QUASIRESONANT RAMAN SCATTERING FROM TlBr CRYSTALS*

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Second-order Raman-scattering spectra have been measured in TlBr single crystals as a function of exciting-light frequency at low temperatures. The results obtained indicate that as the exciting frequency approaches the first exciton peak frequency, a new resonant-scattering mechanism becomes important, as evidenced by the appearance and rapid increase of a sharp peak at twice the LO phonon frequency ($q=0$), and by the absence of such a feature in analogous spectra taken for TlCl, where only off-resonant scattering is expected to occur.

The basic reason for undertaking studies of resonant Raman scattering, apart from simple enhancement of the scattering cross section, is the possibility of determining which are the predominant interactions in the scattering process as the incident light frequency becomes close to an electronic transition, and whether and how the scattering selection rules change with respect to the ordinary off-resonance case. From both these points of view, it is interesting to study cubic crystals, where first-order processes are forbidden in the off-resonance case since every crystal site has inversion symmetry. The only scattering observed is then due to second-order processes which involve the creation and/or destruction of two phonons of wave vectors q and q' such that the selection rule $q+q'=0$ is obeyed. A different situation obtains when the incident light frequency ω_0 is suitably near to the frequency of an exciton transition, ω_{e0}. In this case the polarizability will have contributions caused by the change in the Hamiltonian of the electron-phonon system associated with the electronic transition in question.[1] This results in the appearance of narrow multiphonon peaks originating from iterations of a first-order process caused by the exciton-phonon interaction during the scattering event.[2] A theory that will be presented elsewhere indicates that this should be the case independently of the crystal symmetry.[3] The appearance of such narrow peaks in a cubic crystal would then be exclusively due to a resonance effect, without the ordinary first-order contributions which are present in noncubic crystals. In this respect it would be of particular interest to investigate possible qualitative changes in the Raman spectrum of a cubic crystal as the incident frequency approaches the fundamental absorption region, and in particular the first exciton peak. In this Letter we present the results of such an investigation.

The test system selected was TlBr. It was chosen for a variety of reasons; first and foremost because it is a body-centered cubic crystal and has a direct exciton transition at 3 eV,[4] which puts it reasonably close to the available lines of the argon laser. This exciton transition results in a narrow absorption line which has been shown to possess a fairly strong LO phonon sideband.[4] Furthermore, accurate phonon dispersion data obtained by inelastic neutron scattering are available.[5] More generally, in recent years, interest in the experimental study of thallium halides has grown, because various fundamental characteristics of these materials place them in an intermediate position between wide-band semiconductors and alkali halides. Of particular interest to us here is that the exciton in TlBr has a large radius (~70 Å) and that the hole effective mass is much larger than the electron effective mass.[4] These features indicate that the exciton-phonon interaction in TlBr is very likely of the Fröhlich type, which implies that in approaching resonance, contributions from long-wavelength LO phonons should become dominant.

We can estimate the resonant contributions to the scattering due to the first ($p=1$) and second ($p=2$) order process for the light frequency region determined by the available laser lines. The scattering intensity at frequency Ω was given as[6]

$$I(\omega_0,\Omega)\propto\sum_{p=1}^{\infty}C_p\delta(\Omega-\omega_0+p\omega_{\rm LO}),\tag{1}$$

where

$$C_p=\frac{A^p}{p!}\left|\sum_{s=0}^{p}(-1)^s\binom{p}{s}\Phi(\omega_0-s\omega_{\rm LO})\right|^2,\tag{2}$$

where

$$\Phi(x)=i\pi I(x)+{\rm P}\int_{-\infty}^{\infty}\frac{I(\omega)}{x-\omega}d\omega;\tag{3}$$

$I(x)$ is the normalized absorption intensity at frequency x and 0°K, and the A^p are related to the exciton-phonon coupling in the Fröhlich approximation, which, as we mentioned before, is applicable in the case of TlBr. Restricting our consideration to the Raman scattering only, we find that for $p=1$, A^1 is equal to

$$(4\pi\omega_{\mathrm{LO}})^{-1}(\epsilon_\infty^{-1}-\epsilon_0^{-1})|A_q^e-A_q^h|^2$$

evaluated at $q\simeq 0$; for $p=2$, A^2 is equal to

$$(4\pi\omega_{\mathrm{LO}})^{-2}(\epsilon_\infty^{-1}-\epsilon_0^{-1})^2 \times\sum_q|A_q^e-A_q^h|^2\sum_{q'}|A_{q'}^e-A_{q'}^h|^2$$

