# LUMINESCENCE OF TRIVALENT URANIUM

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## Abstract

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## PHYSICS

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# LUMINESCENCE OF TRIVALENT URANIUM

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Until recently it had been accepted that, among all uranium compounds, only compounds of hexavalent uranium possess the ability to luminesce, especially compounds in which uranium is present in the form of the uranyl ion ( $UO_2^{++}$ ). A large number of works, set forth in a number of monographs (($^{1-4}$)), have been devoted to the bright green luminescence of the latter. The absence of luminescence in compounds in which uranium has a valence different from 6 was specially emphasized (($^4$)). However, since the electronic configuration of the actinides is analogous to the configuration of the elements of the rare-earth group (lanthanides) (see, for example, (($^5$))), whose characteristic luminescence of trivalent ions is well known, it is natural to expect that trivalent actinide ions will also exhibit luminescence. Recently, the luminescence of ($Am^{+++}$) ions (($^6$)) and ($Pu^{+++}$) ions (($^7$)), introduced into ($LaCl_3$) crystals, was described.

In investigating artificial single crystals of fluorite ($CaF_2$), strontium fluoride ($SrF_2$), and barium fluoride ($BaF_2$), containing about 0.1-0.3% uranium and grown under strongly reducing conditions, we discovered intense luminescence whose spectrum lies in the infrared region around 2.0-2.5 ( ).

The single crystals investigated were grown from the melt in vacuum by the method developed by I. V. Stepanov (($^8$)). To create the strongly reducing conditions necessary for the formation in the crystals of uranium ions of lower valence, graphite powder (in an amount of about ($10^{-3}$) g/g) was added to the initial charge (crystals of natural fluorite crushed and subjected to special purification, or specially synthesized fine-crystalline strontium and barium fluorides*). The crystals grown in this way proved to be intensely colored red (($CaF_2$)), orange-red (($SrF_2$)), or orange (($BaF_2$)), owing to the presence of strong absorption bands in the visible part of the spectrum.

The absorption spectrum of a ($CaF_2$) crystal containing uranium and grown under reducing conditions is shown in Fig. 1. In the region up to 1.3 ( ), the spectrum was measured on an SF-4 spectrophotometer; in the interval 0.9-1.9 ( ), on the infrared spectrophotometer of N. G. Yaroslavskii (($^9$)); and in the longer-wavelength region, on an IKS-11 spectrophotometer**. As can be seen, the absorption spectrum consists of a series of bands located in the ultraviolet,

Fig. 1. Absorption and luminescence spectra (shaded) of a $CaF_2$—0.25% U single crystal. Sample thicknesses: 1—30 mm; 2—10 mm; 3—1.5 mm; 4—0.5 mm. Room temperature

Figure 1: Fig. 1. Absorption and luminescence spectra (shaded) of a $CaF_2$ —0.25% U single crystal. Sample thicknesses: 1—30 mm; 2—10 mm; 3—1.5 mm; 4—0.5 mm. Room temperature

visible, and infrared parts of the spectrum. The maxima of the principal bands at room temperature are located at about 2.22, 2.15, 1.84, 1.34, 1.23, 1.045, 1.025, 0.99, 0.95, 0.89, 0.84, 0.71, 0.69, 0.64, 0.55, 0.51, 0.45, 0.34, 0.28 ( ) (the most intense bands are indicated in boldface). The character of the absorption spectra of ($SrF_2$) and ($BaF_2$) crystals containing uranium ions. In these crystals, however, the group of intense bands in the blue-green part of the spectrum is shifted (with the number and shape of the bands preserved) toward the short-wavelength side by ( 25) m( ) in $SrF_2$ and by ( 50) m( ) in $BaF_2$, which determines the differences in the coloration of the crystals.

On cooling to the temperature of liquid air, a large number of extremely narrow lines appear in the spectra, some of which have widths of the order of 1-3 Å.

The luminescence spectrum was investigated on an apparatus consisting of a mirror monochromator with a diffraction grating (300 lines/mm), a receiver—cooled lead sulfide photoresistor, an AC amplifier, and an EPP-09 recorder. A mercury lamp SVD-250 served as the excitation source; its light was passed through a cuvette with water and heat-absorbing glass in order to eliminate infrared radiation. The excitation light was modulated by means of a perforated disk.

