ON THE TETRAGONAL LUMINESCENCE CENTER OF THE Eu^{3+} ION IN CaF_{2}

Corresponding Member of the Academy of Sciences of the USSR G. B. Bokii, L. S. Gaiterova,

1968

SovietRxiv

Abstract

Full Text

UDC 548.0:535.37

PHYSICS

Corresponding Member of the Academy of Sciences of the USSR G. B. Bokii, L. S. Gaiterova,
M. I. Gaiduk, O. F. Dudnik, E. N. Murav' ev

ON THE TETRAGONAL LUMINESCENCE CENTER OF THE Eu^{3+} ION IN CaF_2

In connection with the creation of quantum generators, the study of the structure of luminescence centers of rare-earth ions (TR) is of considerable interest. As is known, a number of quantum generators have been realized on the basis of fluorite activated with TR. The main difficulty encountered in the study of such systems as CaF_2—TR^{3+} is the existence in them of various luminescence centers. This is due to the different possible ways of compensating the excess positive charge of the rare-earth ion replacing divalent Ca^{2+} in the cubic fluorite lattice (^{1}), for example, replacement of a fluorine ion F^- in the nearest environment of TR^{3+} by an oxygen ion or introduction of an F^- ion into the octahedral void nearest to TR^{3+} (types I and II in (^{1}), respectively). The mode of compensation determines the symmetry and magnitude of the crystal field acting on the rare-earth ion and, consequently, also the positions of the Stark components of the energy levels and the probabilities of radiative and nonradiative transitions, which account for the substantial differences in the lasing ability of different luminescence centers. A change in transition probabilities leads to differences in the kinetics of luminescence of the TR ion, which can serve as one of the methods for identifying spectra corresponding to different luminescence centers.

In the present work the luminescence of Eu^{3+} in CaF_2 was investigated. The energy-level scheme of Eu^{3+} is convenient for realizing a four-level lasing system owing to the large separation between the terminal level of the working transition and the ground state. It is no accident that the greater part of quantum generators based on organic liquids has been created using Eu^{3+} ions as the active impurity. Hence the great interest in the spectroscopic study of this rare-earth ion in various media is understandable. In contrast to other TR, the structure of luminescence centers of Eu^{3+} cannot be investigated by means of electron paramagnetic resonance (since the ground state $^7F_0$ is nonmagnetic).

In work (^{3}), by the magneto-optical method, the absorption of the Eu^{3+} ion in CaF_2 (transition $^7F_0 \to {}^5D_1$) was studied, and the assignment of certain lines

Fig. 1. Oscillograms of luminescence decay of the Eu^{3+} ion in CaF_2 for transitions from the levels: a $-^5D_0$, b $-^5D_1$, c $-^5D_2$ and d $-^5D_3$ (time marks every 2 μsec; T = 77°K)

Figure 1: Fig. 1. Oscillograms of luminescence decay of the Eu^{3+} ion in CaF_2 for transitions from the levels: a $-^5D_0$, b $-^5D_1$, c $-^5D_2$ and d $-^5D_3$ (time marks every 2 μsec; T = 77°K)

of this transition to cubic and tetragonal centers was established. In the present work a complete spectroscopic investigation was carried out of the tetragonal center of Eu^{3+} in CaF_2 (type II), which it was possible to isolate in studying the kinetics of luminescence.

Under pulsed excitation of Eu^{3+} in CaF_2, a luminescence build-up effect was found for certain lines, which it was possible to group into a system of transitions belonging to one center (Fig. 1). On the basis of group-theoretical analysis and calculations according to crystal-field theory, the isolated center was classified as tetragonal C_{4v}. The presence of this center is explained by compensation of the excess positive charge of Eu^{3+} by an interstitial F^- (1). It should be noted that this center predominates in fluorite crystals fluorinated by the method developed in the single-crystal department of the P. N. Lebedev Physical Institute of the Academy of Sciences of the USSR (2).

