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ENHANCEMENT OF RAMAN CROSS SECTION IN CdS DUE TO RESONANT ABSORPTION

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We have observed marked resonant enhancement of the Raman cross section for phonons in CdS at frequencies near the absorption edge. The data, taken at 77°K, can be explained on the basis of a simplified model in which the absorption band is replaced by a single effective frequency coinciding with the band edge to within one percent. The experimental technique involved collecting Raman radiation scattered from the surface of the crystal.

Resonant Raman effect in liquids was observed by Tsenter and Bobovich[1] for excitation in the neighborhood of absorption bands. Their experimental data show that the properties of Raman scattering by molecules which have continuous electronic absorption spectra are described satisfactorily by a semiclassical theory. This effect has also been called upon by Worlock and Porto[2] as a device to increase the Raman cross section of *F* centers. We report in this Letter a striking demonstration of this phenomenon for lattice-vibration Raman effect which we believe has never been observed before.

CdS was chosen for this experiment because its absorption edge at 77°K is quite convenient for resonance with the available lines of the Ar^+ laser. The technique and experimental arrangement are quite similar to the one already described by the authors[3] and recently extended to solids.[4] Because of absorption it was necessary to make the laser beam incident on the crystal surface at a glancing angle of about 5 deg, observation being performed on the same face, and perpendicularly to the incident beam. The CdS crystal was immersed in liquid nitrogen.

Measurements of absolute cross section are difficult, particularly near resonance where the scattering volume and effective excitation intensity are not well known because of absorption. But *relative* intensity measurements between two Raman-shifted frequencies in the same crystal are a simpler matter as the mentioned difficulties are largely removed.

We chose in the present experiment the one- and two-longitudinal-optical-phonon processes at 305 and 604 cm^{-1}, respectively. The spectrum in Fig. 1 shows the one-, two-, three-, and four-phonon processes. The emissions at 909 and 1200 cm^{-1} are sufficient evidence to ascribe the 604-cm^{-1} emission to the two-phonon process. In general, the frequency shift of a two-phonon process is not exactly twice that of the one-phonon process because phonons allowed by momentum conservation to participate in the former process are restricted to a narrow range of momentum, whereas in the latter, this is not so. Two phonons with opposite propagation directions may satisfy the momentum-conservation rule in a wider range of energy. This can be verified by the wider band width of the two-phonon process. The 305-cm^{-1} longitudinal-optical-phonon process is observed for incidence parallel to the optical axis because of the strong coupling with the transverse optical phonon. The two-phonon process of 604 cm^{-1} is allowed, and for this configuration is the dominant Raman-shifted radiation away from resonance.[5] For simplicity, the frequencies of those two phonons will be called ω_0 and $2\omega_0$.

Figure 2 shows the four experimental points obtained at 77°K for the ratio of Raman cross sections or intensities at the shifted frequencies ω_0 and $2\omega_0$. The following excitation lines of the cw Ar$^+$ laser were used: 5145, 4965, 4880, and 4765 Å. It should be pointed out here that appreciable (at least one order of magnitude) increase of the 305-cm^{-1} shifted Raman radiation was observed when the excitation wavelength varied from 5145 to 4880. Corrections due to absorption, even though small (less than 20%), are included for the first three points. Here absorption data by Thomas, Hopfield, and Powell[6] were used. For the fourth point no correction is included as no absorption data are available at those wavelengths. The continuous curve in Fig. 2 is a best-fit curve that follows the empirical law

$$I_{\omega_0}/I_{2\omega_0} \sim [1+\omega_0/\Delta\omega]^2. \qquad (1)$$

For solids, first-order Raman cross sections, as calculated by Loudon,[7] are given by expressions proportional to factors of the following general form:

$$\left\{\sum_{\alpha\beta}\left[\frac{P^1_{0\beta}\Xi^2_{\beta\alpha}P^3_{\alpha 0}}{(\omega_\beta+\omega_0-\omega_i)(\omega_\alpha-\omega_i)} + \text{other similar terms}\right]\right\}^2, \qquad (2)$$

where the subscripts on the P and Ξ matrix elements refer to electron-hole pair states with energies $\hbar\omega_\alpha$ and $\hbar\omega_\beta$, and 0 refers to the ground state. The P and Ξ matrices describe the electron-radiation and electron-lattice interactions, respectively. ω_0 is the frequency of the phonon considered and ω_i is the excitation frequency. Each term has two poles, one at $\omega_i=\omega_\alpha$ which is independent of the phonon considered, and the other at $\omega_i=\omega_\beta+\omega_0$.

There are three basic processes responsible for second-order Raman scattering in crystals. Those processes are described by the self-explanatory diagrams of Fig. 3. A simple extension of Loudon's theory for the first-order Raman effect may be obtained for the second-order Raman scattering by the appropriate time-dependent perturbation theory. Process (a) leads to a sixth-order perturba-

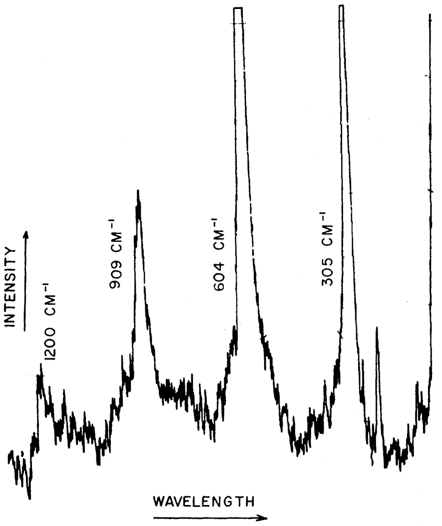

FIG. 1. Room-temperature spectrum of CdS obtained with the 4880-Å line of the Ar$^+$ laser. One can easily observe the three- and four-LO-photon processes. Absorption is here of the order of 10^4 cm^{-1}, and the energy of the incident photon is approximately 200 MeV above the absorption edge.

