Ch. B. Lushchik and I. L. Kuusmann. *Luminescence, Autolocalization and Decay of Excitons in Ionic Crystals*. The idea that free and self-trapped (autolocalized) excitons may exist in crystals was introduced by Frenkel' in[1]. Landau[2] and Rashba[3] analyzed the need for an activation energy for autolocalization of electrons and excitons in solids.

Numerous experiments have indicated that only free excitons exist in narrow-gap semiconductors. An experimental study of excitons in broad-gap ionic crystals has been made at the Estonian Academy of Sciences Institute of Physics; it required the development of methods for measurement of optical characteristics in the region of the spectrum up to 22 eV, methods of registering weak emissions with excitation of the crystals by pulsed electron beams, and the preparation of crystals of high purity.

It has been established that excitons exist in three states in alkali halide crystals: free excitons,[4] self-trapped monohalide excitons (X^0e)[5], and autolocalized dihalide excitons (X_2^-e),[6,7] in which the hole component is spread out over two halogen ions (X^-). Figure 1 shows the luminescence spectra of all three types of excitons under excitation of KI crystals with 5-keV electrons at 67 °K (curves 2, 2′). The strong broad bands at 3.3 and 4.1 eV correspond to triplet and singlet dihalide excitons. The weak narrow band at 5.75 eV, which is nearly resonant with the self-absorption band, is due to radiative annihilation of free excitons. The luminescence of monohalide self-trapped excitons appears in the 5.2 eV range.

The figure (curve 1) presents the 3.3-eV luminescence excitation spectrum measured for KI at 80 °K. There are three different mechanisms by which autolocalized dihalide excitons can be formed: by direct optical creation of monohalide excitons (range 5.7–7.0 eV), by recombination of electrons with autolocalized holes (7–11 eV), and by the creation, by photons, of hot photoelectrons capable of generating excitons by electron impact (11.5–17 eV).

The freezing of the luminescence of dihalide excitons in NI and KI on cooling from 80 °K to 4 °K, and the concurrent intensification of free-exciton luminescence in NaI and of the luminescence of impurity centers in Ki-Tl indicate that the process of two-center autolocalization of excitons requires an activation energy.[7,8] As a result, free and autolocalized excitons coexist in alkali iodides at low temperatures.[4,7,8]

Table I gives the positions of the emission bands (in electron volts) of free excitons (e^0) and one-center and two-center autolocalized excitons (e^0_{A1} and e^0_{A2}) for a number of the ionic crystals that were studied. The symbol + marks the experimentally observed cases of hole autolocalization (e^+_A) and the hypothetical cases of electron autolocalization (e^*_A). As the table shows, coexistence of free and autolocalized excitons is possible in both one-center and two-center autolocalization, both with stopping of the hole exciton component and with self-trapping of the electron component.

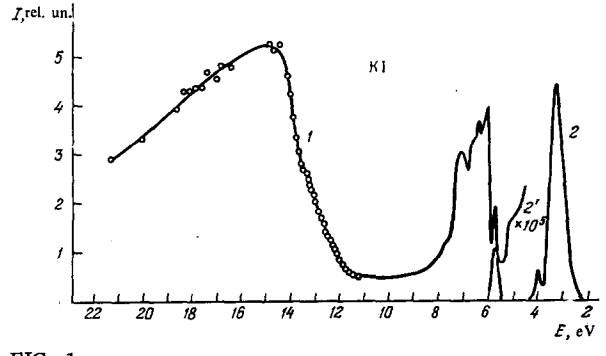

FIG. 1.

TABLE I.

	e^0	e^0_{A1}	e^0_{A2}	e^-_A	e^+_A
NaI	5.55		4.2		+
KI	5.75	5.2	4.1; 3.3		+
RbI	5.58	5.2	3.8; 3.1		+
KCl		6.8	2.4		+
KBr		5.8; 6.3	4.2; 2.2		+
RbBr		5.8; 6.3	4.1; 2.1		+
CsBr		5.45; 6.0	4.95; 3.4		+
LiH	4.92		4.5; 3.3	+	
LiD	5.02		4.5; 3.3	+	
MgO	7.65				
AgCl	5.1	2.4			+
AgBr	2.8				
$PbBr_2$	4.0	2.7		+	
$CaWO_4$		5.8			+

The creation of defects in alkali halide crystals takes place in the same way under irradiation in the reactor and with x-ray and vacuum-ultraviolet radiation.[9] In crystals with autolocalized excitons, the excitons decay with production of Frenkel' defects.[10] Excitons decay most effectively with production of F centers and interstitial halogen atoms.

Analysis of the causes of this unusual phenomenon, which requires joint thoretical analysis of electron excitations and structural defects in solids, has shown that strong local oscillations arise at the time of transition of the monohalide excitons to the dihalide state, leading to displacement of the X_2^- molecule to a single anionic site with release of the other for formation of an F center. In crystals of the MgO type, where excitons are not autolocalized, it is impossible for highly mobile excitons to decay into defects.

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