There are several possible experiments to test these notions; we hope they will be done in the near future.

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Light Scattering from Polaritons in Centrosymmetric Crystals

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Polaritons in centrosymmetric crystals ($SrTiO_3$ and $KTaO_3$) have been studied by small-angle light scattering induced by external electric fields. Measurements of polariton dispersion curves in $SrTiO_3$ have produced new values for oscillator strengths of the infrared-active phonons. Absence of a measurable k dependence for the linewidth of the "ferroelectric" mode bears on the discrepancy between Raman and infrared linewidth measurements previously reported.

EXPERIMENTAL observation of polaritons[1–6] by means of small-angle Raman scattering has proven useful in three ways: It provides determination of the dispersion predicted by the classical oscillator equations[7] used to fit infrared (IR) data; it reveals interference between electro-optic and displacive contributions to the nonlinear susceptibility in the reststrahlen region[8,9]; and it is helpful in distinguishing between first- and second-order Raman features.[10] Since the polariton is a mixed excitation comprised of photon and IR-active TO phonon contributions, its observation in the Raman effect has previously been limited to noncentrosymmetric crystals (in which an excitation may be simultaneously IR- and Raman-active).

In the experiments described here, polaritons in centrosymmetric crystals have been studied for the first time by light scattering through the application of electric fields to induce Raman activity in the normally IR-active modes. The materials studied were $SrTiO_3$ and $KTaO_3$, which at the temperature of our experiments (8°K) belong to space groups D_{4h}^{18} and O_h^1, respectively. Earlier electric-field-induced Raman scattering from the phonon modes in these crystals demonstrated that appreciable scattering cross sections could be induced by the field and revealed some puzzling behavior of the linewidth of the so-called "ferroelectric mode."[11,12] In addition to illuminating this question, the present work provides new values for the oscillator strengths of the IR modes which differ slightly from those obtained in IR experiments.[13]

The experimental techniques involved a combination of those described in Refs. 3 and 12. Samples were provided with Au over Cr evaporated electrodes to which were applied repetitively pulsed electric fields (of 250–2000 V across a 2.4-mm thickness of crystal) of 200-μsec duration every 3–10 msec. Linearly polarized light at 4880 Å from an argon ion laser was focused into the crystal mounted on a cold finger of a liquid-He Dewar. Light scattered through small angles was focused onto the slits of a double spectrometer. Aper-

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tures were used in the collecting optics to reduce the solid angle of scattered light accepted to an equivalent of $\pm 0.3°$ internal scattering angle. Other details relating to the imposition of electric fields and synchronous detection of scattered light appear elsewhere.[12]

Figures 1(a) and 1(b) illustrate the scattering results obtained for two of the polariton branches in $SrTiO_3$ at 8°K. Figure 1(a) shows the field-induced spectrum associated with the component of the "ferroelectric" mode polarized parallel to the applied field. The nature of this mode is discussed below. As the scattering angle is reduced the lower frequency component (the polariton) moves toward lower frequency. The phonon peak remains at its large-angle value—illustrated by the curve at 90°. The remnants of this frequency appearing in the small-angle spectra result from reflected light scattered in the near backward direction. The polariton associated with the 555-cm^{-1} TO phonon is shown in Fig. 1(b). Its behavior is qualitatively similar to the lower-frequency polariton. Again, reflected back-scattered light is responsible for the peak at 555 cm^{-1}. A third IR-active TO mode in $SrTiO_3$ appears[12] at 172 cm^{-1} and was also observed in the electric-field-induced scattering for small angles. However, as expected from previously obtained values of oscillator parameters, the 172-cm^{-1} mode exhibited no measurable dispersion with angle.

The connections between the quantities observed—polariton frequency ω and scattering angle θ—and the dielectric properties of the crystal are briefly reviewed below. Conservation of wave vector in the scattering process requires

$$K^2 = K_L^2 + K_s^2 - 2K_L K_S \cos\theta,$$

which for small θ (using $\cos\theta \approx 1 - \frac{1}{2}\theta^2$) becomes

$$K^2 \approx \omega^2 (\partial K/\partial\omega)_{\omega_L}^2 + \theta^2 \omega_L^2 n_L^2, \qquad (1)$$

where we have approximated $K_L - K_S = \omega(\partial K/\partial\omega)$, since $\omega \ll \omega_L$, ω_S, and we have taken in the second term $K_L = \omega_L n \approx K_S$. Here K, K_L, and K_S are the wave numbers of the polariton, incident photon, and Stokes scattered photon, respectively. [We shall use units of cm^{-1} for both ω and K; consequently, $c = 1$ in Eqs. (1)–(6).] ω_L is the laser frequency and n_L is the crystal's refractive index at ω_L. Using the classical oscillator model for the dielectric response, we obtain

$$\epsilon(\omega) = \frac{K^2}{\omega^2} = \epsilon_\infty + \sum_{i=1}^{m} \frac{\omega_i^2 S_i}{\omega_i^2 - \omega^2}. \qquad (2)$$

