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Method for measuring the contribution of the nonlinear dipole moment to multiphonon absorption*

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A method is proposed by which one may determine the separate contributions of (a) the anharmonic interionic forces, and (b) the nonlinear electric dipole moment (the nonlinear dependence on ionic displacements) to the integral over infrared frequencies of the imaginary part $\epsilon_2(\omega)$ of a material's dielectric function (times the frequency ω). The results can be used to determine parameters needed to calculate other features of multiphonon absorption. The method does not depend on the nature or magnitude of the anharmonic forces, but does require a model for the quadratic term in the dipole moment. The parameters in this model are then determined from measurements of $\epsilon_2(\omega)$ at several temperatures. We use the method to show from existing data that the multiphonon contribution to the integral of $\omega\epsilon_2(\omega)$ for cubic LiF arises predominantly from anharmonic forces.

I. INTRODUCTION

The absorption of infrared radiation by an "ideal" polar crystal occurs only at a small number of discrete fundamental lattice-vibration frequencies called the ($k=0$) transverse-optic (TO) modes of the crystal. In this context, an ideal crystal is one in which the interionic forces are strictly linear in all ionic displacements, and the force on any ion of an external electric field is proportional to the field. In actuality, even the purest real polar crystal exhibits, in addition, a lesser and varying amount of absorption throughout the infrared. 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. Such multiphonon absorption arises from either or both of two possible mechanisms: (a) anharmonic interionic forces, and (b) the nonlinear dependence of the electric dipole moment on ionic displacements (or the "nonlinear moment").

The relative contribution of these two mechanisms to multiphonon absorption in specific crystals is still uncertain to a greater or lesser degree. It is least uncertain for alkali-halide crystals, for which it has been found consistent, in albeit approximate, calculations to neglect mechanism (b).[1] However, for many important infrared-window materials, such as ZnSe, CdTe, ZnTe, and GaAs, the relative importance of the two mechanism is quite uncertain.[2]

In the interest of enabling better calculations of multiphonon absorption, we show here how the foregoing uncertainty in mechanism can be resolved using measurements of the imaginary part $\epsilon_2(\omega)$ of the dielectric constant at infrared frequencies ω. Our method is based on the well-known fact that the changes in peak frequency or frequencies and width(s) of the fundamental infrared lattice-absorption resonance(s) with density or temperature do not depend on the nonlinear moment, whereas multiphonon difference- and summation-absorption bands are sensitive to both mechanisms (a) and (b).[1] In Sec. II we show how it is immediately evident from the measured integral of $\omega\epsilon_2(\omega)$ at two temperatures if the nonlinear moment is negligible. If it is not negligible, its form must be modeled as in Sec. III and an average of an expression quadratic in the ionic displacements must be performed in the harmonic-lattice approximation. There we show how two different models for rocksalt-structure crystals give very similar results for the relative importance of mechanisms (a) and (b), lending confidence in our nonlinear-moment models for the present purposes. In Sec. IV, we apply the method to LiF, for which the data is not accurate enough to conclude more than that the anharmonic force mechanism is mainly responsible for the multiphonon contribution to the integral of $\omega\epsilon_2$. Unfortunately, sufficient data for the more interesting semiconductor materials do not yet exist.

Our method requires the measurement of the imaginary part $\epsilon_2(\omega)$ of the dielectric constant, throughout the infrared, and at two or more temperatures. From this measurement one obtains an experimental determination of the integral in the following exact sum rule, in esu (proved in the Appendix):

$$\int_0^\infty d\omega\,\omega\epsilon_2(\omega)=\frac{2\pi^2}{V}\sum_{\alpha,i}\left\langle\left(\frac{\partial M_x}{\partial r_{i\alpha}}\right)^2\right\rangle\Big/m_\alpha, \qquad (1)$$

in which M_x is the operator representing the macroscopic electric dipole moment in some small fiducial volume V, along the principal dielectric x axis for which ϵ_2 was measured. For optically isotropic materials this x axis can be any axis and all principal dielectric constants are equal. The $r_{i\alpha}$ are the spatial coordinates ($i = x, y, z$) of all the N ions ($\alpha = 1, 2, \ldots, N$), with masses m_α, inside the small but macroscopic volume V of the crystal. The brackets $\langle\,\rangle$ indicate the quantum average.

