

LUMINESCENCE AND ELECTRON-MICROSCOPIC INVESTIGATION OF MOLECULAR COMPLEXES IN THE  $\text{NaCl}:\text{EuCl}_2$  CRYSTAL PHOSPHOR

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Submitted 21 May 1969  
ZhETF Pis. Red. 10, No. 2, 65 - 68 (20 July 1969)

In the study of luminescence in ionic crystal, the main task is to determine the structure and the positions of the luminescence centers of the activator. Most investigations are devoted to single centers, namely impurity ions that replace the cations in the regular host lattice (the Seitz model [1]). In addition, it has been proposed in a number of cases that other types of activator centers can also be produced and can also play an important role in luminescence, namely associations of several pointlike centers [2], adsorption inclusions of complex compounds of the activator with the host material [3, 4], and an activator phase [5]. Optical methods alone are insufficient for the identification of such "non-elementary" luminescence centers.

In the present investigation, we observed a unique "non-Seitz" type of luminescence center in an NaCl crystal doped with 0.1 mol.%  $\text{EuCl}_2$  (in the melt), and used electron microscopy to determine the features of their disposition in the host. The NaCl:Eu crystals are convenient for parallel monitoring, by the electron paramagnetic resonance (EPR) method, of the Seitz-type centers, namely single  $\text{Eu}^{2+}$  ions. It is these centers, or more accurately  $\text{Eu}^{2+}$  in association with the cation vacancy on the (110) axis [6], which predominate in samples quenched by rapid cooling from 600 - 900°K. They correspond to a luminescence band at 425 nm (electronic transitions  $4f^6 5d^8 P - 4f^7 8S_{7/2}$ ). At an  $\text{Eu}^{2+}$  concentration in the NaCl lattice on the order of 0.0n%, the solid solution turns out to be unstable. Storage of the crystals (at 300°K) produces, as a result of the diffusion of the  $\text{Eu}^{2+}$  ions, associations that are energetically more favored and consist of several (two or three [2]) " $\text{Eu}^{2+}$ -vacancy" dipoles. These are characterized by luminescence in the 440 - 460 nm region [7]. This process reaches saturation approximately after three days, without leading to the formation of noticeable phase inclusions. A qualitatively new type of luminescence center appears in the crystals only after they are annealed with a slow (1 day) cooling from 600 - 900°K. The samples become turbid. The decrease of the  $\text{Eu}^{2+}$  concentration in the regular lattice is revealed by the weakening of the EPR signal and of the intensity of the 425 nm luminescence band. Simultaneously, a band at 400 - 410 nm appears in the luminescence spectrum (Fig. 1B), characterized by the fact that it is not excited at room temperature (temperature quenching). Its excitation spectrum (curve B') also differs strongly from the excitation spectra of the pointlike  $\text{Eu}^{2+}$  centers, which are characterized in all the known crystal phosphors by two broad uv bands of the type of curve A' of Fig. 1.

The electron-microscopic investigation has shown that in such annealed crystals the

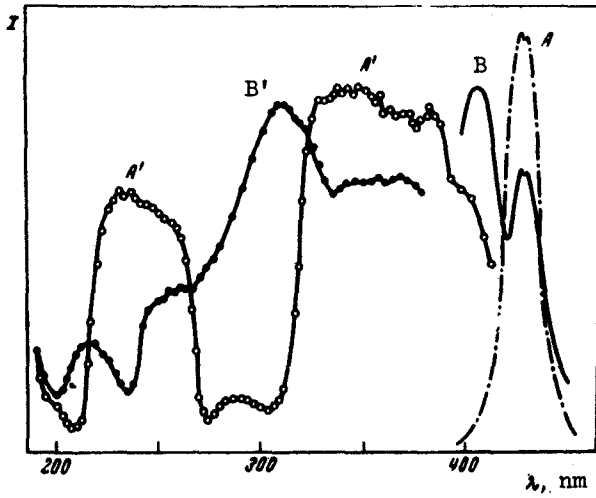


Fig. 1. Luminescence spectra of  $\text{NaCl:EuCl}_2$  at  $77^\circ\text{K}$  and excitation spectra (A', B') at  $90^\circ\text{K}$  of the luminescence bands A and B, respectively.