Luminescence was observed from the levels of the first excited multiplet ^5D_j ($j = 0, 1, 2, 3$) in the range 4000–8000 Å. For example, Fig. 2 shows the luminescence from the level $^5D_3$. The presence of nonradiative transitions $^5D_3 \to {}^5D_2 \to {}^5D_1 \to {}^5D_0$ leads to a build-up of luminescence from the levels ^5D_j ($j = 0, 1, 2$), which can be observed under pulsed excitation of the crystals.

Fig. 1. Oscillograms of the decay of luminescence of the Eu^{3+} ion in CaF_2 for transitions from the levels: a $-^5D_0$, b $-^5D_1$, c $-^5D_2$ and d $-^5D_3$ (time marks every 2 μsec; $T = 77$°K)

Each level corresponds to a definite build-up time $t_{\max}$, and therefore all transitions with the same $t_{\max}$ must be assigned to one excited level.

The transitions between the sublevels $^5D_j - {}^7F_j$ mainly obey the selection rules for electric and magnetic transitions for a center of C_{4v} symmetry. Under the action of the time-reversal operator $\hat{T}$, the wave functions describing a state with angular momentum I, projection $I_z = M$, and parity p transform as follows [4]:

$$\hat{T}\psi(IM) = (-1)^{I-M+p}\psi(I-M). \tag{1}$$

Applying (1) to the matrix elements of the transitions $^5D_I - {}^7F_{I'}$, one can obtain the following selection rules: magnetic dipole transitions are allowed between states for which the sum $(I+I')+(\mu+\mu')+(p+p')$ is odd, while electric dipole

Luminescence spectrum corresponding to the transitions ${}^5D_3 \to {}^7F_j$ $(j = 0, 1, 2)$: a—at 77 K, b—at 300 K

Figure 2: Luminescence spectrum corresponding to the transitions ${}^5D_3 \to {}^7F_j$ $(j = 0, 1, 2)$: a—at 77 K, b—at 300 K

transitions are allowed between states for which this sum is even; here μ is the crystal quantum number.

Fig. 2. Luminescence spectrum corresponding to the transitions ${}^5D_3 \to {}^7F_j$ $(j = 0, 1, 2)$:
a—at 77 K, b—at 300 K.

These selection rules are well obeyed. However, for transitions from the Stark components of the level ${}^5D_3$ there is a slight deviation from these rules, which apparently can be explained by mixing of the level ${}^5D_3$ with higher excited levels. The most intense transitions for the C_{4v} center in CaF_2—Eu^{3+} are magnetic-dipole transitions with changes $\Delta l = 1$, which indicates a small admixture of states of the upper shells $(5d, 5g$, etc.$)$ to the $4f$ shell of Eu^{3+}.

Using the selection rules, it was possible to describe the energy levels corresponding to the irreducible representations of the point symmetry group C_{4v} and to calculate the crystal-field parameters. The crystal-field potential of symmetry C_{4v} has the form

$$V = \alpha B_{20} O_2^0 + \beta \left[B_{40} O_4^0 + B_{44} (O_4^4 + O_4^{-4}) \right] + \gamma \left[B_{60} O_6^0 + B_{64} (O_6^4 + O_6^{-4}) \right], \quad (2)$$

where $B_{mn} = A_{mn} \langle r^n \rangle$ are the crystal-field parameters; α, β, γ are equivalent operators; O_n^m are angular-momentum operators. The parameters B_{20}, B_{40}, and B_{44} are respectively equal to 250, -176, and -1240 cm^{-1}. The values of the parameters α, β, γ for the lower multiplet ${}^7F_j$ and the first excited multiplet ${}^5D_j$ of Eu^{3+} are given in Table 1. The level scheme of Eu^{3+} for the C_{4v} center is presented in Fig. 3.

Fig. 3. Energy-level scheme of the Eu^{3+} ion in CaF_2 for the tetragonal center C_{4v}:
a—ground multiplet ${}^7F_j$;
b—first excited multiplet ${}^5D_j$.

Fig. 4. Positions of the Stark components of the levels of Eu^{3+} in CaF_2:
a—calculated theoretically;
b—observed experimentally.