The usefulness of (1) lies in the fact that the contribution to the averaged expression of the linear term in the dipole moment can easily be calculated exactly for many important types of crystals. To see this, we first write each ion coordinate as

$$r_{i\alpha} \equiv R_{i\alpha} + x_{i\alpha}\,, \tag{2}$$

the sum of its average value $R_{i\alpha} \equiv \langle r_{i\alpha}\rangle$ (for some temperature) and its deviation $x_{i\alpha}$ from this average value. Then the dipole moment in a volume V of the crystal at this temperature can be expanded in a Taylor series in the $x_{i\alpha}$:

$$M_x = \sum_{i\alpha} e_{xi\alpha} x_{i\alpha} + \tfrac{1}{2} \sum_{i\alpha j\beta} f_{xi\alpha j\beta} x_{i\alpha} x_{j\beta} + \cdots\,, \tag{3}$$

where the $e_{xi\alpha}$ and $f_{xi\alpha j\beta}$ are the Taylor-series expansion coefficients, the former being an "effective-charge" tensor for the αth ion. The terms in M_x third and higher order in the $x_{i\alpha}$ may be assumed to contribute less to (1) than the quadratic term whenever the quadratic term gives rise to sum- and difference-absorption bands that contribute less to the integral in (1) than does the fundamental absorption line(s) arising from the leading, linear dipole moment term. (In fact for all potential ir-window materials, we may neglect higher than quadratic terms in M_x when computing the right-hand side of (1) to within the experimental errors in determining the left-hand side.)

II. CRYSTALS WITH LINEAR DIPOLE MOMENTS

If the mechanism of anharmonic forces dominates that of the nonlinear moment, we may neglect all but the term linear in $x_{i\alpha}$ in the expression (3) for the dipole moment. Then we need study only the $e_{xi\alpha}$, whose forms depend on the symmetry of the site at $R_{i\alpha}$. For ions at sites having point symmetries T, T_h, T_d, O, or O_h (such as the ions in the alkali halides, GaAs, ZnSe, and CdTe),

$$e_{xi\alpha} \to e_\alpha \delta_{xi}\,, \tag{4}$$

where e_α is called the effective charge of the ion α and δ_{xi} is the Kronecker delta. For diatomic cubic crystals such as the aforementioned, the two effective charges must be related by

$$e_1 = -e_2 = e^* \tag{5}$$

in order that no moment develops from (3) when all ions are uniformly translated. This charge e^* has been called the Born effective charge and gives the total change in the macroscopic electric moment accompanying an ionic displacement.

If all the prominent features of $\epsilon_2(\omega)$ arise from a linear dipole moment, acting with anharmonic interionic forces, in alkali-halide and other diatomic cubic crystals, then we see from (3)–(5) that (1) reduces to

$$\int_0^\infty d\omega\, \omega \epsilon_2(\omega) \to 2\pi^2 \rho\, e^{*2}/\mu\,, \tag{6}$$

where ρ is the number density of molecules and $\mu^{-1} = m_\alpha^{-1} + m_\beta^{-1}$ is the molecular reduced mass. In this case, furthermore, the crystal must exhibit a dielectric function ϵ_2 that obeys (6) at different temperatures and densities, with an essentially invariant effective charge e^*. This can be seen as follows: As the temperature is raised and the crystal expands, the Taylor series (3) for the dipole moment must be reexpressed in powers of the deviations $x'_{i\alpha}$ about the new average ionic positions $R'_{i\alpha} = R_{i\alpha} + \delta R_{i\alpha}$. Substituting

$$x_{i\alpha} = x'_{i\alpha} + \delta R_{i\alpha} \tag{7}$$

in (3) gives for the effective-charge coefficients of the linear term in the dipole moment expansion, at the new temperature,

$$e'_{xi\alpha} = e_{xi\alpha} + \sum_{j\beta} f_{xi\alpha j\beta}\, \delta R_{j\beta} + \cdots\,. \tag{8}$$

The form of $f_{xi\alpha j\beta}$ must be such as to involve only differences in displacements with respect to not-distant neighboring ions, and hence (8) must involve mainly the relative average lattice displacements ($\delta R_{j\beta} - \delta R_{i\alpha}$). These relative displacement changes with temperature are of the same order of magnitude as the rms thermal fluctuations of the $x_{i\alpha}$ about $\langle x_{i\alpha}\rangle = 0$. Therefore, if the nonlinear moment term can be neglected in (3), then so can the change in effective charge, proportional to the δR, in (8). QED.

