Coexistence of large- and small-radius excitons bound on defects in solids

É. Kh. Fel'dbakh, Ch. B. Lushchik, and I. L. Kuusmann
Institute of Physics, Academy of Sciences of the Estonian SSR

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The coexistence of large- and small-radius excitons bound with defects (Ca^{2+})—the impurity analog of the coexistence of free and self-trapped excitons in crystals—was detected for the first time in MgO–Ca crystals at 5 K.

After the experimental observation of the coexistence of free and self-trapped excitons (FE and STE), whose states are separated by an activation barrier,[1–3] in alkali iodides, this effect, predicted by Rashba (see, for example, Ref. 4), was studied in several ionic and atomic crystals.

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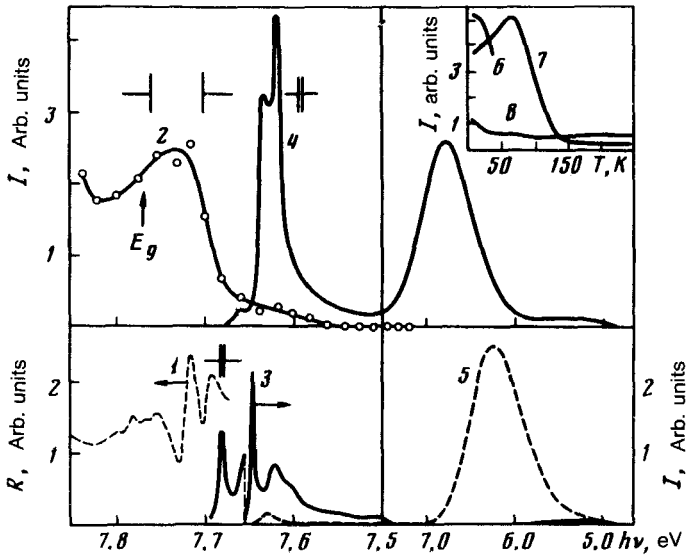

FIG. 1. Reflection spectrum (1), luminescence spectrum at 6.8 eV (2), and cathodoluminescence spectrum (3,4,5) for MgO (1,3), MgO--Ca (2,4) and MgO--Be (5) crystals at 5 K. The widths of the optical slits are indicated : 1 Å and 14 Å for measurement of the excitation spectrum. The temperature dependence of the intensity of cathodoluminescence at 7.62 eV (6), 6.8 eV (7), and 7.5 eV (8) is shown in the insert.

In this work, for the case of MgO--Ca, it is shown for the first time experimentally that excitons with large and small radius, bound with defects of one type, can coexist in solids. The states with large and small radius are separated by an activation barrier, which protects the large-radius excitons from collapsing via a transition to the small-radius excitation.

Edge luminescence, in which it was possible to separate out at 5 K 7.68-eV luminescence corresponding to FE, was observed by Valbis *et al.*,[5] in MgO crystals of high purity.[6] We studied the luminescence of the crystals MgO, MgO--Ca, MgO--Be, MgO--Li, and MgO--Al on a unique apparatus with a double vacuum monochromator for investigating low-temperature luminescence generated by 10-keV electrons[7] in the region of the spectrum from 4 to 8 eV. The introduction of 10^{18}–10^{19} cm^{-3} Ca^{2+}, Be^{2+}, Li^{+}, and Al^{3+} ions into MgO sharply decreases the luminescence of FE and leads to the appearance of wide-band luminescence with a large Stokes shift relative to FE (6.8, 6.25, 5.9, and 5.4 eV, respectively).

As is evident from Fig. 1, the introduction of Ca^{2+} ions into MgO leads not only to the appearance of luminescence at 6.8 eV and 5 K but also sharply intensifies the edge luminescence at 7.62 eV, which is displaced by 60 meV relative to the luminescence of FE. The Be^{2+} and Li^{+} ions sharply quench the edge luminescence. Measurements of thermally stimulated luminescence and ESR measurements have shown that in MgO, Be^{2+} ions serve as traps for electrons, while Ca^{2+} ions serve as traps for holes.

In MgO--Ca it is observed that linear (7.62 eV) and wide-band (6.8 eV) luminescence coexist. At 5 K, the excitation spectrum of 6.8-eV luminescence encompasses

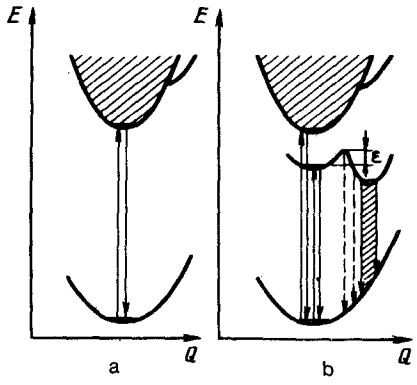

FIG. 2. Schematic dependence of the potential energy of free (a) and large- and small-radius bound excitons (b) on the deformation Q. The arrows indicate transitions in absorption and emission.

the region of interband transitions ($h\nu > 7.80$ eV), the region of optical creation of free excitons (7.68–7.80 eV), and the region of creation of bound excitons with large radius (7.60–7.68 eV). Under heating, the intensity of cathodoluminescence at 7.62 eV sharply decreases, in the region 30–60 K, and the intensity of luminescence at 6.8 eV increases. Under further heating from 60 to 120 K, the luminescence at 6.8 eV is quenched due to the thermal separation of holes from Ca^{2+} ions. In the region between the edge luminescence (7.62 eV) and wide-band luminescence (6.8 eV), MgO--Ca exhibits a weak, temperature-independent continuous luminescence background.

Analysis of the experimental data obtained has led to the conclusion that the excitons with large and small radius, bound with Ca^{2+} ions, which replace the magnesium ions at the sites of the crystal lattice, coexist in MgO--Ca. Figure 2 shows schematically the energy diagrams of free excitons and excitons of large and small radius bound with point defects in the crystal. The large-radius bound excitons correspond to the 7.62-eV luminescence line while the bound small-radius exciton corresponds to the wide-band luminescence with a peak at 6.8 eV. As the system relaxes vibrationally, weak, hot luminescence with a continuous spectrum appears. The correlated change in the intensities of the linear and wide-band luminescence in the region 30–60 K indicates the existence of an activation barrier (ϵ).

A comparison of the characteristics of MgO--Ca and MgO--Be showed that the coexistence of bound large- and small-radius excitons is characteristic in MgO for an impurity (Ca^{2+}) which serves as a non-Coulombic (deformation) trap for heavy holes and which is isovalent with the ions of the matrix. When light electrons are trapped by Be^{2+} ions, a bound large-radius exciton is not formed.

The possibility of coexistence of large- and small-radius excitons bound with defects of one type can be viewed as the impurity analog of the coexistence of free and self-trapped excitons in solids. The activation barrier between neighboring large- and small-radius excitons, as in the case of the coexistence of FE and STE in alkali-halide crystals,[1–3] is due to the necessity of sharply changing the size of the region of localization of the electronic excitation.[4]

It is very likely that large- and small-radius excitons bound with defects of one type can exist in many solids (especially in semiconductors). To observe them, it is necessary to study carefully the edge luminescence and the wide-band luminescence in solids at the same time.

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