RAMAN SCATTERING BY POLARITONS*

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(Received 12 October 1965)

In ionic crystals transverse optical (TO) phonons and photons with nearly the same wave vector and energy are strongly coupled. The propagating state for these energies and wave vectors can no longer be described as a phonon or a photon, but is a mixture of these two elementary excitations known as a polariton.[1,2] We report in this Letter a Raman-scattering experiment in which polaritons covering a considerable range of energy are produced as well as optical phonons.

The dispersion curves for optical phonons and photons of long wavelength in GaP are shown in Fig. 1. In the absence of coupling, the dispersion curves are straight lines which cross at $q = q'$. The phonon-photon interaction removes this crossing, resulting in the well-known dispersion curves[3] given by the solid lines in Fig. 1. It is in the neighborhood of q', where the dispersion curves bend sharply, that the photon and phonon are strongly mixed and must be described as a polariton. In this experiment, the lower dispersion curve was traced out experimentally in the neighborhood of q' by varying the angle between the detected Stokes radiation and the incident laser beam.

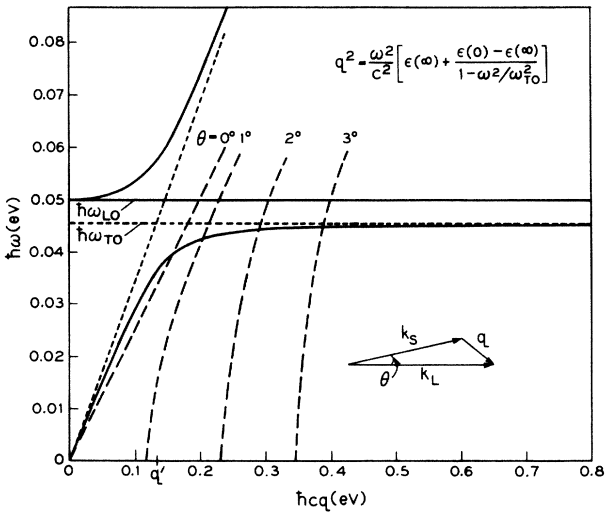

FIG. 1. The dispersion curves of the uncoupled phonons and photons are shown by the short-dashed lines, and those of the LO phonons and the polaritons by solid lines. The equation of the polariton lines is indicated. The long-dashed curves indicate the values of energy and wave vector which kinematically are possible at each angle θ. θ is defined by the vector triangle. $\vec{k}_L$ and $\vec{k}_S$ are the wave vectors of the laser light and the Stokes shifted light, respectively. q is the wave vector of the scattered polariton.

On the lower dispersion curve, as q changes from a value large compared to q' to a value small compared to q', the character of the polariton changes from that of a TO phonon to that of a photon. Similarly, the Raman-scattering event changes from a two-photon–one-phonon scattering process to a three-photon scattering process as q changes from large to small values. Classically, for all values of q, the polariton is an electromagnetic wave propagating in the crystal with a certain complex refractive index. At the surface of the crystal, it will be partially transmitted and partially reflected, as determined by Fresnel's laws.

GaP was chosen for this experiment because it is a cubic material with sharp first-order Raman lines[4] whose refractive indices in the visible[5,6] and infrared have been carefully measured.[7] The lack of inversion symmetry of GaP allows it to be both infrared active and Raman active. The vector diagram in Fig. 1 shows the scattering geometry; $\vec{k}_L$, $\vec{k}_S$, and $\vec{q}$ are the wave vectors of the incident laser photon, scattered Stokes photon, and polariton inside the GaP crystal. In the conventional Raman-scattering experiment, $\theta = 90°$, $q \approx \sqrt{2}k_L$, and the polariton is very phononlike. In our experiment, the Stokes radiation was measured at very small angles with respect to the incident beam. For θ less than three degrees (inside the crystal), the energy of the Stokes radiation becomes shifted to energies significantly below the TO energy.[8] θ was measured down to

zero degrees where the Stokes energy has been shifted by nearly twice the LO-TO energy difference. These results are compared with theory in Fig. 2 and found to be in good agreement. The theoretical dispersion curve was constructed from the infrared data of Kleinman and Spitzer.[7]

The polariton energy $\hbar\omega_q$ is determined experimentally from conservation of energy. The polariton energy is

$$\hbar\omega_q = \hbar\omega_L - \hbar\omega_S, \tag{1}$$

where $\hbar\omega_L$ and $\hbar\omega_S$ are the measured energies of the laser and Stokes radiation. Similarly, the polariton wave vector is determined experimentally from conservation of wave vector. From the vector triangle in Fig. 1,

$$q = (k_L^2 + k_S^2 - 2k_L k_S \cos\theta)^{1/2}$$

$$\approx \left[\left(\frac{\partial k}{\partial \omega}\right)^2_{\omega=\omega_L} \omega_q^2 + k_L k_S \theta^2\right]^{1/2},$$