III. CRYSTALS WITH NONLINEAR DIPOLE MOMENTS

If the imaginary part of the dielectric constant fails to obey (6), then it can only be because the nonlinear quadratic, of "f", term in the dipole moment (3) must be contributing to the average in (1). To see what a deviation from (6) means, one must construct a theory for the form of the f coefficients, and use experimental values of the left-hand side of (1) to determine the parameters in the theory. Fortunately, the averages over the $(fx)^2$ term required in (1) can always in principle be performed because, to the desired order of accuracy, the lattice may be assumed to be perfectly harmonic. We illustrate the foregoing procedure with two models for a rocksalt-structure crystal: (i) the independent-molecule model and (ii) a more complex model in which the nonlinear moment depends only on relative nearest-neighbor displacements. It will be comforting to find that these models give similar results for the small nonlinear moment contribution in LiF when they are applied to existing data on its $\epsilon_2(\omega)$ in Sec. IV.

A. Model of independent molecules with nonlinear moments

The independent-molecule model of the lattice has been used extensively in estimating multiphonon absorption.[3] In this model, each one-dimensional molecule in the crystal contributes independently to the total dipole an amount

$$m_x = ex + \tfrac{1}{2}efx^2 , \tag{9}$$

where x is the deviation from the equilibrium interatomic distance at the temperature under consideration. Equation (1) then reduces to

$$\int_0^\infty d\omega\, \omega\epsilon_2(\omega) \rightarrow 2\pi^2\rho e^2(1+f^2\langle x^2\rangle)/\mu . \tag{10}$$

At another temperature (indicated by primes) the frequency integral becomes

$$2\pi^2\rho' e^2[(1+f\,\delta R)^2 + f^2\langle x'^2\rangle]/\mu . \tag{11a}$$

The linear expansion of the lattice constant with temperature δR and the densities ρ and ρ' are known, and $\langle x^2\rangle$ is easily calculated for the harmonic oscillator at any temperature T, assuming its mass to be the reduced mass μ and its frequency to equal the transverse-optical, or reststrahl, frequency ω_{TO}:

$$\langle x^2\rangle = (\hbar/2\mu\omega_{\text{TO}})\coth\gamma , \tag{11b}$$

where the temperature parameter γ is $\frac{1}{2}\hbar\omega_{\text{TO}}/kT$. Note that now the Born effective charge e does change with temperature as $e[1+f\delta R(T)]$.

The two expressions (10) and (11) can be solved for the two unknowns e and f. Then the contribution to the integral of multiphonon absorption arising from the nonlinear moment is simply the value of the second term in (10) or (11). Subtracting this value from the total measured multiphonon contribution to the integral in (10) gives the estimate of this model for the anharmonicity contribution to the integral. To obtain an estimate of the error of this procedure for rocksalt-structure crystals we develop next a more exact model which can also be evaluated simply.

B. Model with nonlinear moments as functions of nearest-neighbor displacements

Deviations from a linear relation between the crystal electric dipole moments and the ionic displacements are largest when two ions approach one another closely. This nonlinear moment is expected to be directed mainly along the line between the centers of the near ions; the relative positions of more distant neighboring ions ought not to affect it much. Let us use these properties to construct an expression for the component M_x of the total electric moment along a principal axis (x) of a rocksalt-structure crystal. (For a cubic crystal we would of course obtain the same final result for the multiphonon absorption, whatever component we considered.) Since we wish a form that is quadratic in the nearest-neighbor displacements, we are led to an expression (appropriate to a particular temperature T)

$$M_x = \sum_\alpha e_\alpha[x_\alpha + \tfrac{1}{4}f(x_\alpha - x_{\alpha-1})^2] , \tag{12}$$

which is manifestly invariant to translational, and other symmetry operations of the crystal. Here x_α is the x displacement from its average position of ion α and $x_{\alpha-1}$ is the corresponding displacement of the ion nearest α in the negative x direction. The constant f will be determined from experiment and is actually a component of the f tensor in (3) which transforms like xxx.

