SOVIET PHYSICS JETP VOLUME 22, NUMBER 3 MARCH, 1966

ANALYSIS OF THE OPTICAL SPECTRA OF Pr^{3+}, Nd^{3+}, Eu^{3+} *AND* Er^{3+} *IN FLUORITE CRYSTALS (TYPE 1)*[1] *BY THE CONCENTRATION SERIES METHOD*

Yu. K. VORON'KO, A. A. KAMINSKIĬ, and V. V. OSIKO

P. N. Lebedev Physics Institute, Academy of Sciences, U.S.S.R.

Submitted to JETP editor March 10, 1965

J. Exptl. Theoret. Phys. (U.S.S.R.) **49**, 724-729 (September, 1965)

A method is proposed for the analysis of the optical spectra of fluorite-type crystals with rare-earth ion impurities using the concentration dependences of the spectral line intensities—the concentration series method. The absorption and luminescence spectra of fluorite crystals with Pr^{3+}, Nd^{3+}, Eu^{3+} and Er^{3+} impurities are analyzed using the concentration series method. Systems of lines, belonging to rare-earth ion centers of different structure, are isolated from the general spectra. The experimental results obtained are compared with the data of a thermodynamic calculation of the equilibria of the optical centers in $CaF_2—TR^{3+}$ (type 1) crystals.[1]

1. INTRODUCTION

THE optical spectra of fluorite-type (CaF_2) crystals with admixtures of trivalent rare-earth ions (TR^{3+}) consist of sets of line groups, lying in the ultraviolet, visible, and near infrared regions of the spectrum. The spectral positions and the number of these groups are in agreement with the transitions of the corresponding free TR^{3+} ions.[2-4] On the other hand, even at helium temperatures, the number of lines in each of the groups is considerably greater than the theoretical number of lines calculated on the assumption of a uniform distribution of TR^{3+} ions in centers with the same structure. This is because, due to the characteristic features of the crystallochemical structure of $CaF_2—TR^{3+}$, TR^{3+} ions are actually distributed in centers of several types having different structures. Each of these centers has its own set of Stark components and, consequently, its own set of lines in the optical spectrum.

There are several experimental methods for investigating the structure of TR^{3+} centers in fluorite-type crystals. A detailed review of these methods is given in the paper of Feofilov and Kaplyanskiĭ.[5] The fullest information about the structure of TR^{3+} centers (which are paramagnetic) may be obtained by the electron paramagnetic resonance method, which makes it possible to establish quite reliably the symmetry of the electric crystal field of TR^{3+} ions and the relative content of a given type of center at a given concentration of TR^{3+}. Relaxation investigations also make it possible to determine the first excited level. Other methods, which may yield information on the structure of TR^{3+} centers in fluorite-type crystals, include the investigation of the Zeeman effect, the polarized luminescence, and the piezospectroscopic effect. In some cases, these methods make it possible to establish the symmetry of the centers corresponding to given spectral lines. However, none of these methods allows us in practice to obtain anything like a complete analysis of the Stark structure of the optical spectra, i.e., to isolate from the general spectra of $CaF_2—Tr^{3+}$ the systems of lines belonging to different types of TR^{3+} center.

In the present paper we propose an experimental method for the analysis of the optical spectra of $CaF_2—TR^{3+}$ (type 1) crystals using the concentration dependences of the intensities of lines with the Stark structure. This method, which we call the concentration series method, was used to analyze the spectra of Pr^{3+}, Nd^{3+}, Eu^{3+}, and Er^{3+} in the range of concentrations of the rare-earth impurities from 0.003 to 2 wt.%. Using the concentration series method in our earlier investigation[6], we isolated from the general $CaF_2—Nd^{3+}$ (type 1) spectrum, the spectra corresponding to different types of center and we identified the experimentally observed lines of the stimulated radiation of fluorite crystals containing Nd^{3+}.[7]

---

[1] The nomenclature of crystal types is in accordance with the crystallochemical classification given in[1].

