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COMBINED MAGNETIC-ELECTRIC DIPOLE TRANSITIONS IN THE SPECTRA OF ALKALI-FLUORIDE CRYSTALS WITH HEXAVALENT URANIUM

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The problem of determining the nature of the elementary acts of radiation in the green luminescence of hexavalent-uranium compounds was posed in the works of S. I. Vavilov (^1). A solution of the question was obtained recently by P. P. Feofilov in studying the luminescence of single crystals ($^{2,}3$) of alkali fluorides with hexavalent uranium. In the luminescence spectra of LiF—U and NaF—U at $T = 77^\circ$ K, two "principal" electron-vibrational series of lines are observed, present in all specimens, and many "variable" lines, situated mainly on the short-wavelength side of the series. Studies (^2) of the polarized luminescence of LiF—U and NaF—U single crystals showed that the luminescence centers responsible for many lines are anisotropic formations oriented in the lattice along the symmetry axes C_4, while the transitions in the centers for individual lines correspond to electric or magnetic dipoles directed along the axes of the centers. Thus, according to (^2), the total luminescence of hexavalent uranium in MeF—U is a superposition of spectra of magnetic and electric dipole radiation.

In order to obtain further information on the structure of the luminescence centers MeF—U and on the multipolarity of the transitions, we studied the effect of uniaxial-compression deformation on the low-temperature luminescence spectra of LiF—U and NaF—U single crystals (the so-called "piezospectroscopic effect" (^4)); in doing so, we found a variety of patterns of deformation splitting for different MeF—U lines, which indicates, in agreement with the multiplicity of spectra, the existence of different types of complex luminescence centers. The symmetry properties of these centers were found, and models satisfying them were proposed, constructed on the assumption that the centers are uranyl ions UO_2^{2+} embedded in the MeF lattice and substituting for F^-—Me^+—F^-, with different methods of compensation of the excess charge of UO_2^{2+} by oxygen leading to the formation of uranyl centers of different types. The multipolarity of transitions was determined, corresponding for many MeF—U lines to magnetic or electric dipole transitions. It was also established that the optical transitions in some lines correspond to a third type—mixed magnetic-electric dipole radiation. The present communication is devoted to this interesting phenomenon of combined multipolarity of the MeF—U luminescence lines.*

Determination of the multipolarity of a line in the piezospectroscopic effect is based on studying the spatial distribution of the intensity and polarization of the radiation (absorption) for separate components of the deformation splitting (^4). The corresponding experiment consists in comparing, in polarized light, the spectra of uniaxially stressed crystals for two nonequivalent observation directions L_1 and L_2, differing by 90°. In this case, for electric dipole transitions the spectrum observed in pola-

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* A detailed description of the properties of deformation splitting of the luminescence lines of LiF—U and NaF—U is given in (^5).

···polarization with the electric vector $E \parallel N$, where N is the normal to the plane (L_1, L_2). The spectrum in $E \perp N$ will change. For magnetic-dipole transitions the opposite picture is observed: preservation of the spectrum in $E \perp N$ and its change in $E \parallel N$. The indicated criterion follows from the most general properties of the spatial distribution of intensity and polarization of dipole radiation and can be applied in the study of any systems with an anisotropic distribution of radiation (absorption). It is used, in particular, for uniaxial crystals, when spectra observed along the C axis (the so-called "α-spectrum") and across the axis ("π-spectrum" for $E \parallel C$ and "σ-spectrum" for $E \perp C$) are compared (6). In the case of cubic crystals such a study is impossible, since both types of dipole transitions give an isotropic intensity distribution. Directed deformation is a factor that introduces anisotropy, for it leads to splittings in the spectrum, the components of which in principle possess an anisotropic distribution of intensity (in the case of anisotropic centers, for example, these components are associated with centers of a definite orientation in the lattice (4)). The convenience of the piezospectroscopic method lies in the fact that, to determine the multipolarity, a qualitative comparison of the relative intensity of the splitting components in the spectrum at different L is usually sufficient.

