

## Refractive-index measurements and nonlinear moment parameters for polycrystalline ZnSe†

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We have measured the refractive index and its temperature derivative, of polycrystalline ZnSe at seven wavelengths between 3.5 and 15  $\mu\text{m}$  (3 to 14 times the reststrahl frequency). We have used these data to determine relations among the effective ionic charge and the coefficients of the second- and third-order terms in an expansion of the crystal electric-dipole moment in powers of the lattice displacements. Comparison of ours with other data suggests that two-phonon absorption in ZnSe arises mainly from this nonlinear behavior of its electric-dipole moment.

### I. INTRODUCTION

The infrared absorption spectrum of an insulating crystal is characterized by narrow peaks at the ( $k \sim 0$ ) transverse-optic (TO) mode frequencies. These are called "one-phonon" peaks, since the energy of the absorbed photon is given entirely to a single lattice phonon. There are also much lower level and broader features in the infrared absorption spectrum. This additional absorption is called "multiphonon absorption" because the absorption of any infrared photon results in the creation and/or annihilation of two or more phonons in the crystal. This low-level multiphonon absorption arises from either or both of two possible mechanisms: (a) the small anharmonicity of the interionic forces,<sup>1</sup> and (b) the nonlinear dependence of the electric dipole moment on ionic displacements (i.e., the "nonlinear moment").<sup>2,3</sup>

In this paper we present the first direct experimental study of the parameters governing the nonlinear moment in a zinc-blende-structure crystal ZnSe. We assume that the nonlinear moment is a general function of the displacement from equilibrium of nearest neighbors along the vector separating them. We then relate three relevant parameters of this function to our measurements of the dispersion of the refractive index  $n(\omega)$  and its temperature derivative  $dn/dT$ . Unlike previous interpretations of various facets of multiphonon absorption,<sup>2-7</sup> our relations require no knowledge of, or assumptions concerning, the nature of the anharmonic crystal forces. Although our measurements cannot determine the nonlinear-moment parameters uniquely, we are able to specify them further using physical arguments and the nature of thermal expansion data. We conclude that the nonlinear-moment mechanism (b) is mainly responsible for multiphonon absorption in ZnSe, at least at low-phonon multiples. We are able to place strong constraints on the values of the nonlinear-moment parameters which would serve as

a check on any theory which predicts them or their relation to, for example, anharmonic forces.<sup>5,6</sup>

Our approach is based on the Born-Oppenheimer approximation in which the following relation holds between the imaginary part  $\epsilon_2(\omega)$  of the infrared dielectric function of an insulating solid and the derivatives of the (linear and nonlinear) electric-dipole moment  $M_i$  ( $i = x, y, z$ ) with respect to the position vectors  $r_{i\alpha}$  of the  $N$  ions (labeled by  $\alpha$ ) in a small fiducial volume  $V^8$

$$I_1 \equiv \int_L d\omega \omega \epsilon_2(\omega) = 2\pi^2 V^{-1} \sum_{\alpha} \frac{S_{\alpha}}{m_{\alpha}}, \quad (1a)$$

where  $m_{\alpha}$  is the mass of ion  $\alpha$ , and

$$S_{\alpha} \equiv \sum_i \left\langle \left( \frac{\partial M_x}{\partial r_{i\alpha}} \right)^2 \right\rangle. \quad (1b)$$

The subscript  $L$  indicates integration over positive frequencies (rps) encompassing all lattice absorption, which is assumed to occur at frequencies well below the electronic band gap. The dielectric function is for light polarized along a principal axis  $x$  of the crystal (or along any axis for an optically isotropic material). The brackets  $\langle \rangle$  signify a quantum average, which we will find may be calculated to sufficient accuracy assuming the lattice interactions to be harmonic. (Hence no knowledge of lattice anharmonicities is required to analyze the experimental behavior of  $I_1$  in terms of nonlinear-moment parameters.) Note that if the nonlinear moment is too small to be measurable, it means that the derivatives in (1) are  $c$  numbers (i.e., the effective ionic charges  $e_{\alpha}$ ), and the average can be calculated exactly and trivially for any anharmonic forces. For a cubic diatomic crystal like ZnSe, for example,  $I_1$  would be found to obey

$$I_1 = 2\pi^2 \rho e_{\alpha}^2 / \mu \quad (2)$$

exactly if the moment  $M_i$  were linear (in the  $r_{i\alpha}$ ). Here  $\rho$  is the number of molecules per  $\text{cm}^3$ ,  $\mu$  their reduced mass, and  $\pm e_{\alpha}$  are the (temperature-

independent) "Born" effective charges of the two-ion species. In fact, we find that (2) does not describe ZnSe, which therefore has a significant nonlinear moment.