2. CONCENTRATION SERIES METHOD

An approximate thermodynamic calculation of the equilibria of optical centers in CaF_2—TR^{3+} (type 1) crystals was published earlier.[8] Formulas were obtained relating the concentrations of TR^{3+} centers having different structure to the total concentration of the rare-earth element in a crystal and to the equilibrium temperature. Figure 1 shows the theoretical isotherms of the relative concentrations, and Fig. 4 in[6] the absolute concentrations of "cubic," "tetragonal," and "orthorhombic" centers.

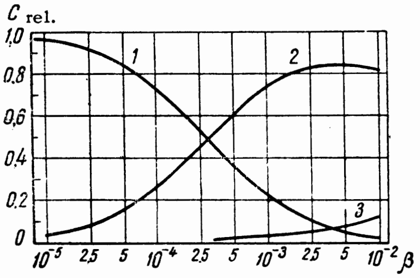

FIG. 1. Theoretical isotherms of the relative concentrations of centers of different structure in $CaF_2 - TR^{3+}$ (type 1) crystals at an equilibrium temperature of 1373°K: 1) centers of cubic symmetry; 2) centers of tetragonal symmetry; 3) centers of orthorhombic symmetry. The abscissa gives the β-fraction of the cation sites occupied by TR^{3+} ions, while the ordinate gives the relative concentrations of the centers (c_{rel}).

It follows from the thermodynamic calculation (Fig. 1) that the dependences of the concentrations of different centers on the total concentration of TR^{3+} are very characteristic. Thus, at low concentrations ($\beta < 10^{-4}$) the majority of TR^{3+} ions should be in cubic environments. On increasing the TR^{3+} concentration, the fraction of tetragonal centers should increase: for $\beta = 10^{-3}$, there should be more tetragonal centers than cubic. At still higher concentrations of TR^{3+}, there should be a considerable fraction of orthorhombic centers.

These characteristic features of the behavior of different centers form the basis of the concentration series method. The basis of the method is as follows. A series of CaF_2—TR^{3+} crystals is grown with the TR^{3+} concentration varying over a wide range, i.e., a concentration series is obtained. For each crystal in the series, the absorption spectrum of the line groups selected earlier is recorded. Next, for each Stark structure line, a dependence is plotted of the absorption coefficient on the TR^{3+} concentration. Since the crystals contain TR^{3+} centers having different structures, the concentration dependences obtained should split into several families of curves, whose behavior should reproduce the concentration curves of the corresponding centers.

For a successful analysis, the investigated CaF_2—TR^{3+} crystals must satisfy the following requirements: 1) the crystals should differ only in their TR^{3+} concentration—they should all be grown from the same raw material under completely identical thermal conditions; 2) the exact concentration of the rare-earth element in a crystal should be known and this element should be distributed uniformly throughout the volume of the crystal; 3) the Stark structure of the spectra should be well resolved; 4) the concentration of the centers should be proportional to the optical density at the maxima of the corresponding absorption lines, i.e., the Lambert—Bouguer—Beer law should be obeyed.

Preliminary investigations showed that the most suitable fluorite crystals for the investigation by the concentration series method were those containing Pr^{3+}, Nd^{3+}, Eu^{3+} and Er^{3+} impurities. These impurity ions have intense groups of absorption and luminescence lines in convenient regions of the spectrum, making it possible to carry out investigations at very low concentrations (down to 0.003% by weight). The crystals used in the investigation were synthesized by the method described earlier.[6]

3. ABSORPTION SPECTRA

The preliminary investigations of the absorption spectra were carried out at 77°K using a spectrophotometer type SP-700 in the region from 0.185 to 2.5 μ. The most convenient groups of lines were selected for further detailed investigation. The absorption in these groups was recorded with a diffraction spectrometer type DFS-12 with a 0.1 Å resolution at 77°K. Photomultipliers with antimony—cesium or oxygen—cesium photocathodes were used as the optical receivers. A signal from a photomultiplier was amplified and then recorded with a potentiometer type ÉPP-09 M1. The linearity of the potentiometer readings was checked first using the output signal. The accuracy of the determination of the spectral line positions was ±1.5 cm^{-1}. An incandescent lamp of 1.8 W (6.3 V), supplied by a storage cell, was used as the source of light. The lamp and the crystal were both immersed directly in liquid nitrogen. The light passing through the crystal was led by a quartz light pipe to the input slit of the spectrometer.