Performing the derivative required in (1), squaring, averaging, and performing the indicated sum gives

$$\sum_\alpha \left\langle \left(\frac{\partial M_x}{\partial x_\alpha}\right)^2 \right\rangle \Big/ m_\alpha = \sum_\alpha e^2[(1+f\,\delta R)^2 + \tfrac{1}{4}f^2\langle(x_{\alpha+1} - x_{\alpha-1})^2\rangle]/m_\alpha , \tag{13}$$

where $\delta R(T)$ is the displacement, if any, of the average nearest-neighbor distance from the average distance at some fiducial temperature for which the original Taylor series (3) was defined. (This is just as in the Secs. II and III A preceding.) Again $e_\alpha = -e_\beta = e$.

We expect (13) to give the nonlinear moment contribution accurately (to within a few percent) for rocksalt-structure crystals, provided the indicated average over relative square displacements is done in the harmonic-crystal approximation with correct force constants. Since the data do not warrant such accuracy we will perform these averages with the following wrong force constants, and as if the ion masses were equal. Since in (13) the average of the light-ion mean-square displacements is always divided by the heavy-ion mass (and vice versa), and since the sum of averages does not change to first order in the deviation of the masses from equality (at fixed reduced mass), the equal-mass approximation should introduce only an extra few percent error. Worse will be our lattice model having only nearest-neighbor forces. After adjusting the force constant to give the correct ω_{TO}, we estimate we may have introduced a 20–30% error in the sum of averages.

For a rocksalt-structure crystal having equal ion masses ($m_\alpha = m_\beta = m$) and nearest-neighbor forces, the average in (13) is easily performed, and is[4]

$$\langle (x_{\alpha+1} - x_{\alpha-1})^2 \rangle = \frac{2\hbar a}{m\omega_0 L} \sum_n \frac{(\sin^2 2\theta_n)\coth(\gamma \sin\theta_n)}{\sin\theta_n}, \tag{14}$$

where the sum is over the integers n labeling ions spaced by a along a fiducial length L of the x axis; $\theta_n \equiv \pi a n/L$; and the temperature parameter is $\gamma \equiv \frac{1}{2}\hbar\omega_0/kT$, where ω_0, the exact transverse-optic frequency for the model, will be chosen to equal ω_{TO} of the crystal.

The sum in (14) is well represented by an integral with n as a continuous variable in the limit $L \gg a$. Changing variables in this integral to $u = \sin\theta_n$ gives for (13) used in our theorem (1)

$$\int_0^\infty d\omega\, \omega\epsilon_2(\omega) \to \frac{2\pi^2 \rho e^2}{\mu}\left((1 + f\delta R)^2 + \frac{2\hbar f^2}{\pi\mu\omega_0} I(\gamma)\right), \tag{15}$$

where the integral

$$I(\gamma) \equiv \int_0^1 du\, u(1 - u^2)^{1/2} \coth\gamma u \tag{16}$$

is plotted in Fig. 1 alongside the corresponding quantity $\frac{1}{4}\pi \coth\gamma$ which occurs in the independent-molecule-model result (11b). It is comforting that the result (15) coincides with (11) in the high-temperature limit and is less by a factor $4/(3\pi)$ in the low-temperature limit. This lowering is expected physically because the difference-band absorption on the low-frequency side of ω_{TO} vanishes at low temperature whereas the summation-band on the high-frequency side does not. The cruder "independent-molecule" model has no "acoustic branch" or difference bands, whereas the "simple-lattice" model here exhibits both difference and summation bands when either a nonlinear moment or anharmonic forces exist, bands which are similar to those in the real crystal.

