Hot edge luminescence in xenon crystals

R. A. Kink, A. É. Lykhmus, and M. V. Sel'g

Institutes of Physics, Estonian Academy of Sciences

(Submitted 7 July 1978)
Pis'ma Zh. Eksp. Teor. Fiz. **28**, No. 8, 505–508 (20 October 1978)

Glow of free excitons in inert crystals optically excited in the exciton region was observed for the first time ever. The free and autolocalized states of the exciton in Xe are separated by a potential barrier $\epsilon = 70 \pm 10$ meV, corresponding to an exciton band width $B = 0.8$–1.2 eV.

PACS numbers: 71.35. + z, 78.55.Hx

We have investigated Xe crystals grown from the liquid phase in an ampule equipped with an LiF window. The initial xenon gas was first cleaned with liquid lithium. The optical measurement system included two vacuum monochromators of the VM-1 type and a flow-through hydrogen excitation lamp. The signal was registered by the photon-counting method.

The edge luminescence of xenon excited by ionizing radiation was observed earlier in Refs. 1–3, where the maximum of the luminescence was observed at energy 8.35–8.33 eV. The data on the maximum of the first exciton (Γ_{15}) absorption band disagree

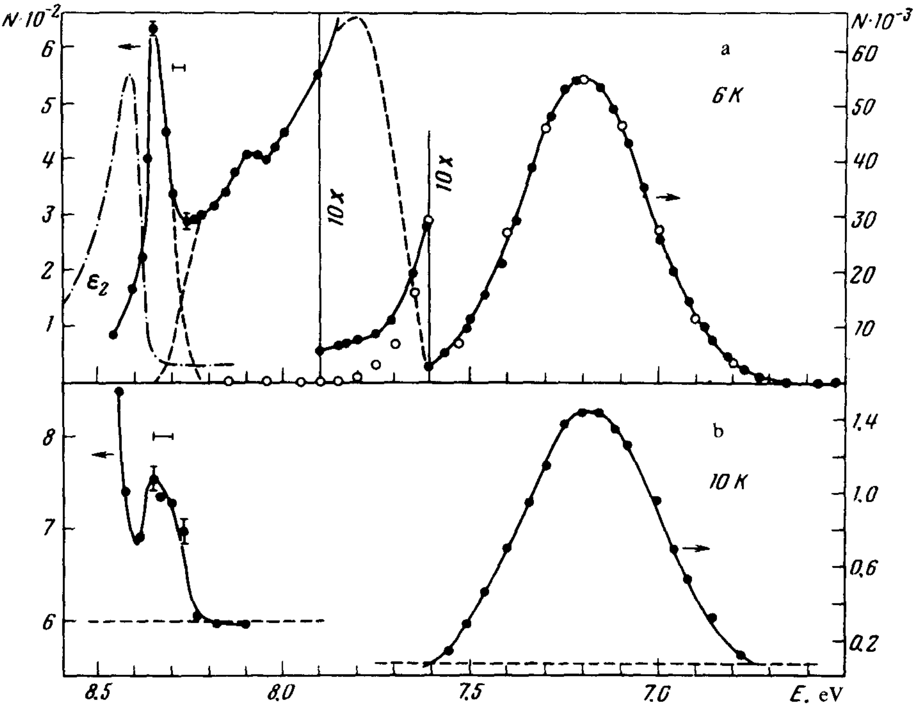

FIG. 1. Intrinsic luminescence spectrum of Xe crystal (number of counts) under x-ray excitation (a) and excitation with light of photon energy $E = 8.8 \pm 0.2$ eV (b).

greatly, owing to the different defect contents of the investigated thin films of xenon. It is more correct to determine the absorption from the reflection spectra of large crystals. In Refs. 4 and 5 the first reflection maximum of xenon crystals near helium temperatures was found to be at 8.42–8.40 eV. Figure 1(a) shows the ϵ_2 spectrum obtained from the reflection spectrum with the aid of a Kramers–Kronig analysis, together with the intrinsic luminescence spectrum of xenon excited with x rays. The narrow edge-luminescence band with half-width $\delta \leqslant 35$ meV is shifted away from a broader ($\delta \approx 130$ meV) absorption band by approximately 60 meV. The intensity of this emission is 0.01 of the intensity of the emission at 7.2 eV. When optical excitation is used, the same bands are observed in Fig. 1(b), and the edge with maximum at 8.35–8.37 eV has a Stokes shift of approximately 50 meV. This band is excited only in the region of the exciton absorption, thus confirming its exciton origin. The position of the band does not depend on the exciting wavelength. At $E > 8.4$ eV, a "tail" of exciting light is registered. The relative yield of the edge luminescence obtained by photoexcitation is on the average 10 times higher than for x-ray excitation. The luminescence band is apparently so narrow that the difference in the reabsorption under photo-excitation and x-ray excitation does not affect substantially the position of the band maximum. The reason why there is no exciton luminescence resonant with the absorption is not yet clear. In fact, the exciton has good mobility. The lower limit of the exciton mean free path is estimated by us at 500 Å. It is possible that the edge luminescence is due to free excitons, but the Stokes shift is determined by the polariton effect. A theoretical estimate of the longitudinal–transverse splitting in xenon yields $\Delta E \approx 100$ meV, which is close to the observed shift.

