. Solin and A. K. Ramdas, Phys. Rev. B 1, 1687 (1970).

[26] R. Brout, Phys. Rev. 113, 43 (1959).

[27] H. B. Rosenstock, Phys. Rev. 129, 1959 (1963).

[28] R. Marshall and S. S. Mitra, Phys. Rev. 134, A1019 (1964); S. S. Mitra and R. Marshall, J. Chem. Phys. 41, 3158 (1964).

[29] S. S. Mitra, C. Postmus, Jr., and J. R. Ferraro, Phys. Rev. Letters 18, 455 (1967).

[30] See J. E. Rowe, M. Cardona, and K. L. Shaklee, Solid State Commun. 7, 441 (1969).

[31] W. B. Daniels, in *Proceedings of the International Conference on the Physics of Semiconductors, Exeter* (The Institute of Physics and the Physical Society, London, 1962), p. 482.

[32] W. B. Daniels and C. S. Smith, Physics and Chemistry of High Pressures Symposium, London, 1962 (unpublished), p. 50; W. B. Daniels, *Lattice Dynamics*, edited by R. F. Wallis (Pergamon, London, 1965), p. 273.

[33] S. I. Novikova and N. Kh. Abrikosov, Fiz. Tverd. Tela 5, 2138 (1963) [Soviet Phys. Solid State 5, 1558 (1964)].

[34] S. S. Mitra and O. Brafman (unpublished).

[35] J. C. Slater, *Introduction to Chemical Physics* (McGraw-Hill, New York, 1939), Chap. XIII.

[36] W. B. Daniels, Phys. Rev. Letters 8, 3 (1962).

[37] H. J. Holland and K. Beck, J. Appl. Phys. 39, 3498 (1968).

[38] M. Blackman, Phil. Mag. 3, 831 (1958).

[39] A. Bienenstock, Phil. Mag. 9, 755 (1964).

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Sum Rule Relating Optical Properties to the Charge Distribution*

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(Received 24 February 1970)

A sum rule is constructed which relates the third moment of the imaginary part of the dielectric function at zero wave vector to an integral of the product of the Laplacian of the crystal potential and the fluctuation of the electron density. This sum rule, though rigorous, will be of real use only when the real solid can be replaced by a solid of pseudoatoms having only valence electrons. A method is found for obtaining an "experimental" third moment from other known moments. In this approximation some of the recent empiricism about bonding in crystals can be given a more rigorous basis. A quantitative application of the theorem to the prediction of the dielectric constant of GaAs is sketched.

I. INTRODUCTION

The recent works of Phillips[1] and Van Vechten[1] have made extensive use of the optical dielectric constant due to electronic polarizability to aid in understanding covalent and ionic bonding in a wide class of materials. This theory is empiricism based on good physical notions, but has not been derived from the Schrödinger equation. More recently, Wemple and DiDomenico[2] have empirically found that the dispersion in $\epsilon_1(\omega)$ as a function of frequency shows a systematic correlation with crystal binding and coordination number. It is obvious that $\epsilon(\omega)$ contains information about the electronic wave function responsible for bonding. What is not clear from this empiricism is whether $\epsilon(\omega)$ directly relates to bonding, or whether wave functions are a necessary intermediate construct of a complete quantum-mechanical theory. In this paper we develop a theorem which provides a direct link between $\epsilon(\omega)$ and some physical quantities of relevance to bonding.

An exact sum rule relating an integral over the dielectric function at zero wave vector to the charge distribution within a unit cell is derived in Sec. II. While this theorem is exact, it is of real utility in understanding binding only if the atomic core is replaced by a pseudopotential (Sec. III). Silicon, for example, will be considered a four-electron atom. In Sec. IV the direct relation between the symmetric and antisymmetric charge distributions and potentials and the magnitude of the optical dielectric constant is demonstrated. A quantitative evaluation of the difference in dielectric constant between Ge and GaAs is obtained by using the theorem.