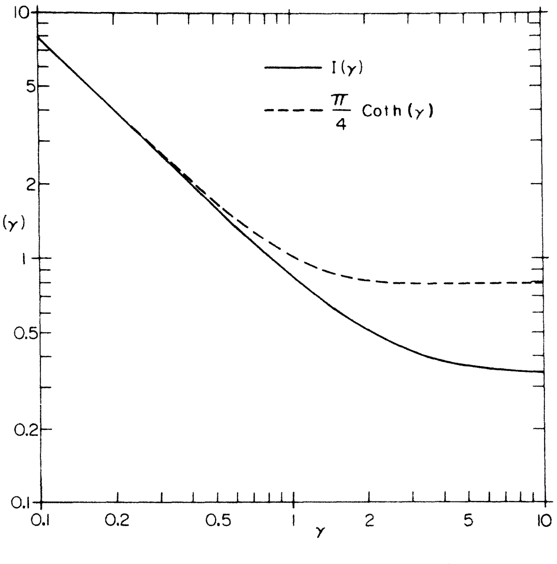

FIG. 1. Plot of the temperature-dependent function $I(\gamma)$ of Eq. (15) with the corresponding function in Eq. (11). $\gamma = \frac{1}{2}\hbar\omega_{TO}/kT$.

We now proceed to calculate the nonlinear moment parameters for LiF, applying both models to data on ϵ_2, and find similar results for both models.

IV. APPLICATION TO LITHIUM FLUORIDE

A. Summary of pertinent data

The only crystal for which $\epsilon_2(\omega)$ has been measured over a wide frequency range at several temperatures is LiF. Klier has measured its ϵ_2 by

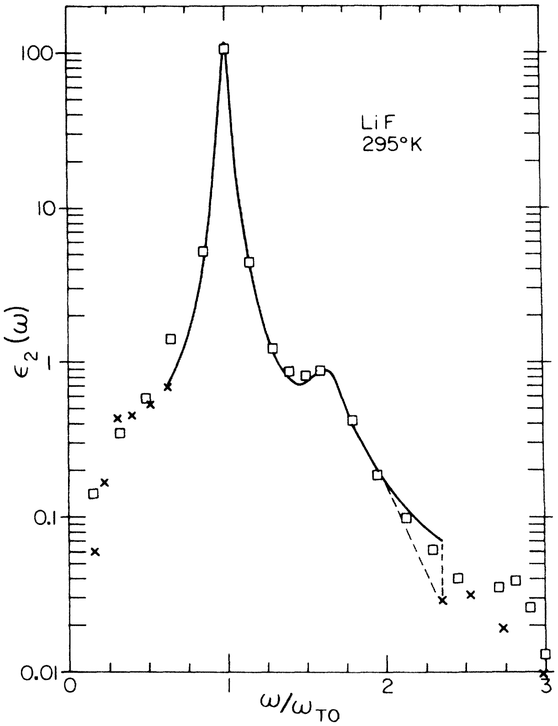

FIG. 2. Measured imaginary part of the infrared dielectric constant ϵ_2 vs frequency for LiF at 295 K. Solid line is from Ref. 7. The points × are from Ref. 5. The square points are from a Kramers-Kronig analysis made of his own unpublished data by A. Kachare (private communication). The dashed lines indicate the range of uncertainty in the ϵ_2 values which we have assumed in estimating the errors quoted in Table I.

TABLE I. Experimental values of the dielectric integral of Eq. (1), the fraction F_{mp} contributed to it by multiphonon absorption, the lattice-constant expansion, and the transverse-optical frequency, at three temperatures. Sources discussed in Sec. IV A.

T (K)	$10^{-26}\int_0^\infty d\omega\, \omega \epsilon_2(\omega)$ (sec^{-2})	F_{mp} (%)	$10^{10}\delta R$ [a] (cm)	ω_{TO} (cm^{-1})
77	365 ± 6	>3	−1.009	317.5 ± 0.8
295	360 ± 6	>6	0	307.5 ± 0.8
573	371 ± 5	16 ± 6	2.060	300 ± 1

[a] Reference 8.

transmission measurements in the ranges 8 to 14μm and 40 to 400 μm, at 300, 22, and −196°C.[5]