The edge luminescence goes over gradually into intense luminescence in the 7.2-eV band. We attribute this to the luminescence of the Xe_2^* exciton localized near a structure defect (vacancy).[3] The autolocalized exciton Xe_2^* in an "ideal" lattice emits in the 7.6 eV, but owing to the high barrier ϵ between the free and autolocalized states, the exciton cannot be autolocalized at low temperature (Fig. 2). The quenching of the luminescence of the free exciton and the redistribution of the intensities among the bands 7.2 and 7.6 eV is characterized by the same value of the potential barrier, $\epsilon = 70 \pm 10$ meV. We note that the high-temperature reverse redistribution is charac-

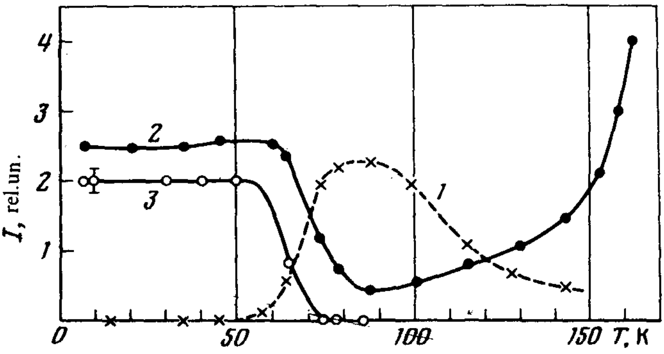

FIG. 2. Temperature dependence of the Xe luminescence-band intensities: 1—7.6, 2—7.2, 3—8.35 eV (the scale of curve 3 is increased 100 times) under x-ray excitation.

terized by an energy 0.15 eV, which coincides in practice with the theoretical enthalpy of vacancy production in the crystal.[6] Xenon is the only crystal known to us in which the height of the barrier ϵ exceeds by more than 10 times the limiting phonon energy. Therefore at low temperature this barrier is practically unsurmountable. The transparency of this barrier to tunneling at $T = 0$ K, determined from the theory of Ref. 7, is also small ($D \sim 10^{-55}$). Consequently, the tunnel process can likewise play no essential role in the autolocalization of the exciton in Xe. The experimental data agree with these conclusions. Theoretically, luminescence from the first vibrational level of the Xe_2^* molecule is described with sufficient accuracy by a Gaussian distribution. It is seen in Fig. 1(a) that the 7.2-eV band agrees in fact quite well with a Gaussian curve (represented by circles) up to an energy 7.6 eV. The intensity of the 7.6 eV band is lower by at least several orders of magnitude than that of the 7.2-eV band. At higher energy the luminescence is substantially more intense. The dashed curve for the energy region 7.6–8.3 eV shows the difference between the corresponding curves. The obtained contour represents the hot luminescence produced by vibrational relaxation of the Xe_2^* quasimolecule. Hot luminescence occurs also in the 7.6 eV band at nitrogen temperature. The entire luminescence spectrum of Xe_2^* is well described by theory of secondary luminescence of impurity centers of crystals.[8]

The barrier ϵ height is closely connected with the width of the exciton band B. In the existing theories of barrier height[9,10] no account is taken of the quasimolecular character of the autolocalized exciton, and their results for Xe can be used only for an approximate estimate. The width B can be estimated from Ref. 9 without using directly the experimental value of the Stokes shift of the luminescence of the autolocalized exciton. On the basis of our "quasimolecular" calculation of the exciton in xenon we could show that the theory parameter that determines the height of the barrier should lie in the range $1.5 < S^2/B < 2$. This corresponds to an exciton-band width $B = 0.8$–1.2 eV.

The authors thank G.G. Liid'ya, Ch.B. Lushchik, and V.V. Khizhnyakov for a discussion.

[1] J.M. Debever, A. Bonnot, A.M. Bonnot, F. Coletti, and J. Hanus, Solid State Commun. **14**, 989 (1974).
[2] I.Ya. Fugol', G.A. Belov, E.V. Savchenko, and B.Yu. Poltoratskiĭ, Fiz. Nizk. Temp. **1**, 203 (1975) [Sov. J. Low Temp. Phys. **1**, 98 (1975)].
[3] R.A. Kink and A.É. Lykhmus, Izv. Akad. Nauk SSSR Ser. Fiz. **42**, 466 (1978).
[4] I.T. Steinberger and U. Asaf, Phys. Rev. B **8**, 914 (1973).
[5] R.A. Kink and A.E. Lykhmus, Fiz. Nizk. Temp. **2**, 277 (1976) [Sov. J. Low Temp. Phys. **2**, 137 (1976)].
[6] M. Doyma and R. Cotterill, Phys. Rev. B **1**, 832 (1970).
[7] S.V. Iordanskiĭ and E.I. Rashba, Zh. Eksp. Teor. Fiz. **74**, 1872 (1978) [Sov. Phys. JETP **47**, 975 (1978)].
[8] V. Khizhnyakov and I. Rebane, Izv. Akad. Nauk Est. SSR Ser. Fiz. Mat. **26**, 260 (1977).
[9] V.V. Khizhnyakov and A.V. Sherman, Tr. Inst. Fiz. Akad. Nauk Est. SSR **46**, 120 (1976).
[10] É.I. Rashba, Fiz. Nizk. Temp. **3**, 524 (1977) [Sov. J. Low Temp. Phys. **3**, 254 (1977)].