Then Eq. (4.3) may be written

$$\frac{1}{L}=\frac{4}{\pi^{1/2}}R\left(\frac{\epsilon_s-\epsilon_\infty}{\epsilon_\infty^{1/2}}\right)f\left(\frac{\omega_0}{\omega}\right)^2\frac{\omega_T}{c}\ , \qquad (4.5)$$

where $\epsilon_s=\epsilon_\infty+4\pi n q_0^2/m_0\omega_0^2$ is the static dielectric constant of the host.

For the purposes of providing a crude estimate of the sensitivity of the absorption coefficient at 10.6 μ to the presence of these anomalous impurities, we set R and $(\epsilon_s-\epsilon_\infty)/\epsilon_\infty^{1/2}$ equal to unity, and suppose $\omega/\omega_0\sim 7$ and $\omega_T=20\ \text{cm}^{-1}$. We then find

$$1/L\approx 5f(\text{cm}^{-1})\ , \qquad (4.6)$$

where f is the impurity concentration.

The quantitative estimate of L displayed in Eq. (4.6) must be regarded as extremely crude, because the model is highly oversimplified. It does suggest that near 10.6 μ, the absorption coefficient of the crystal may be quite sensitive to small concentrations of Li, Ag, Cu, or other impurities which give rise to impurity-induced resonance modes with frequency very much lower than expected on mass defect considerations. It would be extremely interesting to measure the effect on the absorption coefficient of doping KCl with Li, with concentrations in the range of 0.1 at.% to test this conjecture.

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Raman Scattering in Small Crystals

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The Raman scattering of a powder composed of small crystals of a noncentrosymmetric ionic material is considered using the Nyquist-theorem approach of Barker and Loudon. For modes that are both Raman and infrared active, the splitting of the transverse- and longitudinal-phonon frequencies is determined by the local electric field. This local field depends on the shape of the particles and on the powder density. The relative contribution to the Raman scattering from macroscopic electric field fluctuations and from atomic displacement fluctuations is also dependent on the powder density. This effect yields an antiresonance in the Raman intensity scattered by longitudinal phonons.

I. INTRODUCTION

It has been established experimentally that the frequencies of infrared-active modes of vibration can be dependent on the size and shape of the crystal measured.[1] If the crystal is small enough to make an electrostatic approximation, this effect can be attributed to a change in the local field in a unit cell due to the surface depolarization charge.[2] The local field influences the long-wavelength characteristic frequencies. This simplest of descriptions would be applicable to an absorption experiment performed on one crystal with dimensions on the order of 1 μm. The optical-phonon frequency in such a sample would be shape dependent and size independent. It is, of course, not convenient to make optical measurements on only one crystal of microscopic dimensions. The local field in more convenient samples, composed of many small crystals, is additionally influenced by the dipolar interaction of neighboring particles.[3,4] For such a sample, the optical-phonon frequencies would be shape and powder-density dependent. If the particles composing the powder are larger than the wavelength of light at the phonon frequency, then the optical-phonon frequency is size dependent as well as shape and density dependent.[1]

It should be possible to measure, also with Raman-scattering techniques, similar size-shape-density effects on phonons that are both Raman and infrared active. Such measurements should have several advantages over the infrared-absorption measurements. Firstly, one can observe both the shifted transverse and longitudinal optical modes in noncentrosymmetric crystals. In addition, we will show that the relative contribution to the Raman scattering from macroscopic electric field fluctuations and from atomic-displacement fluctuations can be varied by changing the density of a powder sample. These two contributions can be written in the form[5]

$$P(\omega_s) = [d_E E(\omega_{\text{ir}}) + d_Q Q(\omega_{\text{ir}})] E(\omega_l) \ , \qquad (1)$$

where $P(\omega_s)$ is the ω_s Fourier component of a dipole moment induced by the laser field $E(\omega_l)$ which is modulated by the atomic-displacement coordinate Q vibrating at frequency ω_{ir} and its associated electric field $E(\omega_{\text{ir}})$. We will show that Raman scattering measurements on powder samples should allow the relative sign and magnitude of the d coefficients to be determined.