From their reflectance measurements on LiF in the range 7.5 to 1060 K, Jasperse *et al.*[6] obtained a two-pole analytic functional form for $\epsilon(\omega)$ at frequencies near ω_{TO}, where Klier was unable to measure transmission. Kachare *et al.* varied the parameters of this two-pole function so as to improve the agreement between calculated and observed reflectance and to establish better the probable errors in this determination of $\epsilon(\omega)$.[7] A plot of $\epsilon_2(\omega)$ at 295 K from the foregoing measurements is shown in Fig. 2. We have integrated $\omega\epsilon_2(\omega)$ from this and similar plots for 77 and 573 K to obtain the desired values for the integral of (1). These results are given in Table I along with the estimated errors obtained by performing the integrals with slightly different functions consistent with the experimental uncertainties, such as displayed in Fig. 2 and given by the analysis of Kachare *et al.*[7]

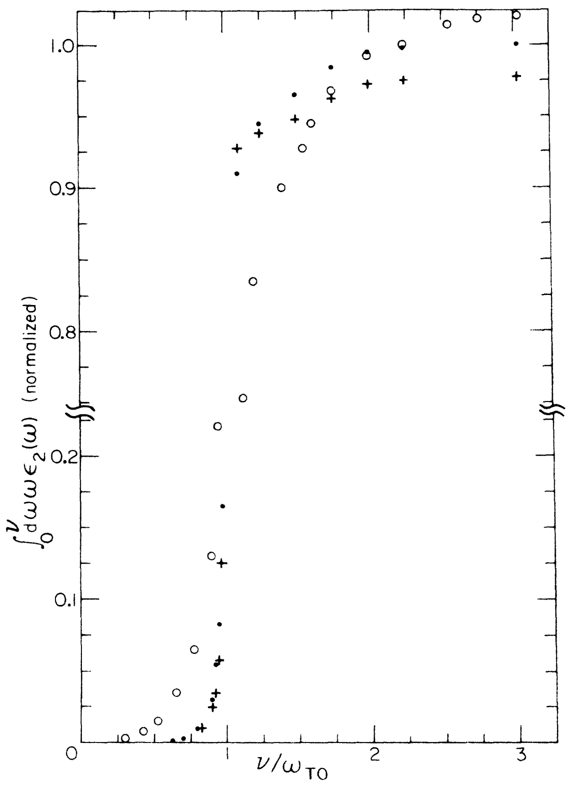

FIG. 3. Imaginary part of the dielectric constant of LiF, integrated as indicated, vs upper frequency limit of integration. The ○ represent values at 573 K from Refs. 5 and 7. The + represent values at 77 K from Ref. 6. The ● represent values at 77 K from Ref. 7.

For completeness, the data for 77 and 573 K are given in Fig. 3, but in a different form: $\int_0^\nu d\omega\, \omega\epsilon_2$ vs ν. When $\nu \gg \omega_{TO}$ this gives the desired integral in (1). In Fig. 3, the sharply rising central portion of each curve derives from one-phonon absorption (a sharp line centered at ω_{TO}) whereas the fillets are contributed by multiphonon absorption (difference and summation bands) whose origin can be either anharmonic forces or nonlinear moments. Kachare *et al.*[7] point out that reflectance data give very inaccurate values for $\epsilon_2(\omega)$ for ω near ω_{TO}, below room temperature (although they give fairly accurate values for our integral) as one can see in Fig. 3. Therefore, we believe that a significant estimate of the multiphonon contribution to ϵ_2 near ω_{TO} can only be made at high temperatures. We have done this as follows.

The full width at half-maximum γ_1 of the main one-phonon peak in ϵ_2 is 0.016 or 0.014 times ω_{TO} at 573 K according to Jasperse *et al.*[6] and Kachare *et al.*,[7] respectively. One can see from Fig. 3 that if one excludes from the integral a range of frequencies $3\gamma_1$, centered about ω_{TO}, then the remainder contributes 20 to 21.5%. If one excludes a range $6\gamma_1$, centered about ω_{TO}, then the remaind-

TABLE II. Results of independent-molecule model. (a) Nonlinear moment parameter f and Born effective charge e (in units of the electronic charge e_0). (b) Calculated fraction of $\int d\omega\, \omega\epsilon_2$ from nonlinear moment and its ratio to the total multiphonon contribution of Table I.