Sufficiently accurate measurements of  $\epsilon_2(\omega)$  over all infrared frequencies and at several temperatures are difficult to obtain by absorption and reflectance measurements. To date such data only exist for LiF and are of barely useful accuracy for our purposes.<sup>8</sup> Therefore we have developed the following method of determining  $I_1$  (and especially its temperature dependence) from refractive-index measurements.<sup>9</sup> This method is of inherently greater accuracy and simplicity than direct measurements of  $\epsilon_2$  and employs the well-known (causality) relation between the real part  $\epsilon_1$  and imaginary part  $\epsilon_2$  of the dielectric function. For crystals whose electronic- and lattice-absorption bands are well separated from each other, this relation may be written

$$\epsilon_1(\omega) = \epsilon_{e1}(\omega) - \frac{2}{\pi} \int_L \frac{\nu d\nu \epsilon_2(\nu)}{\omega^2 - \nu^2}, \quad (3)$$

where the limits of integration are as in (1a), i.e., over the range of lattice absorption only.

In our measurements of the refractive index  $n(\omega)$ ,  $\omega$  was both far enough below the band gap (where the electronic contribution  $\epsilon_{e1}$  is real) and far enough above the transverse-optic mode frequency  $\omega_{TO}$  so that  $n(\omega)$  was real and  $n^2(\omega) \cong \epsilon_1(\omega)$ . Our measurements determined  $\epsilon_1$  over the range of  $\omega$  between 3 and 15 times  $\omega_{TO}$ , where we have verified that the following approximate expansion of both terms on the right-hand side of (3),

$$\epsilon_1(\omega) \cong \epsilon_\infty + A\omega^2 - \frac{2}{\pi} \left( \frac{I_1}{\omega^2} + \frac{I_3}{\omega^4} + \frac{I_5}{\omega^6} \right) \quad (4)$$

is accurate to better than  $10^{-4}$  for ZnSe and most diatomic cubic crystals. Here  $\epsilon_\infty$  is the long-wavelength limit of the optical (electronic) dielectric constant,  $A\omega^2$  is its first dispersion correction at small  $\omega$ , and

$$I_m \equiv \int_L \omega^m \epsilon_2(\omega) d\omega \quad (5)$$

are infrared absorption moments which result from the Taylor expansion of the integral in (3) in powers of  $(\nu/\omega)^2$ . Evidently we need enough measurements of  $n(\omega)$  to obtain all the coefficients in (4); only then will we know  $I_1$  and its temperature derivative to the accuracy we need. Before describing these measurements, we examine how  $I_1$  depends on the nonlinear moment parameters.

## II. THEORY FOR $S_\alpha$

In this section we will develop the required explicit relation between the moment  $I_1$  of (1) which

we measure and the nonlinear moment parameters we wish to determine. These parameters are the coefficients in the Taylor expansion of the moment function  $M_x$  in powers of the deviations (in vector notation)

$$\vec{x}_\alpha \equiv \vec{r}_\alpha - \vec{X}_\alpha \quad (6)$$

of positions  $\vec{r}_\alpha$  of the nuclei from their average positions

$$\vec{X}_\alpha \equiv \langle \vec{r}_\alpha \rangle_T \quad (7)$$

at some fiducial temperature  $T$ . Our final expressions will require only pair correlations of these coordinates calculated in the harmonic-lattice approximation. To proceed, we must first develop a reasonable approximation for the form of the dependence of  $\vec{M}$  on the  $\vec{x}_\alpha$ . The parameters in this expression can then be (nearly) determined from the experiments of Sec. III. At present the main uncertainty in this determination comes from our uncertain knowledge of the pair-correlation functions.