Figure 2 shows some of the concentration series of the absorption curves. It is evident that in each

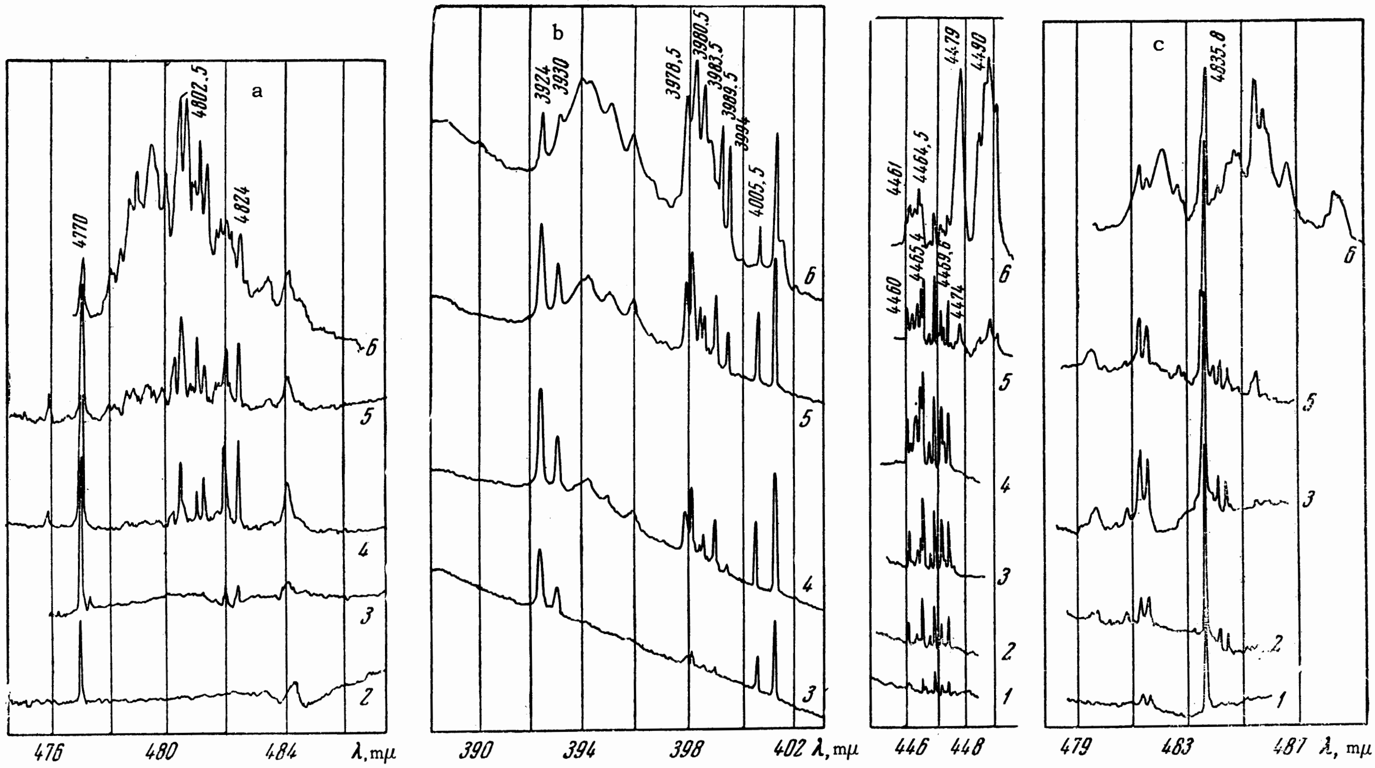

FIG. 2. Concentration series of the absorption curves of CaF$_2$–TR^{3+} (type 1) crystals: a) CaF$_2$–Pr^{3+}, transition $^3H_4 \rightarrow P_0$; b) CaF$_2$–Eu^{3+}, transition not identified; c) CaF$_2$–Er^{3+}, transitions $^4I_{15/2} \rightarrow {}^4F_{3/2,\ 5/2}$ and $^4I_{15/2} \rightarrow {}^4F_{7/2}$. TR^{3+} concentrations: 1) 0.003, 2) 0.01, 3) 0.03, 4) 0.1, 5) 0.3, 6) 1 wt.%.

of the series the line intensities change as the TR^{3+} concentration is increased: some lines become relatively weaker and almost disappear at high concentrations, while other lines which are intense at high concentrations are almost completely absent at low concentrations. For each line (with the exception of very weak and faint lines), we determined the peak values of the absorption coefficient. The dependence of the absorption coefficient on the activator concentration in a crystal is plotted on a double-logarithmic scale in Fig. 3. The curves in Fig. 3 and the absorption