(a)

Data T (K)	f (Å^{-1})	e/e_0
573, 295	1.1 ± 0.5	1.03 ± 0.02
573, 77	0.8 ± 0.4	1.05 ± 0.01
295, 77	0.6 ± 0.6	1.044 ± 0.005
all	0.9 ± 0.3	1.04 ± 0.01

(b)

T (K)	$F^{(1)}_{NLM}$ (%)	$F^{(1)}_{NLM}/F_{mp}$
77	1.0 ± 0.6	<0.5
295	1.5 ± 1	<0.4
573	2.6 ± 1.5	0.23 ± 0.18

er contributes 10 to 11.5% of the integral. Therefore, we feel that the total multiphonon fraction F_{mp} of the integral in (1) may be safely said to be in the range $16 \pm 6\%$ as listed in Table I.

Although $\epsilon_2(\omega)$ is uncertain near ω_{TO} at 293 and 77 K, the reflectance data clearly show a bump near $1.6\omega_{\text{TO}}$ about whose area and central frequency both Refs. 6 and 7 agree well. Klier's absorpiton data in the far wings give a further unambiguous contribution of ~2 and 0.5% at 273 and 77 K, respectively. When added to the above reflectance bumps, these data give the limits on the multiphonon fraction F_{mp} listed in Table I.

B. Determination of nonlinear moment parameter f

In order to determine what part of the multiphonon contribution arises from a nonlinear dipole moment, we use the data of Table I either in Eqs. (10) and (11) or (15) to determine the nonlinear moment parameter f in each of the two lattice models. The last term in these equations represents the nonlinear moment contribution to the integral. Data at any two temperatures give two simultaneous equations for f and for e (the "Born" effective charge). Once a convenient set of average ionic positions is chosen (by choosing a fiducial temperature) about which to write the Taylor series (3), then data from any pair of temperatures should yield the same pair of values for f and e. We now verify this by using the three data sets at (77, 295 K), (295, 573 K), and (573, 77 K), respectively, in each of our model formulas. In these we take the reduced mass μ to be 8.44×10^{-24} g, and the density of molecules at 295 K to be 6.125×10^{22} cm^{-3}.[8] From the derived values of f, each model predicts what part of the multiphonon contribution to (1) arises from the nonlinear moment. The results are as follows.

Independent-molecule model. The nonlinear moment parameter f of (10) and (11) as derived from three sets of data is given in Table II(a) along with the corresponding values of the effective charge e. The higher-temperature data give the most accurate estimates for f because multiphonon absorption is more prominent at higher temperatures. The value 0.9 ± 0.3 Å^{-1} for f as listed is consistent with all estimates with this model.

The fraction $F^{(1)}_{\text{NLM}}$ of the integral over $\epsilon_2(\omega)$ in (10) and (11) contributed by the nonlinear moment term of this first model is seen from these equations to be

$$F^{(1)}_{\text{NLM}} = \left(1 + \frac{(1 + f\delta R)^2 2\mu\,\omega_{\text{TO}}}{f^2 \hbar \coth\gamma}\right)^{-1}. \tag{17}$$

Using the value of f derived in Table II(a) in (17) gives the values of this fraction at the different temperatures in Table II(b). These are compared there with the total observed multiphonon-absorption contributions listed in Table I. According to this first model, the nonlinear moment contributes to a minor fraction of the multiphonon absorption.

Simple-cubic-lattice model. We have calculated the nonlinear moment parameter f of the more accurate lattice model of Sec. III B above by using three sets of temperature data in Eq. (11). The results of this are given in Table III(a) along with the corresponding values of the Born effective charge e. It is comforting that these parameters turn out to have essentially the same values as they did for their counterparts in the first model.

From (15) the fractions $F^{(2)}_{\text{NLM}}$ of the nonlinear moment contribution to the integral of (1) are

$$F^{(2)}_{\text{NLM}} = \left(1 + \frac{\pi(1 + f\delta R)^2 \mu\,\omega_{\text{TO}}}{2\hbar f^2 I(\gamma)}\right)^{-1} \tag{18}$$

as a function of temperature. Using $f = 0.9 \pm 0.3$ Å^{-1} in (18) gives the fractional nonlinear moment contributions listed in Table III(b) at various temperatures. The results are essentially the same as for the first model at 295 and 573 K. However, they give about half the fraction at 77 K. We already noted that this was to be expected at lower temperatures where the difference-band contributions must vanish: The "independent-molecule" model exhibits no difference bands whereas this second "simple-cubic-lattice" model does.