The investigation was carried out on oriented single crystals of LiF—U and NaF—U*, subjected to uniaxial compression along the symmetry axes C_4 or C_2 ($T = 77$°K). The spectra were observed in polarized light along two nonequivalent directions L_1 and L_2: for $P \parallel C_4$ (Fig. 1a)—along the compression axis P ($L_2 \parallel P$, "longitudinal" observation) and perpendicular to it ($L_1 \perp P$, transverse observation); for $P \parallel C_2$ (Fig. 1b)—transverse observation along two axes $L_1 \parallel C_2$ and $L_2 \parallel C_4$. Since the luminescence of MeF—U is polarized (2), the splitting pattern must depend on the conditions of its excitation (4). Therefore the spectra along L_1 and L_2 were studied under fixed excitation conditions (direction M and polarization of the exciting light from an SVDSh-1000 lamp with a UFS-1 filter).

It was found that deformation causes reversible polarized splitting of the majority of MeF–U lines; moreover, for many lines, on passing from L_1 to L_2 (the excitation conditions fixed), the splitting pattern changes only in one of the polarization states $E \parallel N$ or $E \perp N$, which indicates, respectively, the magnetic or electric nature of the lines. At the same time, for a whole series of lines a change of the spectrum was observed in both polarization states. A number of types of deformation splitting were noted for which the indicated phenomenon is characteristic.

A. A close group of NaF–U lines of different intensity ($\lambda\lambda$ 5481, 5479, 5473, 5472, 5470 Å), located on the short-wavelength side of the main series, and the head line λ 5225 Å of the "additional" luminescence series of LiF–U (^{5}), located between the main series. For $P \parallel C_4$ and $P \parallel C_2$ doublet splitting is observed (Fig. 1, top), and for some NaF–U lines the long-wavelength components of the doublets at $P \parallel C_2$ have a "fine" structure.

The spectrograms of Fig. 1a show the deformation doublets of NaF–U for $P \parallel C_4$, taken with the arrangement shown in Fig. 1a at left (excitation by unpolarized light). It is clearly seen that the transition from $L_1 \perp P$ to $L_2 \parallel P$ causes a change of the pattern in both polarization states $E \parallel N$ and $E \perp N$. In $E \perp N$ for L_1 one short-wavelength component is observed, and for L_2–both components of the doublets. In the polarization $E \parallel N$, for L_1 and L_2 both components are visible, but their relative intensity is reversed. The change of the splitting pattern in both sta–

* Single crystals grown at the Institute of Crystallography, Academy of Sciences of the USSR, were used.

states of polarization occurs for $P \parallel C_4$ and upon excitation of luminescence by polarized light with $E_v \parallel P$ and $E_v \perp P$. Figure 1b shows the deformation doublet λ5225 Å for $P \parallel C_2$ and two different conditions of excitation by unpolarized light ($M_1 \parallel C_4$ and $M_2 \parallel C_2$–see Fig. 1b, left). It is seen that in both cases the transition from L_1 to L_2 produces a change in the form of the doublet both for $E \parallel N$, where a qualitative change in the relative intensity of the components occurs, and for $E \perp N$, where the number of observed components changes.

B. The intense LiF–U line λ5052 Å (weaker LiF–U lines $\lambda\lambda$5134 and 4984 Å also have a similar type of splitting). For $P \parallel C_4$, triplet splitting occurs (Fig. 1, top). When observing along L_1 and L_2 (according to the scheme of Fig. 1a), changes occur in the spectrum for $E \parallel N$ and $E \perp N$ (Fig. 1a): for $L_1 \perp P$ the long-wavelength component of the triplet is visible in $E \parallel N$ and $E \perp N$, the middle one in $E \parallel N$, and the short-wavelength one in $E \perp N$; for $L_2 \parallel P$, the entire triplet is visible in $E \parallel N$ and $E \perp N$. For $P \parallel C_2$, the line λ5052 Å undergoes a complex, apparently triplet, polarized splitting which, because of its small magnitude, could not be resolved and investigated.

C. For some LiF–U lines ($\lambda\lambda$5164, 5160 Å, etc.), which possess a very small splitting for $P \parallel C_4$, it was possible to establish the very fact of a change in the spectrum in the two polarization states $E \parallel N$ and $E \perp N$ when observed according to the scheme of Fig. 1a.

