Resonant Raman scattering in the wide-gap dielectrics LiH and LiD

V. G. Plekhanov and A. A. O'Connel-Bronin

Physics Institute, Estonian Academy of Sciences
(Submitted 13 February 1978)
Pis'ma Zh. Eksp Teor. Fiz. **27**, No. 7, 413–416 (5 April 1978)

Resonant Raman scattering of light was observed in the cubic crystals LiH and LiD. The second-order intensity of the scattering has an anomalous temperature dependence.

PACS numbers: 78.30.Gt

Resonant Raman scattering of light (RRSL) is one of the most widely used and convenient spectroscopic method of investigating elementary excitations and their interaction with one another in condensed media.[1-3] The use of this method was highly successful in the physics of elementary excitations of semiconducting crystals ($E_g \lesssim 3$ eV). Laser excitation has made possible the investigation of not only allowed but also "forbidden" RRSL due to the interband Frohlich scattering mechanism, which is the principal mechanism for ionic crystals.

We have registered and investigated for the first time multiphonon RRSL (including those of fourth order) from free excitons in ionic crystals (lattices of the NaCl type) LiH and LiD, with forbidden band widths $E_g = 4.985$ and 5.090 eV, respectively. These crystals are characterized by the presence of large-radius excitons.[4] The proximity of the energy of the exciting quanta to the maximum of the exciton-absorption line leads to a sufficiently high intensity of the scattered light. This makes it possible to investigate with high resolution the spectrum of Raman scattering from a line separated from the continuous spectrum of a deuterium lamp by a monochromator. The measurements were performed in a backscattering geometry or by scattering at a right angle to the exciting light in the temperature interval 2–250 K.

Following excitation with light above the intrinsic absorption edge, the exciton emission spectrum in LiH crystals (and similarly in LiD) consists (Fig. 1, curve a, $E_{\text{excitation}} = 5.5$ eV) of an emission line (4.942 eV) which is almost resonant with the abosrption ($E_0 = 4.948$ eV), and for LO In the case of longer-wave excitation, (curve b, $E_{\text{excitation}} = 4.977$ eV), in addition to the indicated emission lines (Fig. 1 shows only the replica line $2LO$), on the short-wave side of the $2LO$ emission lines separated from the excitation line by double the LO-phonon energy [1]. With further increase of the exciting-light wavelength, this line (curve c, $E_{\text{excitation}} = 4.886$ eV), experiences a shift simultaneously with the excitation line, and the energy difference between them is constant and equal to double the LO phonon energy.

The dependence of the second-order RRLS intensity (and similarly also for LiD) on the frequency of the exciting light (without the correction for the absorption) is shown in Fig. 1d. To verify the $\propto \omega^4$ law we used an LiF plate whose dispersion of the refractive index in the region 4.5–5.5 eV is small. The second-order intensity shown in

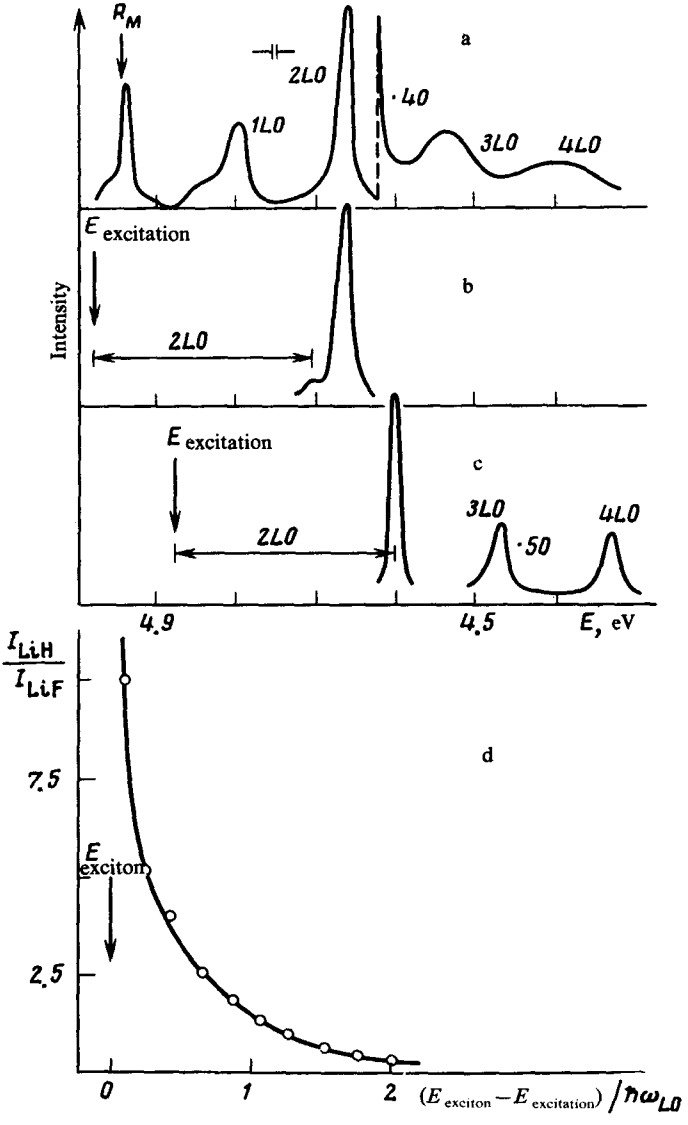

FIG. 1. Emission spectra (a,b) and scattering spectra (b,c) of the excitons and the dependence of the second-order intensity on the frequency of the exciting light (d) of LiH crystals at 4.2 K. The arrow indicates the position of the maximum $n=1$ of the exciton in the reflection spectrum. The resolution of the spectral instrument is indicated.