Strictly speaking, for noncubic crystals ϵ must be written in tensor form.[3] However, for $SrTiO_3$ the tetragonality is so slight that its dielectric properties are essentially those of a cubic crystal.

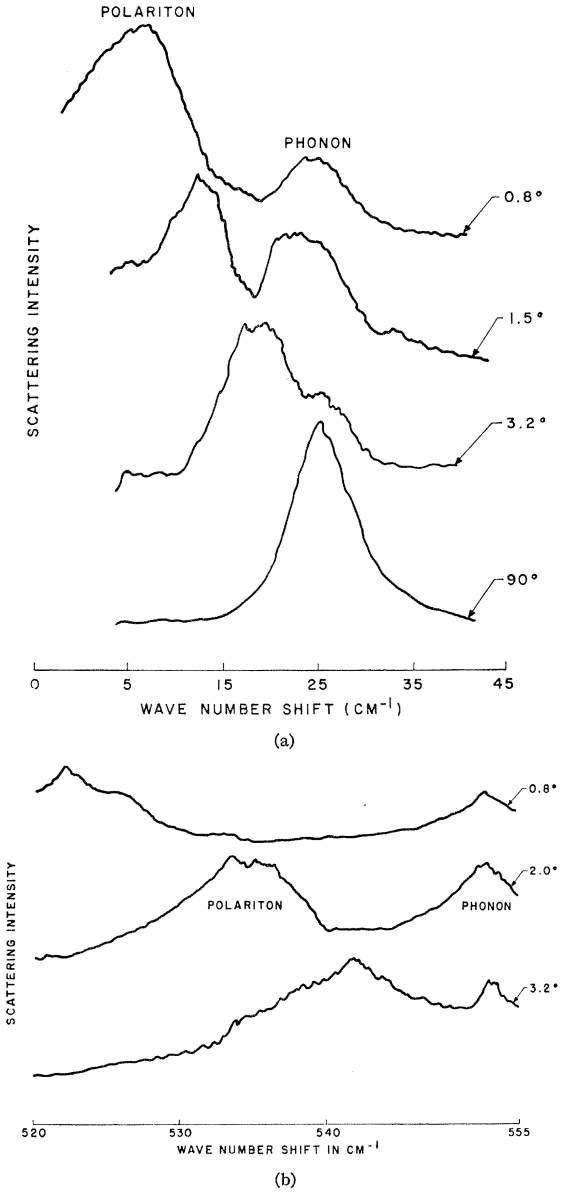
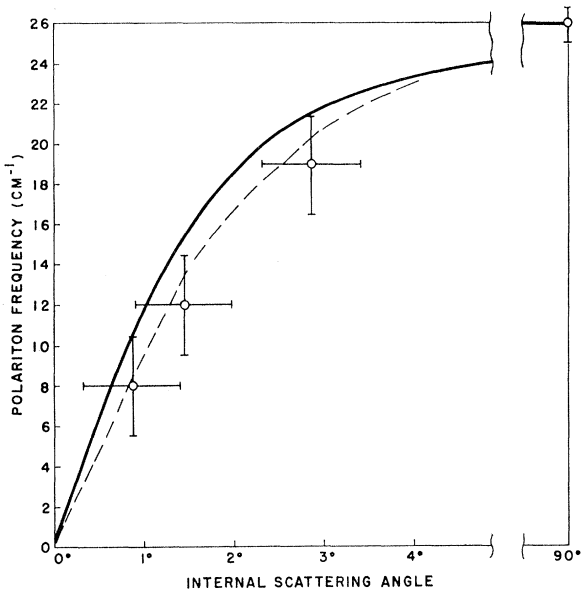


FIG. 1. (a) Electric-field-induced polariton spectrum of $SrTiO_3$ in the 0–25-cm^{-1} region. $F \sim 2.5$ kV/cm, $T = 8°$K. The phonon feature in the scattering is due to large-angle scattering, especially at $\sim 180°$, followed by reflection, and to the effect of damping (Ref. 5) neglected in Eq. (3). (b) Field-induced polariton spectrum of $SrTiO_3$ in the 550-cm^{-1} region. $E \sim 2.5$ kV/cm, $T = 8°$K.