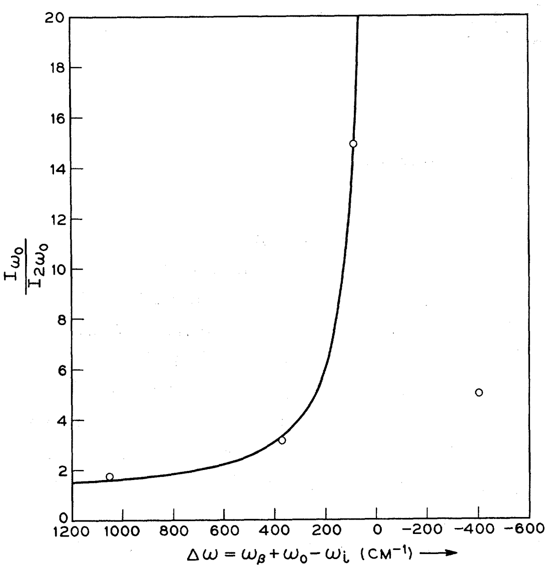

FIG. 2. Plot of $I_{\omega_0}/I_{2\omega_0}$ as a function of $\Delta\omega$. The solid curve is a best-fit theoretical curve as defined by (1). ω_i is the excitation frequency and ω_β is an effective frequency to be determined experimentally.

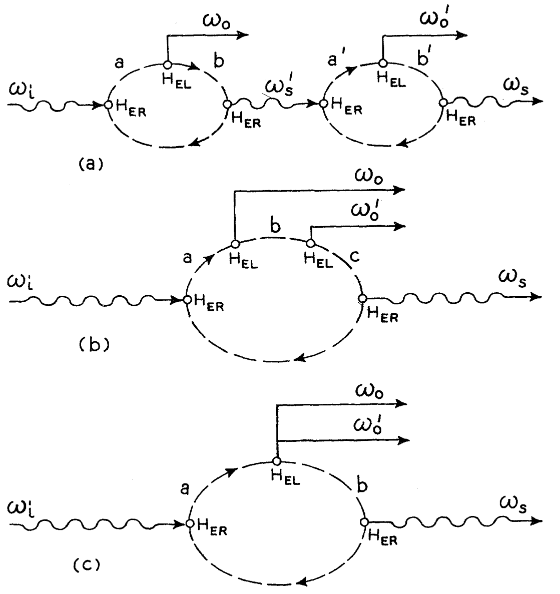

FIG. 3. Diagrams of the three possible processes responsible for the second-order Raman effect in crystals.

tion calculation in which, as expected, the Raman cross sections for overtones are roughly proportional to the square of that of the one-phonon process.[7] Process (b) leads to a fourth-order perturbation which gives Raman cross section for overtones proportional to factors of the following general form:

$$\left\{\sum_{\alpha\beta\gamma}\left[\frac{P_{0\alpha}\Xi_{\alpha\beta}\Xi_{\beta\gamma}P_{\gamma 0}}{(\omega_\alpha-\omega_i)(\omega_\beta+\omega_0-\omega_i)(\omega_\gamma+2\omega_0-\omega_i)}\right.\right.$$

$$\left.\left.+\text{other similar terms}\right]\right\}^2. \qquad (3)$$

The third process in Fig. 3 is essentially the same as the one responsible for the first-order Raman effect, and an expression similar to (2) is obtained for its Raman cross section. The main difference is that the term $(\omega_\beta+\omega_0-\omega_i)$ in the denominator is replaced by $(\omega_\beta+2\omega_0-\omega_i)$. Probably the simplest way to distinguish between those three processes is by means of their frequency dependence near resonance.

Because of difficulties in evaluating the matrix elements in (2) and (3), the experimental verification of these expressions is of course very difficult even for the simplest molecules, but a semiconductor with a high density of states at the bottom of the conduction band may furnish a simple approximation. At low temperatures, the absorption edge is so sharp that we may suppose that the electronic states which dominate the resonance process are in an energy band narrow compared with the phonon energy. Under such circumstances we may compress all the conduction-band states into one single effective ω_β, or we may suppose an equivalent number of states at a characteristic energy $\hbar\omega_\beta$. This rough approximation leads to a simple expression, and (2) may be written as

$$\sim[1/(\omega_\beta+\omega_0-\omega_i)(\omega_\beta-\omega_i)]^2. \qquad (4)$$

For processes (a) and (b), no pole would be obtained for the ratio $I_{\omega_0}/I_{2\omega_0}$, but process (c) may be compared with the empirical expression (1), if we make $\Delta\omega=\omega_\beta+\omega_0-\omega_i$. The pole obtained from the curve in Fig. 2 determines unambiguously the parameter ω_β, and the value thus obtained is 2.521 eV. This value is surprisingly close (within a few meV) to the absorption edge of CdS as reported in Ref. 6.

We have also tried to account for our observations by means of a parabolic approximation as suggested by Loudon.[8] We have found that this was not possible. This is to be expected since the absorption edge of CdS is much sharper than the one based on parabolic bands. In view of our present results we should favor process (c) in lieu of processes (a) and (b) for the two-longitudinal-optical-phonon Raman scattering.

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