**Fig. 1.** Absorption and luminescence spectra (shaded) of a $CaF_2$—0.25% U single crystal. Sample thicknesses: (1)—30 mm; (2)—10 mm; (3)—1.5 mm; (4)—0.5 mm. Room temperature.

The luminescence of $CaF_2$—U crystals is already extremely intense at room temperature and consists of a number of bands located in the region 2.1-2.5 ( ) (Fig. 1)*. At room temperature four bands are observed, with maxima near 2.15, 2.21, 2.42, and 2.49 ( ). The positions of the two most short-wavelength bands in the luminescence spectrum coincide, within the accuracy of the measurement errors, with the positions of the most long-wavelength bands in the absorption spectrum; i.e., resonant transitions occur here.

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* The syntheses were carried out by I. A. Sinyukova and E. G. Chernevskaya.

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The luminescence spectra of SrF(_2)—U and BaF(_2)—U crystals are located in the same region, but differ in structural details. Thus, for example, narrow bands in the spectrum of cooled BaF(_2) crystals are observed near 2.18, 2.20, 2.29, 2.40, and 2.46 ( ). The weak dependence of the luminescence spectrum on the substance in which the uranium ions are located indicates a weak interaction of the levels responsible for the long-wavelength absorption and emission with the surrounding medium. On the contrary, the higher-lying levels corresponding to the shorter-wavelength (visible) absorption are strongly shifted when the parameters of the crystal lattice in which the ions are situated change.

There are a number of grounds for assuming that the luminescence we have found should be attributed to trivalent U(^{+++}) ions: 1) the presence of intense absorption with a characteristic banded spectrum in compounds of trivalent uranium ((^{10-14})); 2) the uniform distribution of coloration throughout the crystal, apparently associated with the closeness of the ionic radius of U(^{+++}) to the radii ions $TR^{+++}$, which, as is known, readily form mixed crystals with $CaF_2$ by the type of isomorphous substitution (15); 3) the recent detection of $U^{+++}$ ions in artificial $CaF_2$—U and $SrF_2$—U crystals by the paramagnetic-resonance method (16). The conditions under which the crystals investigated in the latter work were grown are not stated by the authors; however, they were hardly more strongly reducing than those under which the crystals studied by us were obtained.

The $U^{+++}$ ions have the electronic configuration $[R_n]\,5f^3$. The absorption and luminescence spectra observed by us should apparently be associated with forbidden transitions within the $5f$ shell, just as the spectra of rare-earth ions are determined by transitions within the $4f$ shell. In this case the transitions determining the long-wavelength absorption and luminescence should be identified with transitions between the levels $^4I_{9/2}$ (ground state) and $^4I_{11/2}$. According to Jørgensen' s calculations (14), the separation between these levels is 41008 $cm^{-1}$ (2.44 $\mu$). The following intense absorption bands (1.23 and 0.89 $\mu$) may tentatively be identified with transitions to the levels $^4I_{13/2}$ and $^4I_{15/2}$. Relatively high values of the transition probabilities, which determine the intense coloration of the crystals (crystals containing the uranium analogue—neodymium—are colorless at the same activator concentration), are characteristic of actinide ions (5).

As is known, compounds of trivalent uranium are extremely unstable, which greatly complicates the study of their optical properties. The $U^{+++}$ ions formed in the crystal lattice of $MeF_2$ are quite stable, which is apparently connected with the forced stabilization of the valence of these ions under isomorphous substitution by them of $Me^{++}$ ions.* The high stability of the optical properties

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* The luminescence spectrum shown in Fig. 1 was constructed from recorder traces without taking into account the spectral sensitivity of the apparatus, and the intensity-distribution curves are therefore only qualitative in character.

of single crystals of alkaline-earth metal fluorides activated by trivalent uranium ions makes possible a detailed investigation of their spectral-luminescent characteristics.

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* Compensation of the excess positive charge in such substitution may be accomplished in a number of ways (15).

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