Fig. 1d is normalized to the intensity of the light scattered from the LiF plate, which was measured at the frequency of the $2LO$ phonon. The change of the energy of the exciting light quanta in the interval $0.15 \leqslant (E_{\text{exciton}} - E_{\text{excitation}})/\hbar\omega_{LO} < 2$ leads to an increase of the second-order scattering intensity by twenty five times.[2)]

As seen from Fig. 1 (curves b and c), the second-order scattering can be observed not only on the long-wave side but also on the short-wave side of the $2LO$ emission line of the excitons. Taking into account the known value of the longitudinal-transverse

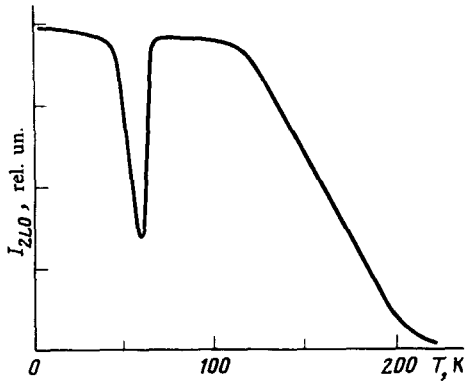

FIG. 2. Temperature dependence of the intensity of the second-order scattering in LiH crystals.

splitting $\Delta E_{LT} \approx 12$ meV,[4] we emphasize that the polaritons that take part in the scattering processes are not only from the lower but also from the upper polariton branch. It follows therefore that the intermediate states in the scattering processes are excitonic states. Evidence in favor of such an explanation is provided also by the experimentally observed anomalous behavior of the second-order scattering intensity with changing temperature (Fig. 2). One cannot exclude the possibility that the appearance of a sharp minimum in this dependence near ~ 50 K can be due to interference of the scattering amplitudes from different intermediate states.[5] When the temperature is raised, the maximum of the $n=3$ exciton (whose binding energy is ≈ 5 meV) becomes resonant with the excitation, and the amplitude of scattering with participation of this state is opposite in sign to the principal scattering amplitude, which is connected with other excitonic states. It is apparently the interference of these amplitudes which seems to cause the observed minimum. It should be noted that the position and the shape of the line and its half-width remain unchanged in the temperature region 2–200 K.

In conclusion, we analyze briefly the cause of the low intensity in the spectra of the "forbidden" first-order RRSL. According to the results obtained by Martin,[6] allowance for the wave vector of the exciting light can lift the forbiddenness of the first-order scattering, especially for large-radius excitons (see, however,[7]). Indeed, the scattering probability is proportional to the square of the phonon wave vector $q \sim 2\pi/r_\beta \sim 4\times 10^7$ cm^{-1}, where r_β is the exciton radius. The wave vector of the exciting light in the resonance region amounts to $K \sim 9\times 10^6$ cm^{-1}. In accordance with the quasimomentum conservation law, the phonons scattered in first order have $q \sim 9\times 10^6$ cm^{-1}, while the phonons with $q \sim 4\times 10^7$ cm^{-1} are significant in the second-order intensity should be smaller by approximately a factor 10–15 than that of the second order. However, we observed no first-order lines when the sensitivity of our apparatus was increased more than twentyfold. We note that the fourth-order intensity of the scattered light is comparable with that of third order.

Thus, the foregoing experimental results attest to observation of resonant and Raman scattering of light in wide-gap dielectrics LiH and LiD. The anomalous temperature behavior of the second order is apparently due to interference of the scatter-

ing amplitudes that are connected with participation of various excitonic states in the scattering processes.

The authors thank V.V. Khizhnyakov, G.S. Zavt, and V.I. Altukhov for useful discussions, and F.F. Gavrilov for supplying the crystals.

[1)]The exact value of the LO phonon energy $\hbar\omega_{LO}=140\pm1$ meV was measured under excitation with a mercury-lamp $\lambda=253.7$ nm line.

[2)]Recognizing that in the indicated energy interval the absorption coefficient changes by six orders of magnitude ($K\approx10^6$ cm^{-1}), we find that the second-order scattering cross section increases by a factor 2.5×10^7.

[1]Light Scattering in Solids, ed. M. Balkanski, Flammarion, Paris, 1971.

[2]Light Scattering in Solids, eds. M. Balkanski, and R.C.C. Leite, and S.P.S. Porto, Flammarion, Paris, 1975.

[3]The Theory of Light Scattering in Solids, eds. prof. V.M. Agranovich, profs. J.L. Birman, Nauka, Moscow (1976).

[4]V.G. Plekhanov, A.A. O'Connel-Bronin, and T.A. Betenekova, Fiz. Tverd. Tela (Leningrad) **19**, 3297 (1977); 20, No. 7 (1978) [Sov. Phys. Solid State 19, 1926 (1977); 20, No. 7 (1978)].

[5]V.V. Khizhnyakov, Author's abstract of doctoral dissertation, Tartu State University, 1972.

[6]R.M. Martin, in [1], p. 25, Phys. Rev. **B4**, 3676 (1971).

[7]P.F. Williams, S.P.S. Porto. Phys. Rev. **B8**, 1782 (1973); S. Permogorov and A. Reznitsky, Solid. State Comm. **18**, 781 (1976).