lines in Fig. 2 are marked with the corresponding wavelengths. In order not to overcrowd Fig. 3 with too many curves, this figure gives the dependences for only some of the lines Several of these lines correspond to absorption line groups not given in Fig. 2. It is evident that all the dependences plotted in Fig. 3 split up, in accordance with the theoretical predictions, into systems of parallel curves, representing different types of center. We were able to detect three such systems: they are denoted by L, M, and N in Fig. 3.

Next, we attempted to carry out the same analysis using the luminescence line intensities. The luminescence spectra were also recorded with the DFS-12 spectrometer at 77°K. A crystal, attached to a quartz light pipe, was immersed directly into

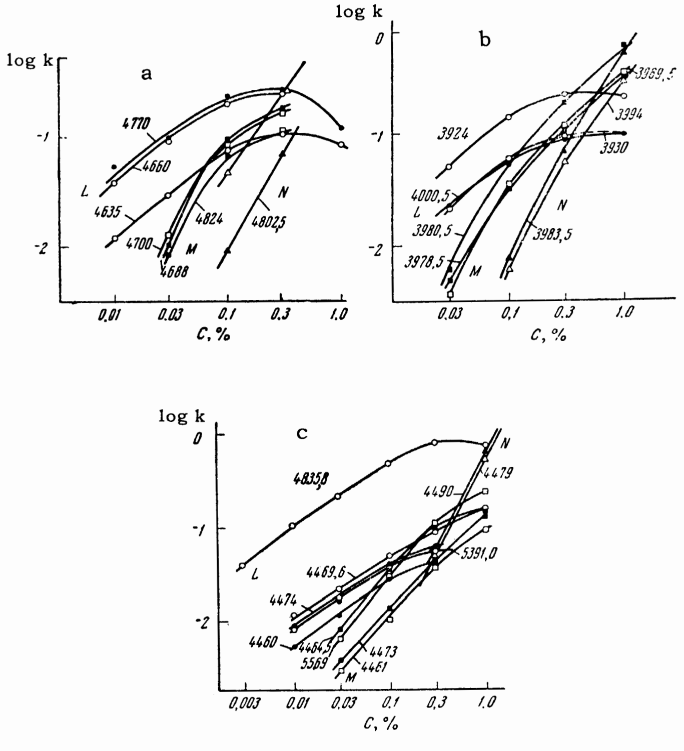

FIG. 3. Concentration dependences of the absorption in individual Stark structure lines of the spectra of CaF$_2$–TR^{3+}: a) CaF$_2$–Pr^{3+}; b) CaF$_2$–Eu^{3+}; c) CaF$_2$–Er^{3+}. Concentration curves are designated with the corresponding wavelengths of the absorption line maxima (cf. Fig. 2).