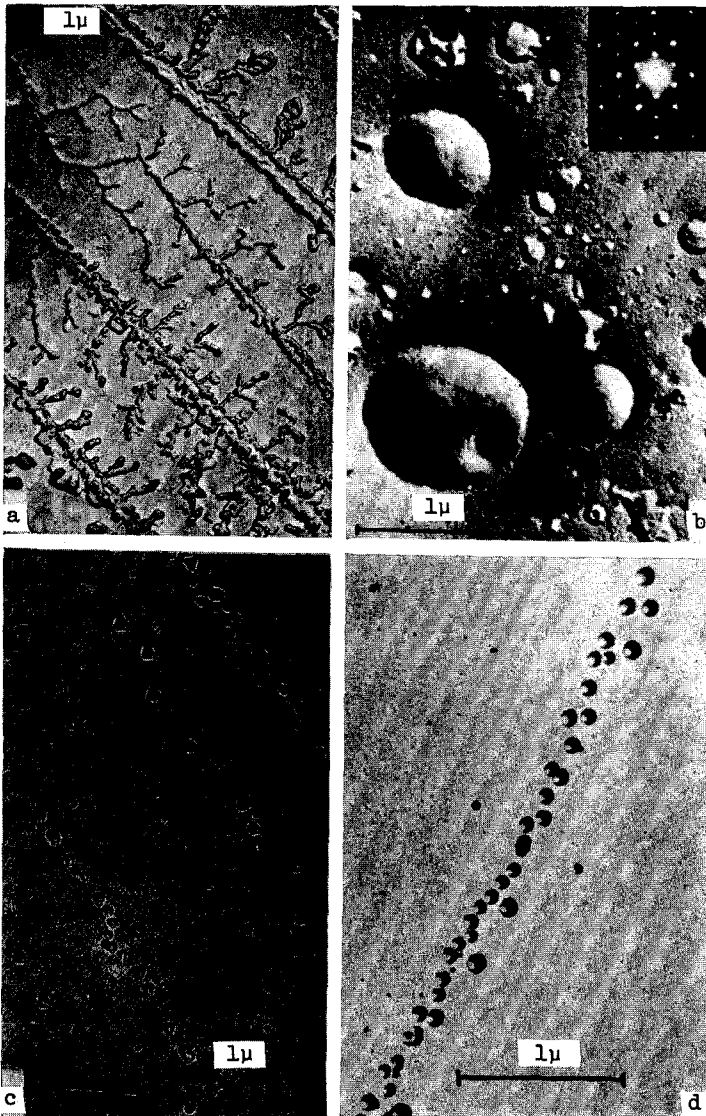
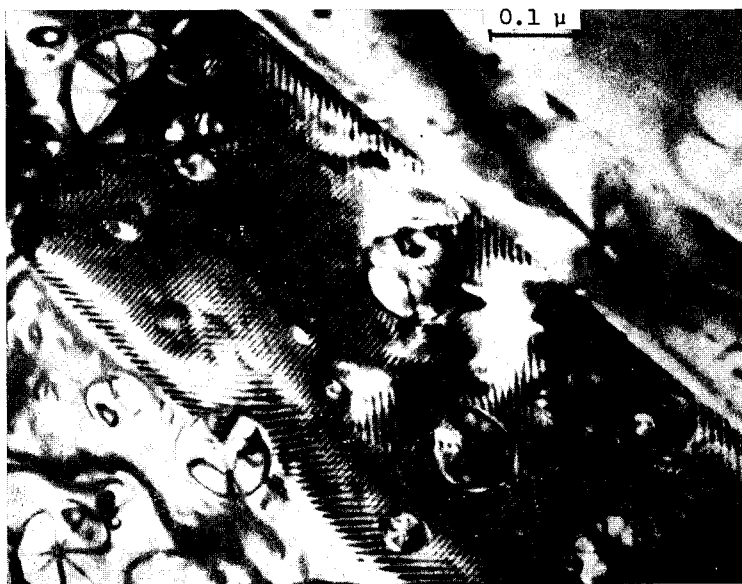


Fig. 2. Replicas from cleaved surfaces of  $\text{NaCl:EuCl}_2$  from various sections of the crystal. a) Microphase segregations in the form of dendrites, b) droplike segregations, with microdiffraction (insert on the right) obtained from an extracted particle (bordered), c) chains of "triangles," d) chain of round microphase particles.