$$k_L = n(\omega_L)\frac{\omega_L}{c},$$

$$k_S = n(\omega_S)\frac{\omega_S}{c}. \tag{2}$$

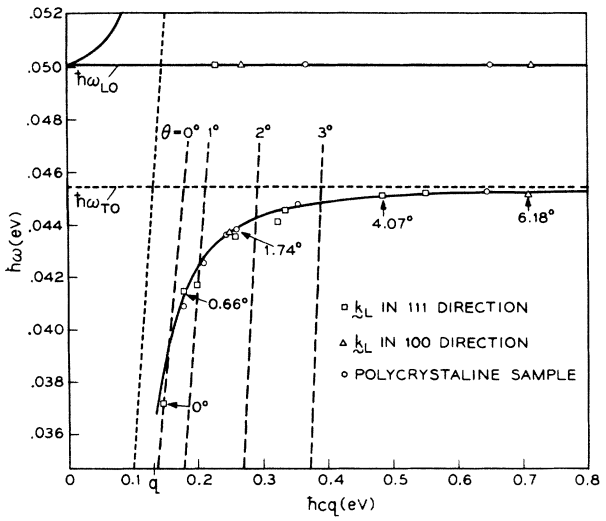

FIG. 2. A plot of the observed energies and wave vectors of the polaritons and of the LO phonons; the theoretical dispersion curves are shown by the solid lines. The dispersion curves for the uncoupled photons and phonons are shown by short-dashed lines. The values of energies and wave vectors which are kinematically possible at angle θ are shown by long-dashed lines. Some of the experimental angles θ are indicated next to the data points.

θ is the measured angle between k_L and k_S. $n(\omega)$, the refractive index of GaP, and its variation in the vicinity of the 6328Å laser light has been measured by Bond[5] and Nelson.[6]

The dashed lines of Figs. 1 and 2 indicate values of (ω, q) which could occur for 6328Å laser light for several different values of θ as determined from Eq. (2). Polaritons can be produced at the crossings of these lines with the polariton dispersion curves. For example, the polariton produced by Raman scattering at $\theta = 0°$ lies at the intersection of the polariton dispersion curve and the dashed curve labelled $\theta = 0°$ in Fig. 1. The latter curve is a straight line with the same slope as the dispersion curve for the laser photon. Polaritons lying to the right of this intersection may also be produced using values of θ greater than zero. It should be noted that the intersection of these two curves depends upon the increase in the refractive index of GaP for visible radiation, causing the dispersion curve to have a smaller slope at $\omega = \omega_L$ than at $\omega = 0$. If the laser wavelength used in this experiment had been greater than 1.5 μ, these curves would intersect only at $q = 0$; in this case, all polaritons on the lower dispersion curve would be allowed.[9]

The light source used was a 35-mW HeNe laser operating at 6328Å. The Stokes shifted light was detected photographically using a two-meter focal-length Bausch & Lomb spectrograph. The angular apertures of the incident light and the scattered light were each 0.6° inside the sample. Exposure times ranged from 30 minutes to seven hours. In order to observe the Stokes radiation at small angles, including 0°, where the Stokes radiation is collinear with the laser beam, a special filter was constructed to attenuate the laser light before it entered the spectrograph. The filter consisted of a crystalline-quartz retardation plate placed between crossed polarizers. The thickness of the plate and its orientation were chosen so that the laser light would be retarded by an even number of waves and hence not pass through the second polarizer; the Stokes radiation was retarded by one-half wave less and passed through the second polarizer. When the filter was oriented with the initial polarizer crossed to the laser polarization, the ratio of the laser energy to the Raman energy entering the spectrograph was reduced by over four orders of magnitude.

Using single crystals of GaP, we observed

Raman scattering with the laser beam in the 100 direction and in the 111 direction. Raman scattering was also observed using a polycrystalline sample.

Rough intensity measurements were made for Raman scattering on single crystals for the Stokes radiation polarized perpendicular to the polarization of the laser light. For the laser beam in the 100 direction, only the component of lattice polarization parallel to this 100 direction can be driven in first-order Raman scattering. The LO intensity will vanish for angles large compared to one degree, where $q \perp k_L, k_S$, and for small angles, where $q \parallel k_L$, k_S, the TO intensity will vanish. After coating the crystal surfaces to eliminate reflected laser beam (which produced substantial Raman back scattering at the LO energy), we were able to observe this selection rule experimentally. For the laser beam in the 111 direction, the predictions of group theory enter differently. For general wave-vector directions and polarizations, both the LO intensity and the TO intensity should be observable. It was indeed found that in the 111 direction the TO intensity was readily observable even at zero degrees.

In this experiment, the Stokes energy and the polariton energy were varied by selecting different values of the polariton momentum. In principle, because of the mixed phonon-photon character of the polariton, infrared quanta at the polariton energy could have been detected outside the crystal. Spontaneous Raman scattering of polaritons thus provides a tunable source of visible and infrared radiation, but radiation of extremely low intensity. Stimulated Raman scattering of polaritons would provide an intense, coherent, and tunable source of infrared and visible quanta.[9]

The authors would like to thank D. G. Thomas for numerous discussions, C. G. B. Garrett and S. P. S. Porto concerning infrared generation, and R. Loudon and J. A. Giordmaine for their helpful comments. We are indebted to C. J. Frosch for providing the crystals used in this experiment and to J. A. May for his technical assistance.

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*Work supported in part by the U. S. Air Force Office of Research, Air Research and Development Command.

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[8]The change in the Stokes energy with angle observed in this experiment results from changing $|\vec{q}|$, the magnitude of the polariton wave vector. This should not be confused with experiments on noncubic crystals in which the Stokes energy changes as the direction of the phonon wave vector in the crystal is varied. For a general discussion of dispersion curves of infrared active phonons in cubic and noncubic crystals, see R. Loudon, Advan. in Phys. 13, 423 (1964).

[9]R. Loudon, Proc. Phys. Soc. (London) 82, 393 (1963) discusses the kinematics of Raman scattering in the forward direction. He points out that in uniaxial crystals, Raman scattering of TO phonons is possible on both the upper and lower dispersion curves, and that infrared light would be emitted at the polariton frequency. In his discussion of cubic crystals, however, he indicated that TO forward scattering does not occur, in contrast with our results. The variation of $n(\omega)$ in the visible spectrum makes possible this forward scattering.