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Abstract

Full Text

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ON THE DECREASE IN THE DECAY TIME CONSTANT OF THE LUMINESCENCE OF EUROPIUM BENZOYLACETONATE UNDER THE INFLUENCE OF HYDROSTATIC COMPRESSION

As is known, the characteristic spectra of rare-earth ions are explained by dipole and magnetic-dipole transitions between levels of the same parity. In particular, for the $4f^6$ configuration the transitions ${}^5D_0 \rightarrow {}^7F_0$ and ${}^5D_0 \rightarrow {}^7F_2$ must be purely dipole (owing to the prohibition of magnetic radiation for the transition $0 \rightarrow 0$ and transitions with $\Delta J = 2$), while the transition ${}^5D_0 \rightarrow {}^7F_1$ is mixed –dipole and magnetic-dipole.

The presence of dipole transitions is due to the odd part of the environmental potential, and their probability is proportional to the quantity:

$$\beta \sim n^2 \left(\frac{U_{\text{odd}}}{E_{\text{even}} - E_{\text{odd}}} \right)^2,$$

where the coefficient n^2 is related to the number of levels of opposite parity that must be taken into account in calculating the influence of the odd part of the environmental potential U_{odd} , and $(E_{\text{even}} - E_{\text{odd}})$ is the energy difference between levels of opposite parity ⁽¹⁾.

It may be assumed that, as pressure is increased, the even and odd levels come closer together in energy (mainly at the expense of the upper, odd levels; Table 1), the quantities n and U_{odd} increase (the latter if the symmetry remains unchanged), and therefore the degree of violation of the parity selection rule increases, i.e., the luminescence decay time constant should decrease.

Table 1

Line positions in cm^{-1}

Transition	Normal pressure	17 kbar
${}^5D_0 \rightarrow {}^7F_0$	17243	17226
${}^5D_0 \rightarrow {}^7F_1$	16928	16896
${}^5D_0 \rightarrow {}^7F_1$	16386	
${}^5D_0 \rightarrow {}^7F_1$	16807	16778
${}^5D_0 \rightarrow {}^7F_2$	16323	16315
${}^5D_0 \rightarrow {}^7F_2$	16308	16296

We have carried out a study of the kinetics of the luminescence of europium benzoylacetate in the region of the transition ${}^5D_0 \rightarrow {}^7F_2$ (see Table 1) as pressure was raised to 17 kbar. Sodium chloride served as the pressure-transmitting medium. The pressure in the chamber was estimated from the force produced on the movable piston and on the piston closing the end of the chamber. The force on the latter was measured by strain gauges.

The results of the lifetime measurements are as follows:

Pressure, kbar	0	6	8	9	12	15	17
Decay constant, 10^{-4} sec	5.6	4.9	4.8	3.9	3.3	3.1	3.3

The decay time constant does indeed decrease. It is necessary to note the following facts: with increasing pressure, the gap between terms apparently changes (as indicated by the successive decrease in the transition frequency ${}^5D_0 \rightarrow {}^7F_0$ —see Table 1). Evidently, still higher odd levels should decrease even more rapidly with increasing pressure.

At the same time, the magnitude of the “crystalline” splitting of the level (in the present case, the difference between the energies of the outer sublevels of the 7F_1 level), which depends on the potential of the surroundings, remains practically unchanged. It is true that in this case an increase in symmetry occurs, as evidenced by the merging of two of the three sublevels of 7F_1 . Nor is any noticeable change observed in the ratio of the intensities of transitions differing in nature, ${}^5D_0 \rightarrow {}^7F_0$ and ${}^5D_0 \rightarrow {}^7F_1$, which indicates preservation of the ratio between the even and odd parts of the potential of the surroundings.

If this is so, then the decrease in the decay time constant is apparently explained by a decrease in the energy gap between the even and odd levels. To explain the observed decrease in lifetime, the magnitude of the displacement of the odd levels must be $\sim 10^4 \text{ cm}^{-1}$.

Since the odd levels of rare-earth ions in solids often lie beyond the limits of possibility for their investigation, the most valuable information consists in determining this gap and the degree of their interaction with the even levels.

It should be noted that between the even and odd levels of europium there are the so-called triplet levels of the organic ligand, which play a major role in the transfer of excitation energy to the rare-earth ion. It is therefore quite probable that, along with the reasons considered for the decrease in the decay constant, there are also other reasons not taken into account by us.

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Note: Figure translations are in progress. See original paper for figures.

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