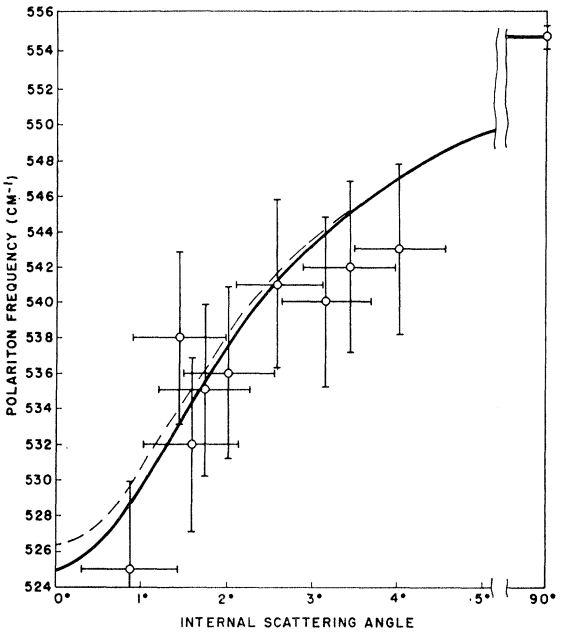
Combining (1) and (2) we get

$$\left(\frac{\partial K}{\partial\omega}\right)_{\omega_L}^2 + n_L^2\theta^2 \frac{\omega_L^2}{\omega^2} = \epsilon_\infty + \sum_{i=1}^{m} \frac{S_i\omega_i^2}{\omega_i^2 - \omega^2}. \qquad (3)$$

For ordinary dielectric materials, Eq. (3) as it stands provides a good description of polariton behavior.[3] However, in the paraelectric crystals such as $SrTiO_3$ and $KTaO_3$, the lowest-frequency TO mode dominates the dielectric behavior. This so-called "ferroelectric" mode (designated hereafter by the subscript F) is



(a)



(b)

FIG. 2. Polariton dispersions in $SrTiO_3$ at 8°K. The applied electric field is ~2.5 kV/cm. Solid curves result from numerical solutions to Eq. (6) using oscillator strengths from Barker's IR data. Dashed curves are drawn for best least-squares fit to the data obtained by varying the S_i. (a) The "ferroelectric" mode, polarized parallel to the applied field. (b) The TO phonon whose large-angle frequency is 555 cm^{-1}.

responsible for the ferroelectric phase transition in displacive ferroelectrics such as $BaTiO_3$ and exhibits striking temperature and electric field behavior.[13,14] The dominant role of the ferroelectric mode in such crystals implies

$$S_F \gg \epsilon_\infty + \sum_{i \neq F} S_i .$$

This relation in combination with the generalized Lyddane-Sachs-Teller relation[15] yields

$$\frac{\epsilon(0)}{\epsilon_\infty} = \frac{1}{\omega_{F,T0}^2(E,T)} \left(\omega_{F,L0}^2 \prod_{i \neq F} \frac{\omega_{i,L0}^2}{\omega_{i,T0}^2} \right) \approx \frac{\alpha}{\omega_{F,T0}^2(E,T)} . \quad (4)$$

(That α is temperature-independent follows the assumption that $\omega_{F,L0}$ is essentially temperature-independent in ferroelectriclike materials.[16]) Hence,

$$\omega_F^2(E,T) S_F(E,T) \approx \text{const} = G , \quad (5)$$

where we have dropped the "TO" subscripts. The polariton dispersion relation can then be written

$$\left(\frac{\partial K}{\partial \omega} \right)_{\omega_L}^2 + \frac{\omega_L^2 n_L^2}{\omega^2} \theta^2 = \epsilon_\infty + \sum_{i \neq F} \frac{S_i \omega_i^2}{\omega_i^2 - \omega^2} + \frac{G}{\omega_F^2(E,T) - \omega^2} , \quad (6)$$

so that all the field and temperature dependence is contained in $\omega_F(E,T)$. No damping constants have been included in Eq. (6), since they are known to be small[14] and therefore to have little effect upon polariton dispersion.[5]

