Experimental manifestation of polarization interaction of excitons with phonons in the wide-gap dielectric NaI

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

Physics Institute, Estonian Academy of Sciences
(Submitted 21 November 1977)
Pis'ma Zh. Eksp. Teor. Fiz. **27**, No. 1, 30–33 (5 January 1978)

We have observed LO replicas of the luminescence of free excitons as well as a doublet structure of the zero-phonon emission line, the latter being apparently due to interaction between the light and the excitons.

PACS numbers: 71.35.+z, 78.60.−b

Recent experiments performed on alkali-halide crystals have shown that besides the well investigated autolocalized excitons (AE) there can simultaneously exist in these systems also free excitons (FE).[1–4] The transition from the mobile state of the excitons to the autolocalized state involves the surmounting of a certain potential barrier,[1–4]which is attributed to short-range interactions of excitons with phonons, which are significant in such systems.[5–8] These theories overestimate the height of the barrier, as already pointed out in[5].

It is also indicated in[5] that an important role is played by the polarization interaction of the excitons with the phonons, since allowance for this interaction in the theory leads to a decrease of the height of the barrier. However, in the theory this interaction was not taken into account, since there were no experimental data on its manifestation. It is known that the polarization interaction is characteristic of large-radius excitons that move coherently in the crystal lattice, and for which the interaction between light and excitons is significant.

Although it is noted in[2,3] that these effects can be realized also in wide-gap dielectrics with autolocalized excitons, to our knowledge neither polarization interaction nor light-exciton effects have been observed in these systems to this day in direct experiements.

In the present study we investigated, with high resolution and high sensitivity, the intrinsic luminescence of NaI crystals. We have observed, for the first time ever, the structure of the zero-phonon emission line of free excitons, as well as its $1LO$ and $2LO$ replicas; in our opinion this is evidence of the importance of the polarization interaction of excitons with phonons. The experimental setup, which includes an immersion helium cryostat, crossed MDR-2 and MDR-4 monochromators, and a sensitive photon-counting system with a cooled FÉU-106 photomultiplier, has been described in[9].

Typical spectra of NaI crystals with a mirror-surface finish, obtained by excitation with photons in the region of the short-wave slope of the exciton ($n=1$) band and at 4.2 K are shown in Fig. 1. Besides the AE emission band with E_M=4.22 eV, we have observed on its short-wave side three equidistant lines separated by an amount

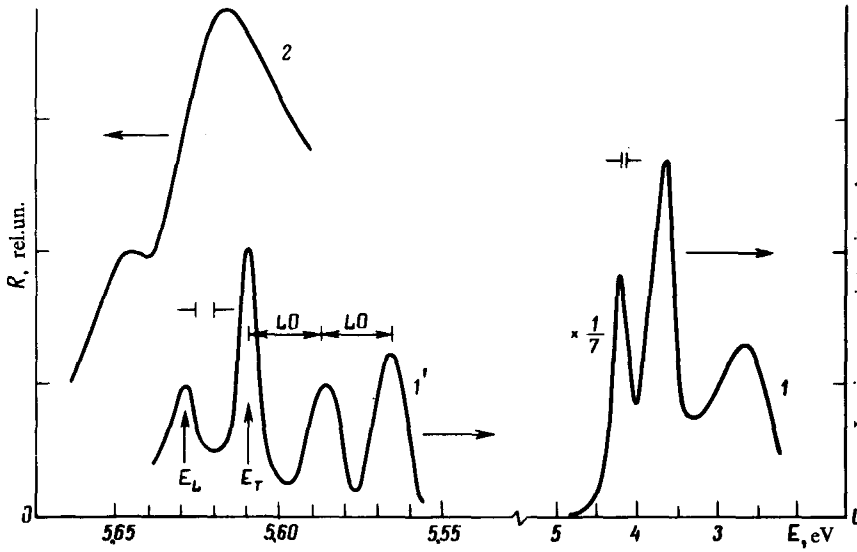

FIG. 1. Photoluminescence (1,1′) and reflection (2) spectra of NaI crystals at 4.2 K. The energy of the exciting photons is 5.75 eV. The arrows indicate the approximate position of the upper (E_L) and lower (E_T) polarization branches. The resolution of the spectral apparatus is indicated.

very close to the energy of the limiting optical phonon: $E_M=22$ meV,[10] and the zero-phonon line has a doublet structure with a splitting ~ 20 meV. The half-width of the long-wave component of the doublet is ~ 7 meV. This is smaller by a factor of more than 40 than the half-width of the AE luminescence band. Raising the temperature and prolonged irradiation of the crystal lead to a quenching of the short-wave radiation.