### A. Form of the nonlinear moment expansion

In its most general form, the expansion of  $\vec{M}$  in powers of the  $\vec{x}_\alpha$  may be written

$$\begin{aligned} \vec{M} = & \sum_\alpha \bar{e}_\alpha \cdot \vec{x}_\alpha + \sum_{\alpha\beta} \underline{f}_{\alpha\beta} \cdot \vec{x}_\alpha \vec{x}_\beta \\ & + \sum_{\alpha\beta\gamma} \underline{g}_{\alpha\beta\gamma} \cdot \vec{x}_\alpha \vec{x}_\beta \vec{x}_\gamma + \dots \end{aligned} \quad (8)$$

Interpretation of our experiments will require only the terms shown, i.e., up to third order. For a diatomic cubic crystal like ZnSe, the linear effective-charge dyadic has the form

$$\bar{e}_\alpha = \bar{I} e_\alpha, \quad (9)$$

where  $e_\alpha$  is  $(\pm)$  the "Born" effective charge, its sign depending on whether  $\alpha$  refers to the positive or negative ion. The tensors  $\underline{f}_{\alpha\beta}$ ,  $\underline{g}_{\alpha\beta\gamma}$ , etc., are third, fourth, etc., rank in coordinate space. Typically, their nonzero elements have magnitudes on the order of

$$\underline{f}_{\alpha\beta} \sim e_\alpha / r_0, \quad (10a)$$

$$\underline{g}_{\alpha\beta\gamma} \sim e_\alpha / r_0^2, \quad (10b)$$

etc., where  $r_0$  is the interionic (nearest-neighbor) distance. Since the  $\vec{x}_\alpha$  undergo thermal fluctuations that are an order-of-magnitude smaller than  $r_0$ , the expansion (8) is usefully convergent. The relations (10) will be crucial in determining which terms we can neglect in calculating  $S_\alpha$  in (1).

We will assume a special form for (8) in which  $\vec{M}$  is a sum over nearest-neighbor pairs only. The contribution of the pair whose labels are  $\alpha, \beta$  must

be expressible as a quadratic form in the difference coordinates

$$\vec{x}_{\alpha\beta} \equiv \vec{x}_\alpha - \vec{x}_\beta, \quad (11)$$

because of translational invariance. The  $n$ th-order term in each pair contribution must be of the form of a product of a tensor  $\underline{m}_{\alpha\beta}^{(n)}$ , of rank  $n+1$ , with  $n$  of the vectors  $\vec{x}_{\alpha\beta}$ . For the zinc-blende lattice, we see from (9) that

$$\underline{m}_{\alpha\beta}^{(1)} = \frac{1}{2} \bar{1} e_\alpha.$$

For the zinc-blende lattice the third rank tensor  $\underline{m}_{\alpha\beta}^{(2)}$  must be constructed of outer products of the unit dyadic  $\bar{1} e_\alpha$  and the unit vector between the nearest neighbors:

$$\hat{R}_{\alpha\beta} \equiv (\vec{x}_\alpha - \vec{x}_\beta) / |\vec{x}_\alpha - \vec{x}_\beta|. \quad (12)$$

The "triadic"  $\underline{m}_{\alpha\beta}^{(2)}$  therefore has three independent terms proportional to  $\hat{R}_{\alpha\beta} \hat{R}_{\alpha\beta} \hat{R}_{\alpha\beta}$ ,  $\bar{1} \hat{R}_{\alpha\beta}$ , and  $\hat{R}_{\alpha\beta} \bar{1}$ , respectively. If the nonlinear moment arises largely from Pauli exclusion between ion cores, then the first of these terms is likely to be dominant. This term alters the dipole moment, depending only on components  $\vec{x}_{\alpha\beta}$  along the interionic separation vector  $\hat{R}_{\alpha\beta}$ . The other terms give nonlinear moments that depend on displacements perpendicular to  $\hat{R}_{\alpha\beta}$ , a dependence that should be small. We neglect the second two terms here; including them does not seem to change the quality of the results as much as their complexity. In fact, we shall assume that all nearest-neighbor contributions to the nonlinear moment are some function of  $\hat{R}_{\alpha\beta} \cdot \vec{x}_{\alpha\beta}$  only. That is, we shall assume that (8) may be approximated by<sup>10</sup>

$$\vec{M} = \frac{3}{8} \sum_{n=1}^{\infty} \sum_{\alpha\beta}' e_\alpha \hat{R}_{\alpha\beta} (\hat{R}_{\alpha\beta} \cdot \vec{x}_{\alpha\beta})^n f_n, \quad (13)$$

an expression which enjoys all appropriate symmetry properties.

To see that (13) gives the same correct linear term as does (9), we use the fact that<sup>10</sup>

$$\sum_{\beta}' \hat{R}_{\alpha\beta} \hat{R}_{\alpha\beta} = \frac{4}{3} \bar{1}. \quad (14)$$

Then, if we take

$$f_0 = 1, \quad (15)$$

we see that the linear term in (13) reduces to  $\sum_{\alpha} e_\alpha \vec{x}_\alpha$  as desired.