These predictions are compared with our experimental observations on $SrTiO_3$ in Figs. 2(a) and 2(b). The solid curves show the predicted behavior of $\omega(\theta)$ for $SrTiO_3$ from Eq. (6), using the values $(\partial K/\partial \omega)_{\omega_L} = 3.1$ (where both K and ω are in cm^{-1}) and $n_L = 2.5$ taken from Bond[17]; $\omega_L = 20\,486$ cm^{-1}; the oscillator parameters $\epsilon_\infty = 5.66$, $G = 2.923 \times 10^6$ cm^{-2} [which implies $S_F(T = 8°K) = 4325$]; and the S_i's of 1.8 and 1.56 for the 172-cm^{-1} and 555-cm^{-1} TO modes, respectively, are inferred from the IR work of Barker.[13] The behavior of $\omega_F^2(E,T)$ has been explored in right-angle electric-field-induced Raman scattering.[14] While disagreement is not serious, the fit to the data of Fig. 2 can be improved by inserting slightly different values for S_i. Using $S_F = 6100 \pm 1500$ from a least-squares fit to the data, we obtain the dashed curves in Figs. 2(a) and 2(b). Thus, the polariton scattering spectrum provides the same information as an IR experiment with the increased sensitivity, in this case resulting from the fact that the light involved all lies in the visible, and that the polariton frequency was observed directly and not determined indirectly by Kramers-Kronig or other similar extrapolation.

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Also of interest with regard to the ferroelectric mode is the previously mentioned[12] discrepancy between the linewidth obtained in scattering experiments and that inferred from IR measurements. In particular, at 85°K the right-angle Raman scattering revealed a linewidth of 3 cm^{-1} for the ferroelectric mode in $SrTiO_3$, while the value obtained from IR work[13] was 61.7 cm^{-1}. Since the IR experiment is constrained to examine the polariton region and the right-angle Raman experiment examines the essentially pure phonon, the possibility arose that the large linewidth discrepancy might be connected with a strongly K-dependent linewidth for the ferroelectric mode. The spectrum in Fig. 1(a) shows clearly that this is not the case. Even at $\theta=0.8°$ the polariton linewidth (including the instrumental contribution) is only slightly larger than the phonon linewidth. This excess width can be attributed largely to the fact that a finite collection angle implies contributions from a spread of frequencies over several cm^{-1} [see Fig. 2(a)].

The low-frequency polariton spectrum of $SrTiO_3$ at low temperatures becomes much more complicated than has been discussed above when the applied electric fields exceed a few kV/cm. There are two sources of this complication. First, the component of the ferroelectric mode which is perpendicular to the applied field becomes visible in the scattered spectrum.[11] The frequencies of both components of the ferroelectric mode exhibit marked electric field dependence, so that whole families of curves twice as complicated as Fig. 1(a) should be generated for different fields. Second, two naturally Raman-active temperature-dependent phonons have recently been identified in tetragonal $SrTiO_3$.[18] (At 8°K their frequencies are 15 cm^{-1} and 48 cm^{-1}.) The electric field induces IR activity in these modes and effects resulting from electric-field-dependent oscillator strengths are expected in the polariton spectra associated with these modes. The combined effects of these complications have thus far precluded satisfactory analysis of the high-field, low-temperature polariton spectra in $SrTiO_3$.

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The second type of complication is not present in $KTaO_3$, but our samples of this material were of inferior optical quality to those of $SrTiO_3$. Thus our polariton observations in $KTaO_3$ were limited to the TO mode, whose large-angle frequency is 556 cm^{-1}. We have followed this dispersion to 540 cm^{-1} for $\theta\simeq 2°$. Better samples of $KTaO_3$ would allow completion of the polariton studies in this material, although from the low-field results in $SrTiO_3$ one already knows what to expect.

We have demonstrated clearly, however, that the technique of electric-field-induced Raman scattering combined with small-angle experiments extends the study of polariton effects to the large class of materials which possess centers of inversion. The question of the ferroelectric-mode linewidth has been clarified by the polariton experiments in $SrTiO_3$ with the resulting implication of some error in the difficult analysis of IR data. The most likely source of difficulty is multiple-phonon processes. In addition, we have shown the small-angle scattering to yield quantitative measurements of oscillator parameters previously available only from IR experiments in centrosymmetric materials. The techniques described here can, of course, be extended to explore other centrosymmetric insulators. Another area of interest is the exploration, through small-angle scattering, of polaritons whose existence (as polaritons) is induced by the electric field. An example is a Raman-active mode in a centrosymmetric crystal whose IR activity is induced by an external field. Modulation of the field would cause a modulation of the dispersion characteristics of the polariton. The low-frequency modes in $SrTiO_3$ mentioned above are less than ideal candidates for such studies because of the complications arising from the ferroelectric mode and their couplings to it.[18]

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