The resonance with the reflection spectrum (see Fig. 1) of the zero-phonon line, as well as the pressure of its two *LO* replicas, shows that the observed radiation is due to large-radius SE. The quantum yield of the SE emission (η_{SE}) at $T \lesssim 20$ K is $(1\text{–}2)\times 10^{-3}$,[3,9] as against $\eta_{AE} \approx 1$ for AE.[11] The slopes of temperature plots of the SE and AE emission yields are opposite and yield the same barrier values $q=16.5\pm 0.5$ meV (see also[2,3,4,11]), but the sum of the yields is not conserved and depends on the temperature. The latter follows from the decrease of η_{AE}, by a factor of 25–30, with decreasing temperature from 70 to 4 K, whereas its decrease, due to the flareup of the SE radiation, should be $(1\text{–}2)\times 10^{-3}$. This discrepancy is due to the energy transfer by the free excitons to the impurities, as manifest by the flareup of the impurity emission with $E_M=3.67$ eV in this temperature interval. It follows therefore that when the temperature is lowered the mean free path (l) of the excitons increases sharply (see also[3]). The experimentally obtained[2,3,12] value of l for NaI amounts to thousands of lattice constants. Assuming, as in[2] that the width of the excition band is $\Delta E \approx 4$ eV and the SE lifetime is $\sim 10^{-11}$ sec,[2,3] we estimated the value of l for coherent motion of the exciton at $l \approx 10^3$ nm. The conclusion that the motion of SE is coherent in alkali iodides was reached in[3] by analysis of the temperature dependence of the diffusion

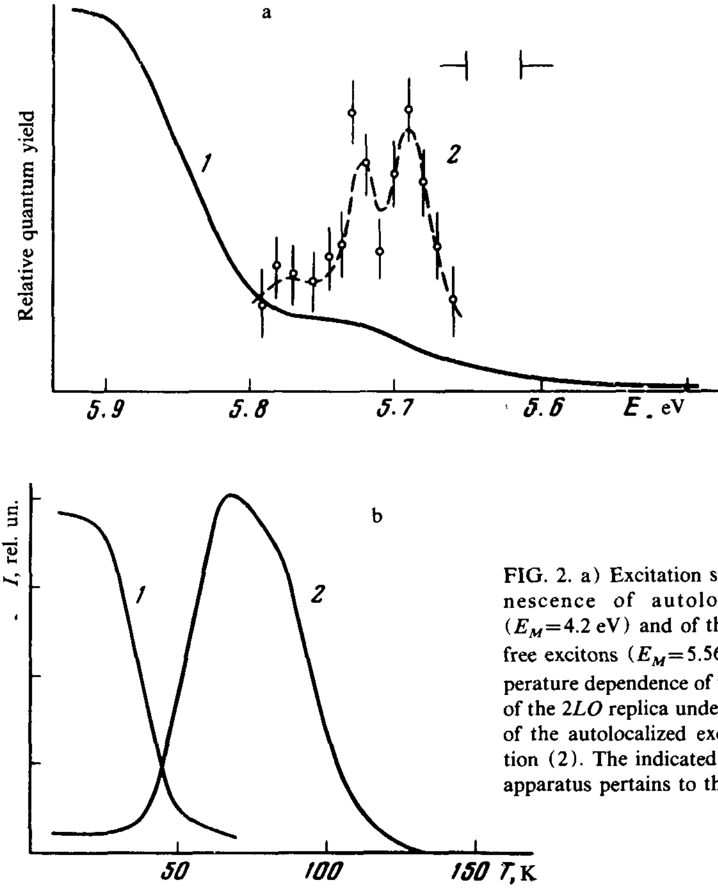

FIG. 2. a) Excitation spectra of stationary luminescence of autolocalized (1) excitons (E_M=4.2 eV) and of the 2LO replica (2) of the free excitons (E_M=5.565 eV) at 4.2 K. b) Temperature dependence of the luminescence intensity of the 2LO replica under x-ray excitation (1) and of the autolocalized excitons under photoexcitation (2). The indicated resolution of the spectral apparatus pertains to the curve 2(a).

coefficient. Thus, in the region close to resonance the excitons in NaI have a good quasimomentum. With increasing kinetic energy of the SE, their mobility decreases, and the probability of autolocalization increases (Fig. 2a). This indicates that the larger the disequilibrium of the excitons in the band the more probable their autolocalization and the faster their coherence loss.

For the excitons whose quasimomentum is a good quantum number it is necessary to take into account the light-exciton interaction, since the true eigenstates of the system in this case are the polaritons. It appears that it is precisely this interaction that causes of the structure of the phononless emission line of the SE. One of the causes of the deviation of the LO-replica contour from Maxwellian is the hot emission of the excitons in the region of the barrier,[8] whose central position lies in the LO-replica region.

Our experimental results lead to two principal conclusions: 1) polarization interaction of excitons with phonons sets in for broad-gap dielectrics such as NaI; 2) at low temperature the probability of autolocalization increases with increasing kinetic energy of the SE.

The authors are deeply grateful to V.I. Altukhov and G.S. Zavt for useful discussions, and to Ch. B. Lushchik, at whose initiative this paper was written.

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