We now proceed to evaluate  $S_\alpha$  in (1) using the form (13). This will allow us to determine  $e_\alpha$  and a relation between  $f_2$  and  $f_3$  from the experimental results of Sec. III B.

## B. Evaluation of averages

With (13), the derivative required in (1b) may be written (in dyadic form)

$$\frac{\partial \vec{M}}{\partial \vec{r}_\alpha} = \frac{3}{4} e_\alpha \sum_{\beta, n}' \hat{R}_{\alpha\beta} \hat{R}_{\alpha\beta} (\hat{R}_{\alpha\beta} \cdot \vec{x}_{\alpha\beta})^{n-1} n f_n. \quad (16)$$

With this in (1b)<sup>10</sup>

$$S_\alpha = \frac{3}{16} e_\alpha^2 \sum_{\beta\gamma mn}' (\hat{R}_{\alpha\beta} \cdot \hat{R}_{\alpha\gamma})^2 f_m f_n m n \times \langle (\hat{R}_{\alpha\beta} \cdot \vec{x}_{\alpha\beta})^{m-1} (\hat{R}_{\alpha\gamma} \cdot \vec{x}_{\alpha\gamma})^{n-1} \rangle. \quad (17)$$

Knowing the nearest-neighbor sum<sup>10</sup>

$$\sum_{\beta\gamma}' (\hat{R}_{\alpha\beta} \cdot \hat{R}_{\alpha\gamma})^2 = \frac{16}{3}, \quad (18)$$

and the fact that  $f_0 = 1$  from (15), the leading term in (17) reduces to  $e_\alpha^2$ , as we anticipated in (2). That is, without anharmonicity, the average required in (1) is simply of a constant, and (1) becomes the analogy of the Thomas-Kuhn-Reich sum rule of atomic oscillator strengths.

The remaining terms of importance for us in (17) are the terms linear and quadratic in the  $\vec{x}_{\alpha\beta}$ . We cannot neglect the linear terms proportional to  $\langle \vec{x}_{\alpha\beta} \rangle$  because we will be comparing data at different temperatures where a small average deviation of  $\vec{r}_\alpha$  from  $\vec{X}_\alpha$  may exist because of thermal expansion. These terms come from the  $(n=1, m=2)$  and  $(n=2, m=1)$  terms in (17). The contribution to  $S_\alpha$  of these terms is

$$4e_\alpha^2 f_2 \Delta, \quad (19)$$

where  $\Delta = \langle \hat{R}_{\alpha\beta} \cdot \vec{x}_{\alpha\beta} \rangle$  is the change in nearest-neighbor distance due to thermal expansion. We take  $\Delta = 0$  at  $T = 295$  K. This term gives the small change in the effective charge that occurs by virtue of lattice expansion.

One can see from perturbation theory that the  $(n=1, m=3)$  and  $(n=3, m=1)$  terms also represent the contribution to  $I_1$  of a change in the effective charge (or one-phonon strength) arising from the nonlinear character of  $\vec{M}$ . These terms are seen to contribute

$$6e_\alpha^2 f_3 \langle x^2 \rangle \quad (20)$$

to  $S_\alpha$ , where

$$\langle x^2 \rangle \equiv \langle (\hat{R}_{\alpha\beta} \cdot \vec{x}_{\alpha\beta})^2 \rangle \quad (21)$$

is obviously independent of which nearest neighbors  $\alpha$  and  $\beta$  are involved. In performing a similar analysis on LiF, we found that the contribution (20) could be neglected compared with that of (19).<sup>8</sup> However, mainly because  $d\Delta/dT$  is 5.5 times smaller for ZnSe than for LiF, we will find

that here (20) cannot be neglected in comparison with (19).

The last term in (17) of consequence to our analysis is the ( $n=m=2$ ) term which reflects the role of the nonlinear moment in all of the two-phonon processes which affect absorption. (The creation of two phonons by a photon is the main contributor.) From (17) this term is

$$e_\alpha^2 f_2^2 \langle 3\langle x^2 \rangle + \langle x_1 x_2 \rangle \rangle, \quad (22)$$

where

$$\langle x_1 x_2 \rangle \equiv \langle \hat{R}_{\alpha\beta} \cdot \vec{x}_{\alpha\beta} \hat{R}_{\alpha\gamma} \cdot \vec{x}_{\alpha\gamma} \rangle, \quad \gamma \neq \beta \quad (23)$$

is independent of  $\alpha$ ,  $\beta$ , and  $\gamma$ .