From a comparison of the experimentally found and theoretically calculated magnitudes of the splittings of the Stark components of the levels ${}^7F_j$ and ${}^5D_j$

(Fig. 4), it follows that the optical spectrum of the isolated center is described rather well by the parameters of the tetragonal center.

As indicated above, the C_{4v} center in CaF_2—Eu^{3+} arises from the cubic center O_h, formed by 8 F^- ions, by addition to the nearest interstice of a compensating F^- ion along the cube axis C_4 (1). The correspondence of the optical spectrum investigated to such a model of the center is, it seems to us, confirmed by the following facts:

1. The position of the Stark components of the levels is determined by a crystal field of predominantly cubic symmetry.
2. The relatively small tetragonal splitting of the sublevels Γ_3, Γ_4, and Γ_5 is due to the appearance of the axial second-order parameter A_{20} and to a decrease in the ratio of the fourth-order parameters A_{40}/A_{44} in comparison with a purely cubic field. Both facts are evidently consistent with the presence of an additional F^- ion along the C_4 axis.

Table 1

Values of the equivalent operators α, β, γ for the two lowest multiplets of Eu^{3+}*

Levels	α	β	γ
$^7F_0$	0	0	0
$^7F_1$	$-2 \cdot 10^{-1}$	0	0
$^7F_2$	$-349 \cdot 10^{-4}$	$-106 \cdot 10^{-4}$	0
$^7F_3$	$-741 \cdot 10^{-5}$	$670 \cdot 10^{-6}$	$-172 \cdot 10^{-6}$
$^7F_4$	$260 \cdot 10^{-5}$	$599 \cdot 10^{-6}$	$63 \cdot 10^{-6}$
$^7F_5$	$741 \cdot 10^{-5}$	$19 \cdot 10^{-5}$	$-12 \cdot 10^{-6}$
$^7F_6$	$101 \cdot 10^{-4}$	$-122 \cdot 10^{-6}$	$1 \cdot 10^{-6}$
$^5D_0$	0	0	0
$^5D_1$	$-536 \cdot 10^{-4}$	0	0
$^5D_2$	$-421 \cdot 10^{-5}$	$292 \cdot 10^{-5}$	0
$^5D_3$	$392 \cdot 10^{-5}$	$-314 \cdot 10^{-8}$	$-40 \cdot 10^{-6}$

* The values α, β, γ were calculated allowing for $L-S$ mixing.

3. In the luminescence spectrum the magnetic-dipole transitions are intense. The relatively small contribution of electric-dipole transitions, allowed for a center of C_{4v} symmetry, confirms the small admixture of the tetragonal state to the cubic one.
4. The largest level splittings for centers with oxygen-free compensation (type II according to (1)) correspond to the center under consideration and may be associated with the close location of the compensating ion.

In conclusion, it is interesting to note the significant shift of the $^5D_0$—$^7F_0$ transition in centers with oxygen compensation (type I in (1)). In the crystals we studied, the energy of the $^5D_0$—$^7F_0$ transition for centers with oxygen compensation is 17 437 cm^{-1} (as also in (1)), whereas for type-II centers it is 17 290 cm^{-1}. This short-wavelength shift of 150 cm^{-1} with an increase in the field strength in centers with oxygen compensation is inexplicable from the standpoint of crystal-field theory and, apparently, is due to the weak covalent Eu–O bond.

Institute of Radio Engineering and Electronics
Academy of Sciences of the USSR

Received
27 IV 1967

REFERENCES

1. P. P. Feofilov, *Izv. AN SSSR, Ser. Fiz.*, **26**, 435 (1962); I. V. Stepanov, P. P. Feofilov, *DAN*, **108**, 515 (1956).
2. Yu. K. Voron' ko, V. V. Osiko et al., *FTT*, **7**, 267 (1965).
3. B. P. Zakharchenya, I. B. Rusanov, *FTT*, **8**, 41 (1966).
4. K. S. Tomas, S. Singh, G. H. Dieke, *J. Chem. Phys.*, **38**, 2180 (1963).

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