The phenomenon described—the dependence of the pattern of deformation splitting of the lines on the direction of observation in both polarization states parallel and perpendicular to the normal to the plane of observation—directly indicates that the radiation in the lines is a mixture of electric- and magnetic-dipole radiation. It should be noted that the very phenomenon of combined multipolarity of transitions is observed in optics extremely rarely, since different types of transitions obey different selection rules, and their intensities usually differ by an order of magnitude.*

Important conclusions about the structure of the centers of mixed emission MeF—U can be drawn from the properties of the deformation splitting of the lines, which point to a complex anisotropic structure of the centers. Thus, the character of the splitting described in A allows one to consider (^{4}) that the corresponding luminescence centers are "rhombic." The formula relating the shift Δ of the transition frequency in such a center to the strain tensor $\{\sigma_{ik}\}$ has the form (^{4})

$$\Delta = A_1\sigma_{zz} + A_2(\sigma_{xx} + \sigma_{yy}) + A_3\sigma_{xy} \tag{1}$$

(in the coordinate system of the crystallographic cube). The calculated splitting pattern for these centers agrees well with that observed for $P \parallel C_4$ and $P \parallel C_2$ (in the number, polarization, and shifts of the splitting components and their dependence on the excitation conditions), if it is assumed that the transition oscillator in the center consists of a magnetic dipole, directed—

* One may cite works (^{7}), where the mixed quadrupole—magnetic-dipole nature of a number of lines of Pb atoms was established from the Zeeman-effect pattern, and (^{8}), where from an analysis of polarized spectra of crystalline salts of Eu^{3+} it was concluded that a number of lines belong to a mixture of magnetic-dipole and electric-dipole transitions.

Fig. 1. Polarized deformation splitting of lines of mixed multipolarity MeF—U. At the top—spectrograms of MeF—U lines without deformation and with deformation, taken in unpolarized light for $L \perp P$. a, b—spectrograms in polarized light and the corresponding schemes of the arrangement of the directions P, M, L, N relative to the axes of the cube for $P \parallel C_4$ (a) and $P \parallel C_2$ (b); for each L, the directions of the polarization vector $\bar{E}$ relative to N ($\parallel$ or $\perp$) are given.

polarized along the $[001]_z$ axis of the center and comparable with it in intensity ($I_e \simeq 2I_m$), a linear electric dipole $\parallel [\bar{1}10]_{xy}$; the absorbing oscillator for λ 365 mμ is electric $\perp z$. In this case in formula (1) $A_3 \simeq 0$ (because of this, the splitting for $P \parallel C_2$ has the form of a doublet with fine structure, which arises owing to the difference of A_3 from zero), $A_1 \simeq -0.01$ (in cm^{-1}/kg$\cdot$mm^{-2}), $A_2 \simeq 0.25$—for λ 5479 Å NaF—U, and $A_1 \simeq -0.2$ and $A_2 \simeq 0.4$—for λ 5225 Å

Figure with absorption-line photographs and polarization/geometric schemes. Labels visible in the image: v; NaF-U, $P \parallel C_4$, $\lambda 5479$ Å, 5473 Å, 5472 Å, 5470 Å; $p = 0$, $p \neq 0$; LiF-U, $P \parallel C_4$, $\lambda 5052$ Å; LiF-U, $P \parallel C_2$, $\lambda 5225$ Å. Panels labeled a and b. In panel a: $L_1 \perp P$, $L_2 \parallel P$, M, N, P, L_1, L_2, $\perp$, $\parallel$; right-side labels: NaF-U $\lambda 5470$-5480 Å, LiF-U $\lambda 5052$ Å. In panel b: N, P, M_1, M_2, L_1, L_2, $\perp$, $\parallel$; $L_1 \parallel C_2$, $L_2 \parallel C_4$; right-side labels: $M_1 \parallel C_4$, $M_2 \parallel C_2$; bottom label: LiF-U $\lambda 5225$ Å.