After estimating the required averages, we will find, as we expected, that the nonlinear moment corrections (19), (20), and (22) are all small (<10%) compared with the leading linear moment contribution  $e_\alpha^2$  to  $S_\alpha$ . One can then see with the aid of (10) that terms of higher  $n$  and  $m$  in (17) are of the order of products of these small terms. Therefore we neglect terms in (17) that are of higher order than those (quadratic in  $\vec{x}_\alpha$ ) we have considered. To the same order of accuracy, or higher, we can also neglect the small corrections to pair-correlation functions that arise from anharmonicity in the lattice forces.

At present, not enough is known of the lattice normal mode frequencies and eigenvectors to calculate  $\langle x^2 \rangle$  and  $\langle x_1 x_2 \rangle$  with precision. We will therefore use the following approximation to calculate them:

$$\langle \vec{x}_\alpha \vec{x}_\beta \rangle = \bar{I} \delta_{\alpha\beta} \bar{\hbar} (2\bar{\omega} m_\alpha)^{-1} \coth \frac{1}{2} \beta \bar{\omega}, \quad (24)$$

where  $\beta \equiv \hbar/kT$ ,  $\bar{\hbar} \equiv$  Planck's constant  $\equiv 2\pi$ , and  $\bar{\omega}$  is the average normal mode frequency weighted by the probability that the displacement  $\vec{x}_\alpha$  excites a mode of a particular frequency. The result (24) is exact for a single oscillator and is the first term in a rapidly converging series for  $\langle x_\alpha^2 \rangle$ . Applying (24) to calculate  $\langle x^2 \rangle$  for the (easily soluble) model for the rocksalt structure lattice discussed in Ref. (8) gives a result that is 23% too high, mainly because this lattice model has far too many low-frequency modes. The error should be considerably less when (24) is applied to a realistic lattice model. We believe that for our estimates, the uncertainty in the actual value of the average mode frequency  $\bar{\omega}$  is more troublesome than the inaccuracy of (24). We shall take  $\bar{\omega}$  to lie somewhere between the transverse-optic mode frequency  $\omega_{\text{TO}}$  and  $\omega_{\text{TO}}/2^{1/2}$ .

Using (24) in (21) and (23) then gives the following approximation for  $S_\alpha$  which we will use in (1) to analyze our data<sup>11</sup>:

$$S_\alpha = e_\alpha^2 [1 + 2f\Delta + (\gamma + \xi)f^2 \langle x^2 \rangle], \quad (25)$$

where  $f \equiv 2f_2$ ,  $\gamma \equiv 3f_3/2f_2^2$ , and  $\xi \equiv \frac{3}{4} - (m_\alpha^2 + m_\beta^2)/12(m_\alpha + m_\beta)^2$ , ( $= 0.708$  for ZnSe).

From (24) we have

$$\langle x^2 \rangle = \bar{\hbar} (2\bar{\omega})^{-1} \coth \frac{1}{2} \beta \bar{\omega}. \quad (26)$$

We have redefined the second- and third-order moment parameters in terms of  $f$  and  $\gamma$  for ease of plotting the relation (25) linking  $e_\alpha$ ,  $f_2$ , and  $f_3$  with the experimental values of  $S_\alpha$  and its temperature derivative.

As we have discussed, the ( $n=m=2$ ) term of (17) represented multiphonon absorption caused by the nonlinear moment. Therefore, the fraction  $F_{\text{NLM}}$  of all absorption as averaged in  $I_1$  that arises from the multiphonon absorption caused by the nonlinear-moment mechanism is, from (25) in (1),

$$F_{\text{NLM}} = \xi f^2 \langle x^2 \rangle / [1 + 2f\Delta + (\gamma + \xi)f^2 \langle x^2 \rangle].$$

We will use this to compare with observed multiphonon absorption intensities, arising from all mechanisms, given our experimental results for  $f$  and  $\gamma$ .

### III. EXPERIMENT

Accurate values for the refractive index  $n(\omega)$  for CVD ZnSe have been previously determined at room temperature over the desired range of wavelengths ( $\omega \sim 3$  to 50 times  $\omega_{\text{TO}}$ ).<sup>12,13</sup> Therefore we have concentrated on measuring the temperature variation of  $n(\omega)$  from 25 to 300 °C and from 3.5 to 15  $\mu\text{m}$  ( $\omega = 3.3$  to 14 times  $\omega_{\text{TO}}$ ), mainly in order to determine  $dn(\omega, T)/dT$ .