Raman scattering measurements on powders also present several difficulties. However, Rayleigh scattering does not appear to be one of them. Although the Rayleigh background may be as high as several thousand counts per second, the Raman signal is also enhanced in powder. This increase in signal is due to inelastic scattering occurring only after many elastic scatterings have occurred. One might say that the effective volume is increased in a powder sample. In fact, if the material is absorbing, a powder sample may give a better signal-to-noise ratio than a bulk sample. One real disadvantage of using powders is that only back-scattering experiments can be made conveniently. This geometry is necessitated by the large scattering losses. In addition, one loses all polarization information owing to the random orientation of the small crystals composing the powder. Another disadvantage is that the size of the crystals should be much smaller than 2π divided by the momentum transferred in the scattering process. In practice, this means that the particles should be appreciably smaller than 1000 Å, that is, more than one order of magnitude smaller than particles appropriate for a simple interpretation of infrared-absorption data. It is often difficult to prepare samples of such small particles.

Two experiments have been reported which claim to have seen a shift in the Raman lines of small crystals. Nair and Walker[6] have reported the Raman scattering from the mixed crystal system $\text{KBr}_x\text{I}_{1-x}$. For a certain range of x this system consists of small crystals of three different phases. They interpret one of their lines as due to depolarization-field-shifted Brillouin-zone-boundary modes. However, it seems physically unrealistic to expect a uniform depolarization field to change the frequency of a short-wavelength mode. Scott and Damen[7] have reported experimental results on a simpler system. They have observed Raman scattering from CdS films deposited onto glass. These films were found to be composed of small crystallites. Raman scattering was observed at a frequency shifted by the crystallite depolarization field. However, they found that they could explain their shift quantitatively only if the crystallites were assumed to be long, thin cylinders.

In this paper, we formulate a model for Raman scattering in powders which will help interpret experiments of this type. The model includes interaction between the particles in the powder. We will see that this interaction greatly influences not only the frequencies of the Raman lines but also the relative intensities. In the model used each small crystal is described completely by a frequency-dependent complex dielectric function. The crystal is assumed to be able to support a polarization wave but its atomicity is in other respects ignored. We will make the further assumption that the only mode with appreciable Raman activity is the mode with uniform polarization. This assumption can be shown to be valid if the particles are small enough. For an isolated sphere it has no meaning to characterize the mode with uniform polarization as being either transverse or longitudinal. The modes which would normally be called transverse or longitudinal are identical. However, a powder composed of interacting particles can support plane-wave-like modes that have either transverse of longitudinal character. More specifically, the powder layer behaves optically as a homogeneous isotropic medium.

II. FORMULATION

According to the classical theory of radiation, the energy flux from an oscillating dipole in a direction perpendicular to the dipole is

$$I(\omega_s) = \frac{v^2 n_s}{2\pi c^3} \, \frac{\omega_s^4}{R^2} \, \langle P^2(\omega_s) \rangle \ . \qquad (2)$$

Here, $\langle P^2(\omega_s)\rangle$ is the ω_s Fourier component of the mean-square fluctuations of the dipole moment per unit volume. The index of refraction at ω_s has been denoted by n_s, the speed of light by c, the distance to the dipole by R, and the volume of the sample by v. As we have already indicated in Eq. (1), the dipole moment has two contributions. A similar separation may be made in writing an expression for the fluctuations in the dipole moment. Both fluctuations in the macroscopic electric field $\langle E^2(\omega_{ir})\rangle$ and fluctuations in the atomic displacements $\langle Q^2(\omega_{ir})\rangle$ result in Raman scattering in the presence of an intense laser field $E(\omega_l)$. In addition, a correlation term proportional to $\langle EQ(\omega_{ir})\rangle$ must also be included:

$$\langle P^2(\omega_s)\rangle = |E(\omega_l)|^2[d_E^2\langle E^2(\omega_{ir})\rangle + 2d_E d_Q\langle EQ(\omega_{ir})\rangle + d_Q^2\langle Q^2(\omega_{ir})\rangle] \ . \qquad (3)$$

This expression is particularly useful if d_E and d_Q are real and frequency independent. Such a simplification can be made only when all frequencies are far from electronic transitions.