evaluated under the condition $q+q'\simeq 0$. For the evaluation of C_2 it is possible to use the square of the value of the exciton-phonon coupling as determined by the intensity of the LO sidebands in the absorption.[5] This represents only an approximation; nevertheless the values predicted in this way indicate that this process should make a significant contribution near resonance. By comparison the contribution of the Fröhlich interaction to the first order process is very low and C_1 in the region studied is almost zero. The first order process, which is actually hot luminescence, will appear only when the incident light is above the exciton edge. Then the first-order process peak will be at the same phonon frequency as that observed in the absorption band structures.[5] For the second order contribution the dependence of the 2LO-phonon scattering on the frequency of the incident light is shown in Fig. 1. It shows the increase of scattering cross section with light frequency due exclusively to the resonant-scattering process described by Eqs. (1)-(3). Our calculations also show that contributions for higher orders ($p>2$) to the scattering are small in our light frequency region. The quasi-resonant scattering contribution should result in a narrow peak at 227 ± 8 cm^{-1} which is twice the LO (Γ) phonon frequency as measured by Cowley and Okazaki.[5] Also, the $p=1$ and $p>2$ resonant LO phonon scattering peaks should be very weak.

Single crystals of TlBr grown by the Harshaw Chemical Company were cut and polished and placed in a temperature-controlled cryostat. Excitation light was provided by a commercial cw argon laser. The scattered light was analyzed through a double monochromator at a resolution of 0.4 Å and standard photon-counting techniques were used for the detection. Although measurements were performed at temperatures varying between 20 and 300°K, in this paper we shall concentrate on the low-temperature data; a more comprehensive report is in preparation.

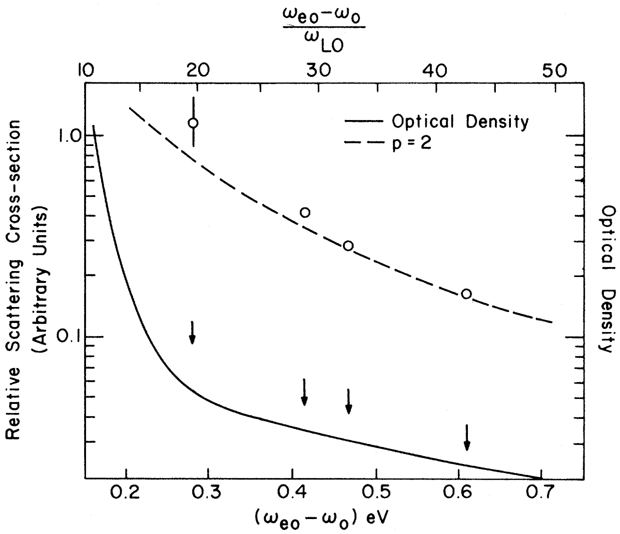

FIG. 1. Scattering cross sections for the resonant second ($p=2$) order process versus energy separation between the first exciton peak and laser lines. The circles represent the experimentally determined 2LO phonon peak intensities for various laser lines at 20°K. The intensities have been normalized to the scattering intensity at 122 cm^{-1}. For convenience in this figure we report also the optical density of a TlBr sample (uncorrected for reflection losses). The small vertical arrows show the position of the laser lines used.

In Fig. 2 we show the dependence of the recorded spectra at 20°K on the frequency ω_0 of the incident light. The intensities of the spectra in this figure are arbitrary. The most prominent feature is the narrow (half-width 12 cm^{-1}) peak at 227 ± 2 cm^{-1}. This frequency is equal, within the experimental accuracy, to the expected 2LO frequency for the $p=2$ resonant peak. Therefore we shall label this the 2LO peak. The most interesting feature of this peak is the behavior of its intensity relative to the rest of the spectrum as ω_0 increases. As we shall see, the remaining features of the spectra can be assigned accurately to ordinary off-resonant second-order scattering in which the rule $q+q'=0$ is obeyed. Thus the observed relative increase of the 2LO peak intensity indicates that it cannot be attributed to the same process. In Fig. 3 we show a more precise spectrum taken at 85°K with the 4759-Å laser line. Temperature and frequency were chosen so that both normal second order and the 2LO peak would show equally well. All of the labeled peaks can be assigned accurately to sums and differences of phonons with $q+q'=0$ using the phonon dispersion curves determined by Cowley and Okazaki.[5] In particular, peaks A and B are