#### A. Apparatus

For our measurements we have used the special prism refractometer shown schematically in Fig. 1. In terms of the ZnSe prism-sample geometry indicated, the refractive index is given by

$$n(\omega) = \sin\beta(\omega)/\sin\alpha, \quad (27)$$

when the angle  $\beta$  is adjusted so that the light of frequency  $\omega$  is refracted by the front surface and reflected collinearly by the back surface of the prism.

Our prism was cut from a sample of (1-cm thick) polycrystalline chemical vapor-deposited (CVD) ZnSe grown by Raytheon Co. It was optically clear along the growth direction but contained very faint light and dark bands when observed in the perpendicular direction (along the planes of growth). The prism was cut from this sample with an apex angle  $\alpha$  of 22.5° to obtain maximum dispersion and minimum reflection loss at the front surface (close to Brewster's angle). The back surface was aluminum coated to serve as a mirror.

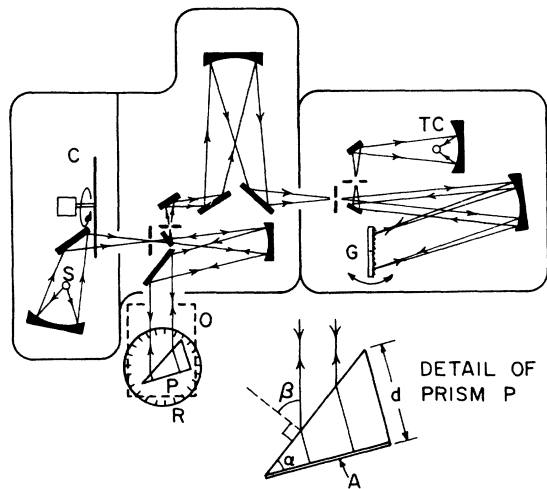


FIG. 1. Schematic of the infrared prism refractometer. Major components are: Nernst glower source *S*, light chopper *C*, oven *O* containing ZnSe prism *P* on rotating stage *R*, diffraction grating *G*, and thermocouple detector *TC*. ZnSe prism of apex angle  $\alpha = 22.5^\circ$  base  $d = 2$  cm, and 1-cm thickness is aluminized on back surface *A*.

The arrangement shown in Fig. 1 was constructed by converting a Perkin-Elmer Model 13 spectrophotometer into two monochromators in tandem, with the prism serving as the dispersive element in the first one. The prism was housed in a stationary oven, and connected to a rotation stage with a thin rod.

At each of the seven wavelengths, the prism was heated to six temperatures  $T$ , the angle  $\Delta\beta$  for this  $\omega$  and  $\Delta T$  was measured, and  $\Delta n$  was calculated using (27). A small correction ( $\sim 3\%$ ) to  $\Delta n$  due to expansion of air was included in calculating  $\Delta n$ .<sup>14</sup> The measurement temperatures were 30, 80, 157, 232, 271, and 328 °C.

#### B. Data

Within our experimental uncertainty we could discern no variation of  $\Delta n/\Delta T$  in the temperature

TABLE I. Measured values of  $\Delta n/\Delta T$  for  $25 < T < 200$  °C.

$\omega$ (cm <sup>-1</sup> )	$10^5 \times \frac{\Delta n}{\Delta T}$ (K <sup>-1</sup> )
2851.7 ± 0.1	6.9 ± 0.2
1583.0	6.7
1327.2	6.66
1154.0	6.57
1028.2	6.56
760.7	6.5
663.5	6.4

range from 20 to 200 °C. At higher temperatures a small increase in  $\Delta n/\Delta T$  ( $d^2n/dT^2 \sim 5 \times 10^{-8}$  K<sup>-2</sup>) was observed at all wavelengths, but it was not possible to ascertain its frequency dependence. Our experimental results for  $dn/dT$  at seven wavelengths between 3.5 and 15  $\mu\text{m}$  are presented in Table I.

Other workers have also measured  $dn/dT$ , both interferometrically at 10.6 and 3.39  $\mu\text{m}$ ,<sup>12,15,16</sup> and with a minimum-deviation prism method from 1 to 18  $\mu\text{m}$ .<sup>12</sup> The reported values of  $dn/dT$  at 10.6  $\mu\text{m}$  are scattered between  $5.2 \times 10^{-5}/\text{K}$  and  $7.4 \times 10^{-5}/\text{K}$ , but the data of Refs. 12 and 15 indicate a small decrease of  $dn/dT$  at lower frequencies, in general agreement with our data in Table I.