A. Nyquist's Theorem

Barker and Loudon[8] have recently developed a technique for calculating the frequency dependence of the fluctuations in Eq. (3) in terms of a quantum-mechanical Nyquist theorem. More recently, this technique has been presented in a more convenient matrix form by Hon and Faust.[9] According to this method two pairs of conjugate variables must be defined. The product of each pair gives the energy inside a unit cell. One pair of variables will be taken to be the macroscopic electric field E and an external driving polarization field divided by the number of unit cells per unit volume, P_{free}/fN. Here N is the number of unit cells per volume in a bulk sample. In a powder sample, however, N must be reduced by a factor f, the fraction of the total sample volume occupied by small particles. The other pair of conjugate variables consists of Q, the relative displacement of plus and minus ions in a diatomic unit cell, and F/fN, an external force per unit volume divided by the number of unit cells per unit volume. With these conjugate variables we can define a linear response matrix $\underline{T}$ defined by

$$\begin{pmatrix} E \\ Q \end{pmatrix} = \underline{T}\begin{pmatrix} P_{\text{free}}/fN \\ F/fN \end{pmatrix} \ . \qquad (4)$$

Nyquist's theorem can now be used to express the fluctuations in E and Q in terms of the response matrix $\underline{T}$. Since we are interested in the fluctuations within a unit volume, the fluctuations within a unit cell must be multiplied by fN:

$$\langle E^2(\omega)\rangle = \frac{fN\hbar}{2\pi}[n(\omega)+1]\,\text{Im}\,T_{11}(\omega) \ ,$$

$$\langle EQ(\omega)\rangle = \frac{fN\hbar}{2\pi}[n(\omega)+1]\,\text{Im}\,T_{12}(\omega) \ ,$$

$$\langle Q^2(\omega)\rangle = \frac{fN\hbar}{2\pi}[n(\omega)+1]\,\text{Im}\,T_{22}(\omega) \ . \qquad (5)$$

The familar quantum-mechanical thermal factor has been denoted by $n(\omega)$.

It is more convenient to find first the matrix elements of the inverse of $\underline{T}$ rather than $\underline{T}$ directly.

If $\underline{R} = \underline{T}^{-1}$, then Eq. (4) becomes explicitly

$$R_{11}E + R_{12}Q = P_{\text{free}} \ , \qquad (6a)$$

$$R_{12}E + R_{22}Q = F \ . \qquad (6b)$$

The procedure for a calculation is now clear. We will derive equations with the form of (6a) and (6b). The coefficients of E and Q will define a matrix $\underline{R}$. The matrix $\underline{R}$ can then be inverted to find the elements of $\underline{T}$ used in Eq. (5).

In the long-wavelength approximation, the equation of motion for an optical mode can be written in terms of local quantities defined within a unit cell. For a diatomic lattice, the appropriate equation is

$$(\omega_0^2 - \hat{\omega}^2)Q = (e_l/\mu)E_{\text{loc}} + F/fN\mu \ , \qquad (7)$$

where

$$\hat{\omega}^2 = \omega^2 - i\omega\gamma \ . \qquad (8)$$

The reduced mass has been written μ and the local ionic charge e_l. A phenomenological damping has been introduced with the term γ. The characteristic frequency in the absence of a local field E_{loc} has been denoted by ω_0. Since F was defined as a force per unit volume, the appropriate driving force per unit cell in the powder is F/fN.

The equation of motion (7) must be modified if it is to have the form of Eq. (6b). That is, the local field must be expressed in terms of the macroscopic field E and Q. The derivation of such an expression for a bulk sample has become well known.[10] However, some new approximations must be made when deriving a local field for a powder sample.

B. Local Field in a Powder

The powder is considered in some respect to be a homogeneous medium capable of sustaining the propagation of a long-wavelength optical phonon. This presents no conceptual difficulties if the powder is so dense that there are many particles per phonon wavelength and if the particles are much smaller than the wavelength. Although the particles have no short-range interaction, they do interact through their long-range dipole fields, providing the necessary coupling for phonon propagation. It is well known that in a homogeneous medium the macroscopic field of a longitudinal and a transverse phonon are given by

$$E^{l} = -4\pi P \,, \tag{9}$$

$$E^{t} = \frac{-4\pi P}{1 - c^2 q^2/\omega^2} \,. \tag{10}$$

In addition to this macroscopic electric field, the local field will have three other contributions. Firstly, there is the usual Lorentz $\frac{4}{3}\pi P$ term. Secondly, there is a depolarization field which is dependent on the shape of the particle. This term is normally written $-4\pi g P$, where g is the so-called depolarization factor. An ellipsoid will, in general, be defined by three depolarization factors, one for each principal axis. However, to simplify the following algebra, we will assume the powder to be composed of oriented ellipsoids. Therefore, the depolarization field in a properly oriented sample can be defined by just one g. The local field has one additional contribution which arises from the interaction of the particles. This term will be chosen so that for f equal to 1 the local field of the powder equals the local field in the bulk material. An additional requirement will be that for f equal to 0, the local field of the powder equals the local field of a single isolated ellipsoid. The interaction term which satisfies these requirements is $4\pi g P^{\text{av}}$. P^{av} is defined as

$$P^{\text{av}} = f P \,, \tag{11}$$

where P is the polarization inside one particle. The local field can now be written as the sum of the four terms we have described:

$$E_{\text{loc}}^{l,t} = E^{l,t} + 4\pi g P^{\text{av}} - 4\pi g P + \tfrac{4}{3}\pi P \,, \tag{12}$$

