Edge luminescence of excitons in MgO crystals in the vacuum ultraviolet region of the spectrum

Ya. A. Valbis, K. A. Kalder, I. L. Kuusmann, Ch. B. Lushchik, A. A. Ratas, Z. A. Rachko, M. E. Springis, and V. M. Tiit

Physics Institute, Estonian Academy of Sciences
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Edge luminescence in the vacuum ultraviolet region, due to radiative annihilation of free excitons, is observed in magnesium oxide for the first time in the case of ionic crystals.

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Gross has observed in the spectra of crystal with narrow forbidden bands ($E_g < 3$ eV) hydrogenlike series connected with the production and luminescence of large-radius excitons.[1] In ionic crystals of the NaI type with $E_g = 6$ eV, the edge luminescence of excitons was observed in[2]. Of fundamental interest is the investigation of crystals with even large E_g, in which the exciton luminescence can appear in the vacuum ultraviolet (VUV) region of the spectrum.

We have observed luminescence of MgO crystals in the region 7.60–7.75 eV which is at resonance with the long-wave intrinsic-absorption bands studied in[3–5]. The thermoreflection spectra of MgO at 85 °K reveal minima at 7.662 and 7.687 eV (the latter has a 7 meV splitting), as well as minima at 7.739 and 7.765 eV.[3] In accordance with a theoretical calculation of the band structure of MgO,[4] the long-wave doublet is ascribed by the authors to the production of the excitons $\Gamma_{1/2}$ and

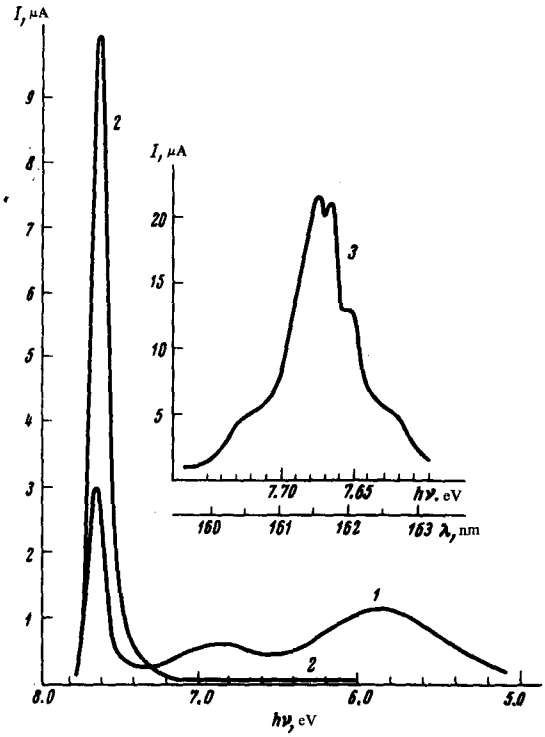

FIG.

$\Gamma_{3/2}$ with spin-orbit splitting 25 meV. The doublet 7.739 and 7.765 eV can be attributed either to the formation of an exciton-phonon complex[3] or with the production of excitons at the X point,[5] or else with $n = 2$ members of Γ excitons. The start of the interband transitions is assumed to lie at 7.83 eV.[3]

We have investigated the luminescence of MgO single crystals excited by electrons of energy from 2 to 25 keV at current densities 10–300 $\mu A/cm^2$. In the first experiments, the luminescence was registered through a Seiya-Namioka monochromator with the aid of an FÉU-79 photomultiplier and a sodium-salicylate light converter. To obtain details of the spectrum we used a Johnson-Onaka double vacuum monochromator[6] and a gas-discharge photon counter.

The figure shows the cathode luminescence spectrum of an MgO single crystal, measured at 90 °K at a resolution 0.1 eV, with excitation by 25-keV electrons (curve 1). Broad bands due to electron and hole recombination on various defects are observed in the 5.0–7.3 region. Of particular interest is the narrow band in the region of 7.64 eV, its shape and position of the maximum being somewhat distorted by absorption. The 7.64-eV emission was observed for all the MgO single crystals in our possession, which were grown in eight different laboratories and differed considerably in their impurity content. It was also seen for increased-purity epitaxial single-crystal MgO layers grown by the gas transport method (curve 2). The intensity of the 7.64-eV luminescence was larger in the samples with the lower impurity concentration.

To decrease the influence of reabsorption, the cathode luminescence spectra were measured as an electron energy 3 keV. An increase of the resolution to 0.01 eV has revealed a fine structure of the MgO single-crystal luminescence spectrum, with maxima at 7.62, 7.65, 7.67, 7.68, and 7.73 eV (curve 3). The structure of the emission spectrum coincides, within the measurement errors (0.01 eV), with the structure of the MgO reflection spectrum.[3] The 7.65, 7.67, and 7.68-eV bands correspond to the luminescence of $\Gamma_{1/2}$ and $\Gamma_{3/2}$ excitons. A 25-meV spin-orbit splitting appears in the spectrum, as well as a weaker splitting of the levels of the $\Gamma_{3/2}$ exciton. The shift of the emission bands relative to the extremal thermoreflection points is less than the energy of the extremal longitudinal oscillations (89 meV), indicating that free nonrelaxed excitons appear in the spectrum. The 7.73-eV luminescence can be ascribed to Γ excitons with $n = 2$ or to X excitons.

When the MgO is heated to 300 °K, the luminescence of the Γ excitons is quenched, and the intrinsic and impurity recombination radiation becomes stronger. These effects are probably the result of thermal dissociation of the excitons. At 300 °K one can also see a weak luminescence in the 7.8–8.7 eV region, which probably corresponds to interband recombinations.

The absence of superlinearity in the dependence of the edge luminescence (7.65 eV) on the current density indicates that the excitons are produced in the MgO mainly not by recombination binding of electrons and holes, but by excitation by electron impact and decay of plasmons into excitons. The edge luminescence in the better samples has at 90 °K an energy efficiency not lower than 0.1%, which greatly exceeds the efficiency of the edge luminescence of NaI. This is natural, since the autolocalization of holes and excitons, which serves in NaI as an additional channel for the decay of the free excitons, is not present in MgO.

The edge luminescence of the Γ excitons in MgO, which is at resonance with the intrinsic absorption, consists of three narrow bands, the half-width of each being less than 15 meV. These bands are narrower by a factor of several dozen than the emission bands in the 5–7 eV region, which correspond to luminescence of local centers. The strong electron-phonon interaction typical of ionic crystals does not appear in the edge-luminescence region; this is natural if this luminescence corresponds to excitons with broad band $E(k)$.

A similar regularity was observed by us in the comparison of the narrow absorption bands corresponding to migrating excitons in NaI with the broad absorption bands of immobile electron excitations of iodine ions in NaBr:I (0.01%) crystals.

The existence of exciton luminescence that is at resonance with absorption in MgO calls for a rigorous analysis of the question whether opto-excitonic effects are present in MgO and in other broad-band ionic crystals.

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