We have used a standard least-squares algorithm to obtain the temperature dependence of the parameters in Eq. (4) from our data (and the indices of Ref. 12) on CVD ZnSe. Our results for these parameters are given in Table II, along with several other known parameters which we shall need for theoretical interpretations.

#### IV. INTERPRETATION

We examine here the constraints placed by our data on the nonlinear-moment parameters  $f$  and  $\gamma$  of (25). By physical argument and examination of thermal-expansion data, we can increase these constraints to obtain probable values.

We obtain a relation between  $f$  and  $\gamma$  by taking the logarithmic derivative of (1) with (25). This eliminates the effective charge parameter (to

TABLE II. Values and temperature derivatives of various parameters of CVD ZnSe at 295 K, derived from experiment. A prime indicates the logarithmic temperature derivative ( $A' \equiv A^{-1} dA/dT$ , etc.). The uncertainty in the last digit, if any, is given in parentheses after the number.

Parameter	Ref.
$\epsilon_\infty = 5.925(5)$	12, a
$A = 2.51(5) \times 10^{-9}$ cm <sup>2</sup>	12, a
$I_1 = 7.27(3) \times 10^{27}$ sec <sup>-2</sup>	12, a
$I_3 = 1.77(7) \times 10^{55}$ sec <sup>-4</sup>	12, a
$I_5 = 6(1) \times 10^{82}$ sec <sup>-6</sup>	12, a
$\epsilon_\infty' = 5.35(20) \times 10^{-5}$ K <sup>-1</sup>	a
$A' = 3(1) \times 10^{-4}$ K <sup>-1</sup>	a
$I_1' = 7(1) \times 10^{-5}$ K <sup>-1</sup>	a
$I_3' = 1.0(5) \times 10^{-4}$ K <sup>-1</sup>	a
$\rho = 2.20$ mol cm <sup>-3</sup>	17
$r_0 = 2.45$ Å	17
$\alpha = r_0^{-1} d\Delta/dT = 7.79(7) \times 10^{-6}$ K <sup>-1</sup>	12
$\omega_{\text{TO}} = 203$ cm <sup>-1</sup>	18
$\omega_{\text{TO}}' = -1.2 \times 10^{-4}$ K <sup>-1</sup>	18

<sup>a</sup> This work.

which we return later) and gives

$$\frac{1}{I_1} \frac{dI_1}{dT} - \frac{1}{\rho} \frac{d\rho}{dT} = \frac{2fd\Delta/dT + (\gamma + \xi)f^2 d\langle x^2 \rangle/dT}{1 + (\gamma + \xi)f^2 \langle x^2 \rangle} \quad (28)$$

at 295 K, where  $\Delta = 0$ . Using the data of Table II, we have plotted the relation (28) between  $f$  and  $\gamma$  in Fig. 2 for two values of  $\bar{\omega}$  which, when used to estimate  $\langle x^2 \rangle$  by (26), give its probable limits. We see that the uncertainty in  $\langle x^2 \rangle$  is much more troublesome than is the uncertainty in our experimental value for  $dI_1/dT$ , which places the small error bars shown on the curves.

The fractional contribution (27) of the nonlinear moment to the absorption (as averaged in  $I_1$ ) is also plotted in Fig. 2. By examination of the absorption and reflection data of Aven *et al.*,<sup>19</sup> we have determined that the total fractional multiphonon contribution  $F_{mp}$  to  $I_1$  is  $5 \pm 1\%$ . Therefore,  $F_{NLM} < 0.06$ , thus placing the limits on  $f$  shown by the vertical dashed lines in Fig. 2.

The main contribution to the nonlinear moment is expected to arise from Pauli exclusion forces between electronic clouds when two ions approach closely. The first ( $n=2$ ) correction to the linear moment in (13) should therefore reflect the fact that the electrons are tending to remain behind