Figure 1: Figure with absorption-line photographs and polarization/geometric schemes. Labels visible in the image: v; NaF-U, $P \parallel C_4$, $\lambda 5479$ Å, 5473 Å, 5472 Å, 5470 Å; $p = 0$, $p \neq 0$; LiF-U, $P \parallel C_4$, $\lambda 5052$ Å; LiF-U, $P \parallel C_2$, $\lambda 5225$ Å. Panels labeled a and b. In panel a: $L_1 \perp P$, $L_2 \parallel P$, M, N, P, L_1, L_2, $\perp$, $\parallel$; right-side labels: NaF-U $\lambda 5470$-5480 Å, LiF-U $\lambda 5052$ Å. In panel b: N, P, M_1, M_2, L_1, L_2, $\perp$, $\parallel$; $L_1 \parallel C_2$, $L_2 \parallel C_4$; right-side labels: $M_1 \parallel C_4$, $M_2 \parallel C_2$; bottom label: LiF-U $\lambda 5225$ Å.

LiF—U. The properties of the splitting B for $P \parallel C_4$ are likewise explained on the assumption of rhombic centers with a formula of the type

$$\Delta = A_1\sigma_{xx} + A_2\sigma_{yy} + A_3\sigma_{zz}, \tag{2}$$

for which the oscillator consists of two mutually perpendicular linear dipoles of comparable emission intensity—electric and magnetic—oriented in the center along the cube axes (for example, z, y).

Additional information on the symmetry of the rhombic centers is obtained from the mixed character of the multipolarity of the transitions. First of all, since the selection rules for magnetic-dipole radiation allow transitions between states of the same parity, and for electric radiation between states of opposite parity, the combined multipolarity of the observed type means that the luminescence centers do not possess inversion (if the selection rules are determined by the "static" symmetry of the luminescence center). Further, from the mutually perpendicular arrangement of the electric and magnetic dipoles in centers of both types it may be concluded that the symmetry of the rhombic centers belongs to the group C_{2v}. It is precisely in this group that there is a representation (B_1 or B_2 (9)) according to which mutually perpendicular components of the matrix elements of the electric and magnetic dipole moments, lying in the plane perpendicular to the C_2 axis of the group C_{2v}, transform simultaneously. In the MeF—U centers under consideration, their C_2 axis is directed, as follows from (1), (2), and the arrangement of the dipoles, along $[110]_{xy}$ (case A) or along $[100]_x$ (case B).

Obviously, models of centers satisfying only the required symmetry properties are not unique. In particular, uranyl complexes have symmetry C_{2v} in which, in the equatorial environment of a linear ($\parallel z$) uranyl ion, of the four nearest F^- ions two neighboring ions (A) or one (three) ions (B) F^- are replaced by

O^{2-}, partially or completely compensating the excess charge of UO_2^{2+}. The absence of information on the electronic states of the free uranyl does not, unfortunately, permit fuller use of the data obtained on the symmetry of the MeF —U luminescence centers and the multipolarity of the transitions.

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CITED LITERATURE

1. S. I. Vavilov, *Vestn. LGU*, No. 1, 5 (1946); *Collected Works*, 2, 1952, p. 252; *Trudy Gos. optich. inst.*, **20**, no. 132, 4 (1950).
2. P. P. Feofilov, *Optika i spektroskopiya*, **7**, 842 (1959); **8**, 824 (1960); **11**, no. 3 (1961); L. M. Belyaev, G. F. Dobrzanskii, P. P. Feofilov, *Izv. AN SSSR, ser. fiz.*, **25**, 548 (1961).
3. L. M. Belyaev, Z. B. Perekalina et al., *Kristallografiya*, **5**, 757 (1960).
4. A. A. Kaplyanskii, *Optika i spektroskopiya*, **5**, 677 (1959); **10**, 165 (1961); *Izv. AN SSSR, ser. fiz.*, **25**, 20 (1961); *Proc. Int. Conf. Semicond. Phys.*, Prague, 1960, p. 356.
5. A. A. Kaplyanskii, N. A. Moskvin, *Optika i spektroskopiya*, **13**, no. 4 (1962); **14**, no. 4 (1963).
6. D. McClure, *Solid State Phys.*, **9**, 1959, p. 400.
7. F. A. Jenkins, S. Mrozowski, *Phys. Rev.*, **59**, 808 (1941); **60**, 225 (1941).
8. K. H. Hellwege, H. G. Kahle, *Zs. Phys.*, **129**, 62, 85 (1951).
9. L. D. Landau, E. M. Lifshitz, *Quantum Mechanics*, 1959.

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