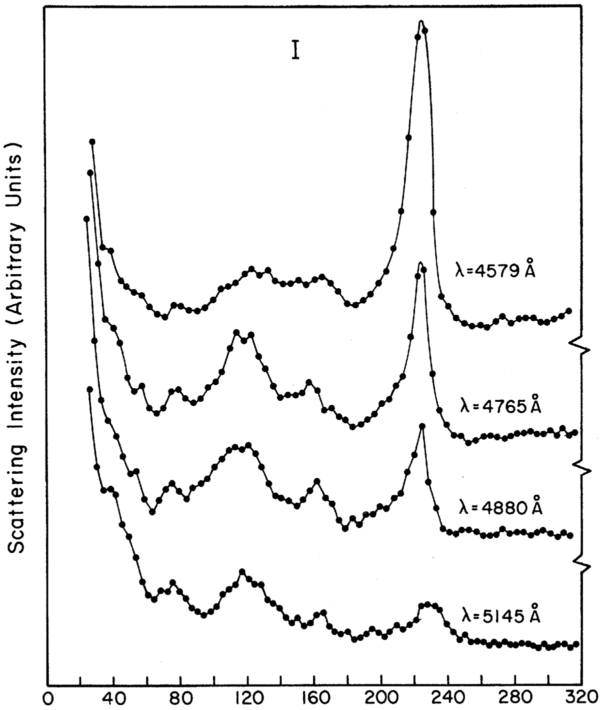

FIG. 2. Raman scattering spectra for TlBr taken at 20°K with the laser lines at 5145, 4880, 4765, and 4579 Å, respectively. The intensities are arbitrary. The resolution is 0.4 Å. The increase in the intensity for λ = 4579 Å at the largest shifts is due to the onset of luminescence.

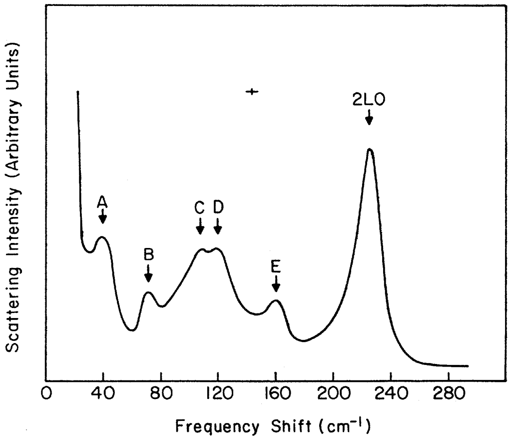

FIG. 3. Raman scattering spectrum from TlBr at 85°K. Excitation at 4579 Å. The 2LO peak is due to quasiresonant scattering (see text), and the other labels refer to peaks due to off-resonance two-phonon scattering.

difference peaks and C, D, and E are sum peaks. These assignments were found consistent with the observed temperature dependence of the relative peak intensities.

In order to test our conclusion that the 2LO peak is not due to ordinary second order scattering, we performed a control experiment by studying the Raman scattering in TlCl. Thallium chloride is very similar to TlBr, but its first exciton-peak energy is shifted by about 0.4 eV towards the uv with respect to TlBr. Therefore we can expect that in TlCl only off-resonance second-order scattering should be observed. The spectra we observed,[7] which will be reported in a later communication, were very similar to those seen in TlBr with the 5145-Å laser line (the farthest from resonance). In particular, a small broad peak was observed in the TlCl 2LO region, of the same relative intensity as that observed for TlBr with excitation at 5145 Å. Furthermore, this relative intensity did not change appreciably as ω_0 was increased, contrary to what we have observed in TlBr. Therefore we can conclude that the spectrum observed in TlBr for the lowest ω_0 is essentially ordinary two-phonon scattering and resonance effects are negligible. As ω_0 increases, the resonant interactions become appreciable, and begin to dominate the spectrum for the highest frequency, as indicated by the fast increase of the 2LO peak with respect to all other parts of the spectrum. Thus we interpret the 2LO peak as the second order process due to the onset of resonance with the excitonic transition. This conclusion is in good agreement with the theoretical prediction reported in Fig. 1. In the same figure we have plotted the measured 2LO peak intensities normalized to the scattering intensity at 122 cm^{-1}, which is a convenient frequency where only ordinary second-order scattering is observed. The intensity increase follows reasonably closely the curve for $p = 2$. The absence of a detectable first order LO peak in our data is also in good agreement with our expectations. The predominance of the $p = 2$ peak indicates that we are not yet in a region which can properly be labeled "resonant." Rather, our results indicate that we are in a quasiresonant region, where the resonance-induced scattering and the off-resonant scattering give comparable contributions. This feature makes this region very interesting since it is then possible to vary essentially continuously the relative weight of the two processes by varying the laser wavelength.