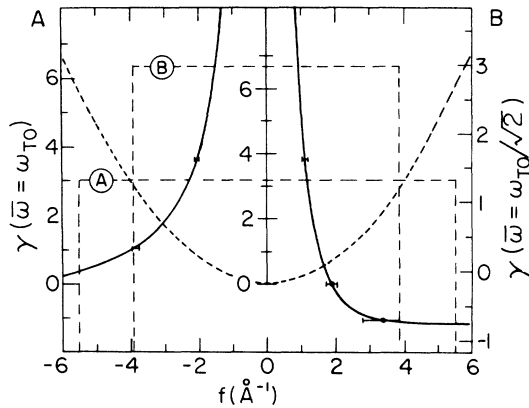


FIG. 2. Solid curve represents the dependence of the third-order moment coefficient  $\gamma$  on the second-order moment coefficient  $f$ , as derived from our data. The left and right scales are for two values of the average phonon frequency  $\bar{\omega}$  which are expected to bracket the true average. The dashed rectangles A and B probably contain the true  $\gamma, f$  values for the left and right scales respectively; the vertical dashed lines correspond to the limit imposed by the observed two-phonon absorption in Ref. 18, and the horizontal lines are at  $\gamma=3$ . The error bars represent the uncertainty in our measurements. The dashed curve represents the fraction  $F_{NLM}$  of the multiphonon contribution to  $I_1$  arising from the nonlinear moment only; the center scale gives  $F_{NLM}(\bar{\omega}/\omega_{TO})^2$  in percent.

when two nuclei approach. This circumstance is easily seen to require

$$f_2 < 0 \quad (29)$$

in the form (13). Because of the suddenness of hard-core interactions, it has been suggested that the nonlinear moment be exponential in form. That is  $f_n \sim f^n/n!$ , where  $f$  is a parameter such as the one we have defined. This would require  $\gamma=1$  by our definition, a value which our data allows when  $f < 0$  (see Fig. 2). Intuitively we feel it to be likely that the magnitude of  $\gamma$  will not exceed 3, a condition which would place the limits indicated in Fig. 2 by the horizontal dashed lines.

In both ZnSe and LiF,  $F_{mp} \sim 5\%$ .<sup>19,8</sup> However, the thermal expansion coefficient  $\alpha$  of ZnSe is only 22% of that of LiF. This shows that ZnSe is much less anharmonic than LiF. The two-phonon absorption caused by the cubic anharmonic potential  $V^{(3)}$  scales as  $|V^{(3)}|^2$ , whereas  $\alpha$  scales proportionally as  $V^{(3)}$ . In LiF we showed that  $F_{mp}$  arises mostly from  $V^{(3)}$ . If  $F_{mp}$  arose mainly from  $V^{(3)}$  in ZnSe, then its smaller  $\alpha$  would suggest that its multiphonon fraction  $F_{mp}$  should be much less than 1%. That  $F_{mp}$  is actually near 5% strongly suggests that in ZnSe, two-phonon absorption arises mainly from the nonlinear-moment mechanism. This is what we would have deduced from our data if we had assumed the series (13) to represent an exponential function, or, at least, taken  $\gamma=1$ . We summarize in Table III the moment parameters which we derive from our data with this assumption (and the requirement that  $f$  be negative), parameters which we feel most probably give the correct nonlinear moment on the basis of our, and thermal-expansion, data.

Using all values of  $f$  and  $\gamma$  enclosed by the dashed rectangles in Fig. 2, together with the value of  $I_1$  in Table II to calculate the effective ionic charge  $|e_\alpha|$  in (1), we obtain values for  $q \equiv |e_\alpha|/e_0$  in the range  $2.0 \pm 0.1$ . ( $e_0$  is the electron charge.) With the probable parameters in Table III, the range for  $q$  narrows to  $2.01 \pm 0.01$ .

TABLE III. Quadratic moment parameter  $f$ , effective ionic charge  $e_\alpha$  (in terms of the electronic charge  $e_0$ ) and corresponding two-phonon contribution  $F_{NLM}$  of the nonlinear moment to the integral  $I_1$ , given for two values of the average lattice frequency  $\bar{\omega}$  which, used in (26), are expected to set the bounds on the parameters. An exponential moment function (or  $\gamma=1$ ) has been assumed.

$\bar{\omega}/\omega_{TO}$	$f$ ( $\text{\AA}^{-1}$ )	$ e/e_0 $	$F_{NLM}\%$
1	-4	2.02	3
$2^{-1/2}$	-2.6	2.00	3

## V. SUMMARY

We have determined experimentally for CVD ZnSe the value and temperature derivative of  $I_1$ , which is an average of  $n$ -phonon contributions to the imaginary part of the dielectric function. Using a sum rule, we have also calculated  $I_1$  in terms of parameters governing nearest-neighbor contributions to the nonlinear-moment function. This calculation is valid in the Born-Oppenheimer approximation regardless of the form of the anharmonic forces, which also cause multiphonon absorption. Fitting the theory to experiment, we have ob-

tained the effective ionic charge and a relation between second- and third-order moment parameters. From previous measurements of the two-phonon absorption and thermal expansion coefficients, we further limit the probable values of these parameters to those for which the nonlinear moment contributes much more to the multiphonon part of  $I_1$  than do the anharmonic forces.

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