A more convenient form is

$$E_{\text{loc}} = E + \tfrac{4}{3}\pi\beta P^{\text{av}} \,, \tag{13}$$

where

$$\beta = 3g + (1 - 3g)/f \,. \tag{14}$$

Here, we have suppressed the superscripts distinguishing the transverse and longitudinal phonons. The expression for the local field can be further reduced by separating the polarization into a lattice contribution and an electronic contribution. Such a separation may be made either in terms of local quantities[11,12]

$$P^{\text{av}} = fP = fNe_l Q + fN\alpha_\infty E_{\text{loc}} \tag{15}$$

or in terms of macroscopic quantities

$$P^{\text{av}} = fP = fNe_{\text{av}} Q + \frac{\epsilon_\infty^{\text{av}} - 1}{4\pi} E \,. \tag{16}$$

The local effective charge e_l and the unit cell polarizability α_∞ have the standard definitions. However, the average effective charge e_{av} and the average electronic dielectric constant must be defined to characterize a powder sample. Comparing Eqs. (15) and (16) and using the Clausius-Mossotti relation and Eq. (13), we obtain

$$e_{\text{av}} = \frac{e_l}{1 + f\beta(\epsilon_\infty - 1)/(\epsilon_\infty + 2)} \tag{17}$$

and

$$\epsilon_\infty^{\text{av}} - 1 = \frac{3f(\epsilon_\infty - 1)}{\epsilon_\infty + 2 - f\beta(\epsilon_\infty - 1)} \,. \tag{18}$$

Note that for f equal to 1, Eq. (17) reduces to the Szigeti effective-charge relation. According to Eq. (18), for f equal to 1, $\epsilon_\infty^{\text{av}}$ is equal to ϵ_∞. That is, the limiting values of both equations are correct.

Strictly speaking, Eq. (15) together with Eq. (12) is not always valid. For a semiconductor, it is often assumed that the electronic polarization does not contribute to the Lorentz field. We could treat the case of semiconductors properly by defining yet another effective charge. However, since our results are indepedent of such considerations, we will continue with a notation that is strictly valid only for insulators.

C. $\underline{R}$ Matrix

Using Eqs. (13) and (16), the local field can be expressed in terms of Q and E. Substituting such an expression into the equation of motion (7) and combining terms linear in Q,

$$(\omega_{ST}^2 - \hat{\omega}^2) Q = \frac{e_{\text{av}}}{\mu} E + \frac{F}{fN\mu} \,. \tag{19}$$

This equation has a characteristic frequency ω_{ST} which is related to ω_0 by the expression

$$\omega_{ST}^2 = \omega_0^2 \, \frac{\epsilon_\infty^{\text{av}} - 1 + 3/\beta}{\epsilon_0^{\text{av}} - 1 + 3/\beta} \,. \tag{20}$$

Equation (19) has the form of Eq. (6b). The coefficients R_{12} and R_{22} can immediately be seen to be

$$R_{12} = -fNe_{\text{av}} \,, \tag{21}$$

$$R_{22} = fN\mu(\omega_{ST}^2 - \hat{\omega}^2) \,. \tag{22}$$

An equation with the same form as Eq. (5a) can be derived from the general requirements of Maxwell's equations on transverse and longitudinal waves. For a longitudinal wave, according to Eq. (9),

$$E^{l} = -4\pi P_{\text{tot}} = -4\pi(P^{\text{av}} + P_{\text{free}}) \,. \tag{23}$$

Using Eq. (16) to express P^{av} in terms of E and Q, we arrive at an equation with the appropriate form:

$$-(\epsilon_\infty^{\text{av}}/4\pi)E - fNe_{\text{av}} Q = P_{\text{free}} \,. \tag{24}$$

This allows the remaining element of R to be defined for a longitudinal wave:

$$R_{11}^{\text{long}} = -\epsilon_\infty^{\text{av}}/4\pi \,. \tag{25}$$

According to Eq. (10), for a transverse wave,

$$(c^2q^2/\omega^2 - 1)E^t = 4\pi P_{\text{tot}} = 4\pi(P^{\text{av}} + P_{\text{free}}) \tag{26}$$

or, using Eq. (16),

$$(1/4\pi)(c^2q^2/\omega^2 - \epsilon_\infty^{\text{av}})E^t - fNe_{\text{av}}Q = P_{\text{free}} \; . \tag{27}$$