In summary, we have developed an experimental method for determining the absolute contributions of (a) the anharmonic forces, and (b) the nonlinear electric dipole moment of a polar crystal to its absorption of infrared radiation by multiphonon processes. The method makes no assumption about

TABLE III. Results of nearest-neighbor-moment model. (a) and (b): quantities as in Table II.

(a)

Data T (K)	f (Å^{-1})	e/e_0
573, 295	1.1 ± 0.4	1.034 ± 0.015
573, 77	0.8 ± 0.3	1.049 ± 0.007
295, 77	0.6 ± 0.3	1.044 ± 0.004
all	0.9 ± 0.3	1.04 ± 0.01

(b)

T (K)	$F^{(2)}_{\text{NLM}}$ (%)	$F^{(2)}_{\text{NLM}}/F_{\text{mp}}$
77	0.5 ± 0.4	<0.3
295	1.3 ± 1	<0.4
573	2.5 ± 1.5	0.23 ± 0.18

the nature of the anharmonic forces, but requires a model of the nonlinear moment. We developed two models for the nonlinear moment in rocksalt-structure crystals and found that they lead to the same qualitative results for the multiphonon mechanisms. Applying the method to LiF (the only crystal for which the required data exist) we find that its nonlinear moment contributes a minor fraction of a certain average of its multiphonon absorption, and we determine parameters which can be used for other multiphonon calculations.

APPENDIX

According to a well-known quantum-mechanical formula (in esu),[9]

$$\epsilon_2(\omega) = 4\pi^2 V^{-1}\sum_{m,n}(P_m - P_n) \times |\langle m|M_x|n\rangle|^2 \delta(\hbar\omega - E_n + E_m), \qquad \text{(A1)}$$

where P_m is the probability of the material inside V being in state $|m\rangle$ with energy E_m. Integrating (A1) by $\omega\, d\omega$ from $-\infty$ to ∞ replaces the δ function in (A1) by $(E_n - E_m)/\hbar$. Then the P_n terms give the same result as do the P_m, and may be dropped if the latter are doubled. Next, use the identity

$$\sum_n (E_m - E_n)|\langle m|M_x|n\rangle|^2 \equiv \tfrac{1}{2}\langle m|[[H, M_x], M_x]|m\rangle, \qquad \text{(A2)}$$

and then evaluate the commutator using

$$H = \frac{1}{2}\sum_{i\alpha} p_{i\alpha}^2/m_\alpha + U. \qquad \text{(A3)}$$

Since both the full lattice potential energy U and M_x are functions of the ion positions only, U does not contribute to the commutator. Using the commutator identity

$$[M_x, p_{i\alpha}] \equiv i\hbar \frac{\partial M_x}{\partial x_{i\alpha}} \qquad \text{(A4)}$$

in (A2) leads then directly to the desired sum rule, Eq. (1).

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[*] Research sponsored by the Defense Advanced Research Projects Agency under Contract No. F19 628-72-C-0275 monitored by Air Force Cambridge Research Labs.

[1] The best-known argument for neglecting the anharmonic moment in alkali-halide crystals is that of P. Keating and G. Rupprecht, Phys. Rev. 138, A866 (1965).

[2] There exist a number of theoretical arguments that one, or the other, or both, mechanisms are important in III-V compounds. See, for example, (a) D. A. Kleinman, Phys. Rev. 118, 118 (1960); (b) D. A. Kleinman and W. G. Spitzer, Phys. Rev. 118, 160 (1960); (c) R. Geick, Phys. Rev. 138, A1495 (1965); (d) C. Flytzanis, Phys. Rev. Lett. 29, 772 (1972). For example, the most recent of these, (d), argues that the contributions of the two mechanisms to microwave harmonic generation are of opposite sign, and therefore measurement of the sign of the total contribution determines which contribution is the larger. The theory of the sign of the nonlinear moment's contribution is, however, uncertain.

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