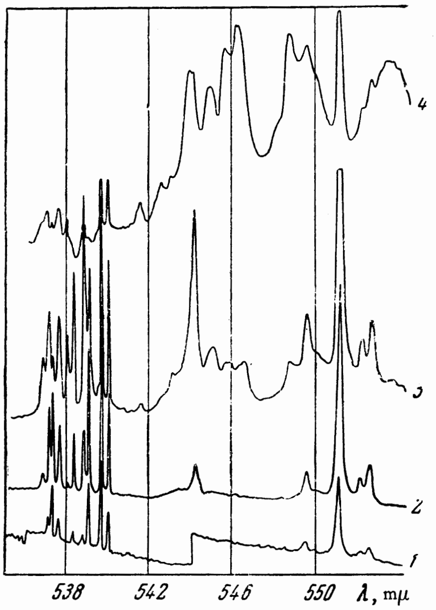

FIG. 4. Concentration series of the luminescence spectra of CaF_2–Er^{3+} crystals ($^4S_{3/2} \rightarrow {}^4I_{15/2}$ group), T = 77°K; Er^{3+} concentrations: 1) 0.003, 2) 0.03, 3) 0.3, 4) 1.0 wt.%

liquid nitrogen. The cryostat was placed in an elliptical mirror system; a tungsten photoflood lamp of 300 or 500 W was used as the exciting light source. Figure 4 gives, by way of example, one of the luminescence groups of CaF_2—Er^{3+} (the $^4S_{3/2} \rightarrow {}^4I_{15/2}$ transition). It is evident from Fig. 4 that, as in the case of the absorption spectra, the line intensities change as the TR^{3+} concentration is increased.

A qualitative analysis of the luminescence spectra of Pr^{3+}, Nd^{3+}, and Er^{3+} established the existence of at least three systems of lines, which differed in their concentration dependence.

A quantitative analysis of the luminescence spectra using the peak values of the intensities was found to be difficult because of the strong re-absorption of the resonance lines, which distorted the concentration dependences.

4. DISCUSSION OF RESULTS

The investigations carried out by the concentration series method established the possibility of complete analysis of the optical spectra of TR^{3+} ions in fluorite-type crystals. For the absorption spectra, this analysis can be carried out quantitatively, but only qualitatively in the case of the luminescence spectra. In carrying out the concentration series method analysis of the spectra at helium temperatures, we can deduce the system of energy levels for each type of center.

Unfortunately, the concentration series method does not make it possible to assign directly the isolated systems of spectral lines to centers of given structure. In this connection, it may be convenient to combine the concentration series method with one of the methods referred to above, by means of which the symmetry of centers can be determined.

In conclusion, the authors express their gratitude to S. P. Afanas'ev for growing the crystals, and to V. B. Aleksandrov for his help in carrying out the experiments.

---

[1] V. V. Osiko, in collection: Rost kristallov (Growth of Crystals), Izd. AN SSSR, 1965, Vol. 5.

[2] S. A. Pollack, J. Chem. Phys. **40**, 2751 (1964).

[3] Z. Kiss, J. Chem. Phys. **38**, 1476 (1963).

[4] M. A. El'yashevich, Spektry redkikh zemel' (Spectra of Rare Earths), Gostekhizdat, 1953.

[5] P. P. Feofilov and A. A. Kaplyanskiĭ, UFN **76**, 201 (1962), Soviet Phys. Uspekhi **5**, 79 (1962).

[6] Voron'ko, Kaminskiĭ, and Osiko, JETP **49**, 420 (1965), Soviet Phys. JETP **22**, 295 (1966).

[7] Kaminskiĭ, Kornienko, and Prokhorov, JETP **48**, 476 (1965), Soviet Phys. JETP **21**, 318 (1965).

[8] V. V. Osiko, FTT **7**, 1294 (1965), Soviet Phys. Solid State **7**, 1047 (1965).

Translated by A. Tybulewicz
94