Since this equation has the form of Eq. (6a), the coefficient of E^t defines R_{11} for a transverse wave:

$$R_{11}^{\text{tran}} = \frac{1}{4\pi}\left(\frac{c^2q^2}{\omega^2} - \epsilon_\infty^{\text{av}}\right) \; . \tag{28}$$

As we have used an electrostatic approximation in defining the local field, for consistency c should here go to infinity:

$$R_{11}^{\text{tran}} \to \infty \; . \tag{29}$$

D. Fluctuations and Raman Scattering

It is an easy matter to invert the $\underline{R}$ matrix defined by Eqs. (21), (22), (25), and (29) in order to find the elements of the response matrix $\underline{T}$. Then using Nyquist's theorem, Eq. (5), the fluctuation spectra follow immediately. The results can be summarized as follows: For transverse waves,

$$\langle E^2(\omega)\rangle = 0 \; , \tag{30}$$

$$\langle Q^2(\omega)\rangle = \frac{\hbar}{2\pi\mu}\,[n(\omega)+1]\,\frac{\omega\gamma}{(\omega_{ST}^2 - \omega^2)^2 + \omega^2\gamma^2} \; , \tag{31}$$

$$\langle EQ(\omega)\rangle = 0 \; . \tag{32}$$

For longitudinal waves,

$$\langle E^2(\omega)\rangle = \frac{2fN\hbar}{\epsilon_\infty^{\text{av}}}\,[n(\omega)+1]\,\frac{(\omega_{SL}^2 - \omega_{ST}^2)\omega\gamma}{(\omega_{SL}^2 - \omega^2)^2 + \omega^2\gamma^2} \; , \tag{33}$$

$$\langle Q^2(\omega)\rangle = \frac{\hbar}{2\pi\mu}\,[n(\omega)+1]\,\frac{\omega\gamma}{(\omega_{SL}^2 - \omega^2)^2 + \omega^2\gamma^2} \; , \tag{34}$$

$$\langle EQ(\omega)\rangle = -\left(\frac{fN}{\mu\pi\epsilon_\infty^{\text{av}}}\right)^{1/2}\hbar[n(\omega)+1] \times \frac{(\omega_{SL}^2 - \omega_{ST}^2)^{1/2}\omega\gamma}{(\omega_{SL}^2 - \omega^2)^2 + \omega^2\gamma^2} \; , \tag{35}$$

where

$$\omega_{SL}^2/\omega_{ST}^2 = \epsilon_0^{\text{av}}/\epsilon_\infty^{\text{av}} \; , \tag{36}$$

and ϵ_0^{av} is defined by Eq. (18) with ϵ_∞ everywhere replaced by ϵ_0. It is useful to discuss these expressions in two limiting cases. For f approaching zero, the powder sample behaves as one isolated particle; that is, the expressions for the transverse fluctuations become identical to the expressions for the longitudinal fluctuations. In particular, $\langle E^2\rangle$ and $\langle EQ\rangle$ are zero for both polarizations and ω_{ST} and ω_{SL} are equal. For f approaching the value 1, the sample behaves as the bulk material. In particular, the poles ω_{ST} and ω_{SL} in the expression for the fluctuations approach the bulk values ω_T and ω_L. The dependence of ω_{ST} and ω_{SL} on f is evaluated from Eqs. (20) and (36) and is displayed in Fig. 1 for parameters appropriate to CdS. A set of curves is shown for each of three different shape factors; g equal to $\frac{1}{3}$ corresponds to a sphere, g equal to $\frac{1}{2}$ is the appropriate shape factor along an axis perpendicular to an infinite needle, and g equal to $\frac{1}{20}$, along an axis parallel to a long but finite needle. It should be possible to compare these calculated values with the experiment of Scott and Damen.[7] The value of f for the polycrystalline thin films used in their experiments is not reported, but it should be at least 0.9. For such large values of f, ω_{SL} is almost independent of shape factor and has a value approximately 0.3% below ω_L. The experimental value of ω_{SL}, however, is about 3% below ω_L. Only if the film used in this experiment was extremely rough or porous could the experimental result be interpreted according to our model as a depolarization-field effect. The discrepancy between the experiment and our calculation is probably due to the fact that we have used a continuum model which neglects microscopic effects such as domain boundaries. Microscopic effects may be important in high-density samples where the depolarization-field effects are small. Measurements using a low-density powder would provide a better test of our model.