Fig. 3. Diffraction effects from two parallel NaCl:EuCl<sub>2</sub> layers; segregations in the form of points (A) of the microphase, leading to the appearance of Kossel lines of fourfold symmetry, are seen against the moire background.



excess activator impurity is segregated in the form of particles of various shapes, with a dimension usually smaller than  $1 \mu$  ("microphase"), decorating the structural defects<sup>1)</sup>. Such a microphase is segregated along the boundaries of the disoriented blocks in the form of dendrites (Fig. 2a) and in the form of droplike particles (Figs. 2b, 2c). In addition, unique chains are encountered at a distance of  $\sim 1 \mu$ , consisting of "triangles" ( $< 0.1 \mu$ ) with a strictly identical orientation in each chain, with the triangles of two neighboring chains being either identically oriented, or at an angle of  $180^\circ$  to each other (Fig. 2c). The question of the type of defect that is revealed by such a decoration requires a separate study. The minimum dimension of the microphase particle that could be observed by studying thin NaCl:EuCl<sub>2</sub> layers in transmitted light (Fig. 3) was  $\sim 0.01 \mu$ .

The extracted particles of the microphase produced a microdiffraction pattern in the form of a regular hexagonal grid (Fig. 2b). It has been established that the material of the microphase has a hexagonal syngony with a parameter  $a = 8.60 \pm 0.03 \text{ \AA}$ . An identical microdiffraction was registered many times by us for particles of different form from different sections of annealed NaCl:EuCl<sub>2</sub> crystals. No other types of diffraction by the segregations of the microphase were observed. It follows therefore that the microphase is at any rate not identical with the inclusions of the activator salt EuCl<sub>2</sub> (rhombic syngony). The volume density of the microphase inclusions in various annealed samples correlates with the intensity of the low-temperature luminescence at 400 - 410 nm. We thus propose that this luminescence is due to Eu<sup>2+</sup> ions that form a complex compound of hexagonal syngony, with a probable formula  $\text{Na}_n \text{Eu}_m \text{Cl}_{2m+1}$ . We note that molecular complexes of this type were established

1)

Neither such segregations nor luminescence are observed in pure NaCl crystals used as a control.

by x-ray structure analysis in the NaCl: CdCl<sub>2</sub> system [8], where they form the compound Na<sub>6</sub>CdCl<sub>8</sub>, which also has hexagonal syngony. The latter system, however, is not a crystal phosphor, and the question of the occurrence of a new type of luminescence center was, of course, not raised in [8]. A study of NaCl:EuCl<sub>2</sub> shows that a molecular type of center in inclusions of a complex activator compound can arise in crystal phosphors, and then electron microscopy can help identify it.

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#### TEMPERATURE DEPENDENCE OF THE PITCH OF THE MAGNETIC HELIX IN RARE-EARTH METALS

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 Submitted 29 May 1969  
 ZhETF Pis. Red. 10, No. 2, 68 - 71 (20 July 1969)

Detailed neutron-diffraction investigations [1] have established that in the ordered antiferromagnetic phase the heavy rare-earth metals (Tb, Dy, Ho, Er, and Tu) are characterized by a noncollinear arrangements of the magnetic moments in space. In a sufficiently wide interval below the Neel temperature  $T_N$ , terbium, dysprosium, and holmium have a simple helical structure (HS). In these metals, which have a close-packed hexagonal lattice, the average magnetic moments along the c axis are "twisted" along a helix, and in a specified basal plane they are oriented to one side. The helical configuration of the magnetic moments can be described by a vector  $\vec{k}_0$ , the direction of which defines the axis of the helicoid, and the length determines its pitch. The angle  $\phi_0$  through which the magnetic moments are turned in neighboring basal planes is given by the relation  $\phi_0 = ck_0/2$ .

As indicated in [2], in a number of rare earth metals an important role may be played by the exchange magnetoelastic energy due to the strong dependence of the exchange interaction between the ions on the lattice parameter along the c axis. The aforementioned magnetoelastic effects were investigated in detail in [3], where it was possible, within the framework of a rather simple scheme, to reconcile the observed anomalous temperature dependence of the lattice parameter  $c(T)$  in the antiferromagnetic phase with the temperature variation of the helicoid  $\phi_0(T)$  in dysprosium.

In [2, 3], the temperature dependence of the pitch of the magnetic helix was analyzed in terms of the long-range order parameter (magnetization) at  $T < T_N$ . It is undoubtedly of interest to observe magnetic neutron scattering in the region  $T > T_N$ , where the critical fluctuations of the long-range-order with a large spin-correlation radius are significant. Naturally, these fluctuations should have a helicoidal character and it is desirable to extend the investigation of the temperature dependence of the helicoid parameters to the