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[1] A. T. Lubchenko and B. P. Pavlik, Fiz. Tverd. Tela 5, 1714 (1963) [Sov. Phys. Solid State 5, 1246 (1964)]; A. K. Ganguly and J. L. Birman, Phys. Rev. 162, 806 (1967).

[2] J. F. Scott, R. C. C. Leite, and T. C. Damen, Phys. Rev. 188, 1285 (1969). See also references quoted herein.

[3] E. Mulazzi, in preparation. The theory is valid for large-radius excitons whose lifetime γ is larger than the phonon relaxation time. The different contributions coming from Raman effect, hot luminescence, and their interference [V. Hizhnyakov and I. Tehver, Phys. Status Solidi 39, 67 (1970)] will be discussed by considering also the change of the phonon frequencies in the exciton state due to the exciton phonon coupling. In a previous publication [see E. Mulazzi, Phys. Rev. Lett. 25, 228 (1970)] the two effects, Raman scattering and hot luminescence, have not been discussed in a separate way.

[4] R. Z. Bachrach and F. C. Brown, Phys. Rev. B 1, 818 (1970).

[5] E. R. Cowley and A. Okazaki, Proc. Roy. Soc., Ser. A 300, 45 (1967).

[6] Mulazzi, second paper of Ref. 3.

[7] Because of the nearness to the fundamental absorption region, the ordinary second order spectra for both TlBr and TlCl were found to have an intensity about one order of magnitude higher than for alkali halides in the same experimental circumstances. This higher intensity could be very profitable in studies in which high precision and high resolution are important, such as the search for critical-point singularities in two-phonon density of states.

NONLINEAR PROPAGATION OF HEAT PULSES IN SOLIDS

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We have observed self-steepening and narrowing of transverse heat pulses in pure NaF at high input-pulse powers when the ambient temperature is in the ballistic regime of the thermal-conductivity curve. The details of such nonlinear propagation of heat are found to be in agreement with the theory proposed by Tappert and Varma, which shows that under certain conditions heat pulses develop an instability.

In comparison with other systems in which nonlinear phenomena have been observed, the nonlinear parameters for the vibrational properties of solids are quite large. For example, for a typical insulating crystal the quantity $\epsilon = a_3h/a_2$, where a_2 and a_3 are the second (harmonic) and third derivatives, respectively, of the interatomic potential and h is the lattice spacing, is of order unity. However, it is usual to linearize the equations of motion for the atoms in the solid and obtain for example a diffusion equation or a wave equation for propagation of heat in solids. Experimentally, the vibrational properties of solids are studied either at very low frequencies, where the available power input is insufficient to drive the nonlinearities, or by studying propagation of heat by introducing a differential increase of temperature. By the second method the phenomena of thermal conductivity, second sound, and ballistic propagation of heat have been studied. In this paper we describe experiments in which we have observed propagation of heat under conditions in which the nonlinearity and dispersive nature of the vibrational properties of solids is dramatically illustrated.

Recently a great deal of mathematical and numerical-analytic work has been devoted to the study of nonlinear dispersive waves and a variety of interesting effects are predicted. The work relevant to our experiment, and its extension to cover our special experimental situation, is discussed in the succeeding paper.[1]

Our experiment is performed in the ballistic regime of the thermal conductivity curve, and we use the method of heat pulses.[2] In this method an alloyed metal film, serving as a heater, is deposited on one end of the solid to be studied and a superconducting film, serving as a bolometer, on the other. The typical lifetime of a phonon in a metal is 10^{-13} sec and since the typical width of our pulses is 10^{-7} sec, the heat pulse is "thermalized" in the heater, so that a heater temperature T_h can be defined. The vibrations so generated are transmitted to the solid under study. In the ballistic regime the mean free path of phonons is of the order of the size of the sample so that a temperature in the heat pulse cannot be defined. The heat pulse merely serves to launch a packet of phonons at one end of the solid which travel down the crystal; the