It is well known that interference often occurs between Raman scattering from electric field

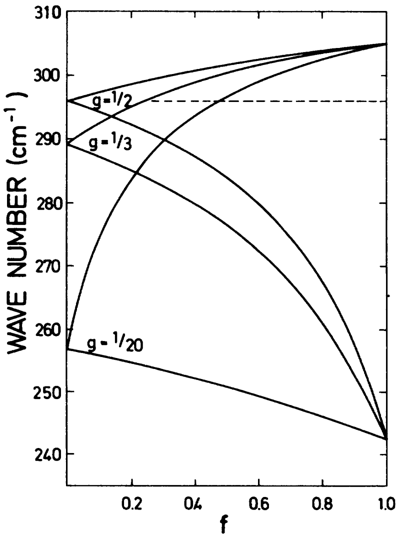

FIG. 1. Longitudinal phonon frequencies (upper branch) and transverse phonon frequencies (lower branch) of a powder as a function of the fraction f of the volume occupied by particles. The parameters are chosen to represent CdS for three different particle shape factors g. The dotted line indicates the frequency observed by Scott and Damen (Ref. 7).

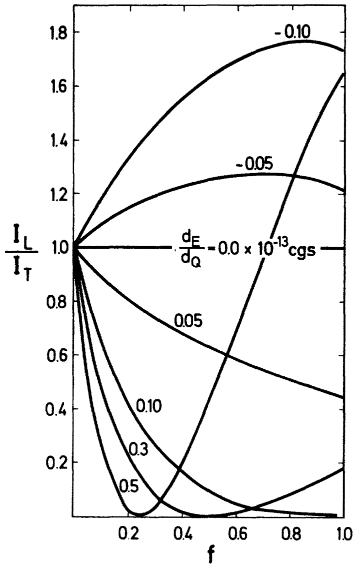

FIG. 2. Ratio of the integrated Raman intensity of a longitudinal phonon line to the corresponding intensity for a transverse phonon as a function of the fraction f of the sample volume occupied by particles. The parameters are chosen to represent CdS for several values of d_E/d_Q.

fluctuations and from atomic-displacement fluctuations.[5] The fact that the electric field fluctuations of a longitudinal wave are f dependent while the atomic-displacement fluctuations are independent of f indicates that an exact cancellation should sometimes be possible. In order to examine this effect more carefully, it is useful to write down an expression for the ratio of the integrated scattered intensity from a longitudinal wave to the corresponding intensity from a transverse wave. For the case of small damping, this ratio has the simple form

$$\frac{\int I_{\text{long}}(\omega_s)\,d\omega_s}{\int I_{\text{tran}}(\omega_s)\,d\omega_s}=\left(\frac{\omega_l-\omega_{SL}}{\omega_l-\omega_{ST}}\right)^4\frac{\omega_{ST}}{\omega_{SL}}$$

$$\times\left\{\left(\frac{4\pi f N\mu}{\epsilon_\infty^{\text{av}}}\right)^{1/2}\frac{d_E}{d_Q}\right.$$

$$\left.\times(\omega_{SL}^2-\omega_{ST}^2)^{1/2}-1\right\}^2 . \qquad (37)$$

This ratio is plotted in Fig. 2 as a function of f for several values of d_E/d_Q. Note that for a certain range of values of d_E/d_Q, the intensity of the scattering from a longitudinal wave should have an antiresonance as f is varied through a realistic range of 0.1 to 1.0.

Scott *et al.*[13] have determined d_E/d_Q to be approximately -0.2×10^{-13} (in cgs units) for CdS. This value indicates that the intensity of the transverse phonon scattering should be relatively weak in small-crystal samples with large f, in agreement with the measurement of Scott and Damen.[7]

III. CONCLUSIONS

If a powder is composed of crystals smaller than the wavelength of the incident laser light, this sample may be considered optically as a homogeneous material with well-defined transverse and longitudinal long-wavelength phonons. The frequency of these phonons will depend on the density of the powder sample and on the shape of the particles.

The relative contribution to the Raman scattering from electric field fluctuations and from atomic-displacement fluctuations is also dependent on the density of a powder sample. This leads to an antiresonance in the intensity of scattering from longitudinal phonons for certain values of sample density.

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