Edge luminescence of excitons in ionic crystals

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Electron-excited edge luminescence of nonrelaxed electrons, adjacent to the long-wave absorption bands and quenched by heating, was observed for the first time in the crystals NaI, KI, RbI, and CsI at 67 °K.

Narrow bands of fundamental absorption of alkali-halide crystals (AHC) were observed in 1930.[1] They were interpreted on the basis of the exciton concept introduced by Frenkel.[2] Intrinsic luminescence of AHC (broad bands, appreciably shifted relative to absorption), were observed in 1955.[3] This luminescence follows radiative decay of the excitons after their vibrational relaxation and loss of mobility as a result of localization of the hole component of the exciton at the two ions of the halide X^-, with production of the quasi-molecular formation X_2^-e.[4]

The hopping diffusion of the relaxed electrons of AHC is quenched at $T < 80$ °K, but even at 5 °K the excitons produced by light can migrate, prior to axial vibrational relaxation, over a distance amounting to hundreds of

lattice constants, and to transfer energy to impurity luminescence centers.[5,6] It was noted in[5-7] that the lifetime of the nonrelaxed excitons can be appreciably increased as a result of the existence of an activation barrier when the "single-nucleus" free exciton (X^0e) is transformed into a "two-nucleus" autolocalized exciton (X_2^-e).

The need of a search for radiative annihilation of the excitons prior to their axial relaxation has been long obvious.[5] Attempts to observe luminescence of AHC at the edge of the intrinsic absorption by producing excitons with ultraviolet radiation were made many times, but all ended in failure.[6,7] We have observed edge luminescence of nonrelaxed excitons in the crystals NaI, KI, RbI, and CsI bombarded with 1–10 keV electrons (depth of penetration $10^{-5} - 10^{-4}$ cm).

The cathode luminescence was investigated with a specially produced installation for a spectra-kinetic investigation of solids. A vacuum of 10^{-7} Torr was produced by absorption pumps in an experimental chamber with a nitrogen-helium cryostat. The crystals were excited by an electron gun operating in the pulsed regime (pulse duration 1–10 μsec, frequency 4 kHz, current in pulse 1–10 μA/mm^2). The luminescence was registered with an FÉU-71 photomultiplier through a DMR-4 double monochromator with the aid of an S7-5 stroboscopic oscilloscope.

The figure shows the absorption spectrum (1) of NaI, measured in[8] at 66 °K, and also the cathode luminescence spectrum (2,2′), measured at 67 °K, of an NaI single crystal grown by the Stockbarger method from specially purified raw material. The intense luminescence in the region of 4.15 eV corresponds to the emission of triplet autolocalized excitons.[4] In photoexcitation, the quantum yield of the 4.15-eV luminescence is approximately 0.5. Particular interest attached to the narrow luminescence band with maximum 5.5 eV, adjacent to the intrinsic (exciton) absorption with maximum 5.62 eV, and having an intensity lower by a factor 10^3. At a monochromator-slit optical width 0.037 eV, the half-width of the emission band is ~0.07 eV. The band is asymmetrically elongated in the direction of lower energies. At the maximum of the emission band, the reabsorption of the emission by the thin emitting layer of the crystal is low ($\kappa d < 0.01$). The reabsorption can distort the contour on the short-wave wing of the band. Heating the crystal to 100 °K lowers the 5.55-eV luminescence intensity by a factor of ~5.

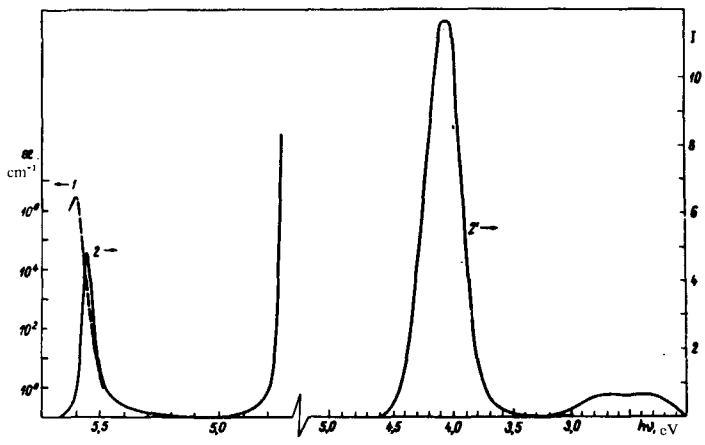
The edge luminescence (EL) was observed by us in single crystals of KI (5.75 eV), RbI (5.58 eV), and CsI (5.65 eV). The emission was adjacent to the exciton absorption bands and was quenched upon heating. In[6,7], the activation barrier q between the states of nonrelaxed and relaxed excitons in AHC was determined from the partial quenching of the emission of the autolocalized excitons at low temperatures. $q = 15$ meV for NaI.[7] The EL quenching in NaI, with allowance for the possible change in the reabsorption upon heating (by an approximate factor of 2) yields an activation energy that is close to q. For CsI, the barrier is one-third as small, and the EL at 67 °K is weaker than the emission of the autolocalized excitons by a factor 10^5. We observed no EL in RbBr, where the anions are quite far from each other.

It is natural to attribute the temperature-dependent EL of AHC to radiative annihilation of the free excitons of the X^0e type prior to their axial relaxation and autolocalization in the form X_2^-e. It is necessary to attempt in the future to separate also the temperature-independent hot luminescence excitons of type X_2^-e.[9]

When electrons act on a crystal, excitons are produced by recombination of the electrons and holes, and also when the ions are excited by electron impact. The sublinear dependence of the intensity of the EL on the current density seems to indicate that the nonrelaxed excitons are produced when the anions are excited by electron impact. Their state can differ somewhat from the state of excitons produced by light.

The mobility of the excitations whose annihilation gives rise to the EL becomes manifest in the quenching of the EL by small amounts (< 0.01 mol.%) of radiation defects and impurities. In NaI, a total of 10^5–10^7 electron-beam pulses attenuates the EL by a factor ~100. The luminescence is at the same time greatly strengthened in the region 3–2 eV, corresponding to the emission of bound excitons near the radiation defects (probably cation vacancies in the case of NaI). The edge luminescence can be obtained again after increasing the energy (depth of penetration) of the electrons, thus indicating that EL is produced in the volume rather than on the surface of the crystal, and making it possible to estimate the role of the reabsorption.

Edge luminescence of excitons has been long known for many semiconductors in which there is no autolocalization of excitations. Our experiments demonstrate that both autolocalized and mobile excitons can exist simultaneously, and produce luminescence, in ionic dielectrics with clearly pronounced autolocalization of the excitons. The simultaneous existence in one crystal of migrating and immobile excitons conforms qualitatively to Frenkel's initial idea concerning free



Absorption spectrum of NaI at 66 °K[8] (1) and emission spectrum of nonrelaxed (2) and autolocalized (2′) excitons at 67 °K.

and trapped excitons[2] and to the interpretation presented in[10] for the fluctuation nature of the activation barrier.

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