

PSEUDO-STARK SPLITTING OF THE $4f \rightarrow 5d$ LINES OF Ce^{3+} IONS IN CaF_2 CRYSTALS

A. A. Kaplyanskii and V. M. Medvedev

A. F. Ioffe Physico-technical Institute, USSR Academy of Sciences

Submitted 25 June 1965

When the ions of a lattice are in a crystalline field without an inversion center, their levels can experience a linear shift in an external electric field [1,2]. A linear doublet splitting (pseudo-Stark splitting) of the bands of the optical spectra of Cr^{3+} and of other $3d^3$ ions in Al_2O_3 in an electric field was observed in [2,4]. This splitting is due to the opposite shifts of the levels and of the transition frequencies at the ions occupying non-equivalent positions with different inversions in the lattice.

We have observed linear pseudo-Stark splitting of the $4f \rightarrow 5d$ bands in the ultraviolet absorption spectra of the cubic crystals of CaF_2 with Ce^{3+} [5]. We investigated primarily CaF_2-Ce^{3+} crystals of the first type [5], in which the Ce^{3+} are in a local field of trigonal symmetry [6], and studied the influence of the electric field at 4.2°K on narrow long-wave lines, the 3383.6 Å absorption line and the neighboring weak 3383.0 Å line of $CaF_2-Ce^{3+}(I)$, corresponding to pure electronic transitions from the ground sublevel $^2F_{5/2}(4f)$ to the lowest crystalline sublevels of the 5d state of Ce^{3+} . The static field ϵ_0 was applied to single-crystal samples along the [111] axis; the spectra were observed in the directions $L \perp \epsilon_0$ and $L \parallel \epsilon_0$.

It was established that in an electric field the 3383.6 and 3383.0 Å lines experience reversible splitting in symmetrically-arranged quartets (Fig. 1a). When $L \perp \epsilon_0$ the two external components of the quartets are completely polarized with the electric vector $E \perp \epsilon_0$ for 3383.6 Å line and with $E \parallel \epsilon_0$ for the 3383.0 Å line (this is why the outer components of the 3383.0 Å quartet are not seen in the spectrum for $L \parallel \epsilon_0$). The splitting is proportional to the voltage applied to the electrodes.

The linear character of the splitting shows directly that there is no inversion center in the trigonal field in which the Ce^{3+} ions are situated in the CaF_2 crystals. This confirms convincingly the model proposed in [7] for triply charged rare-earth centers in CaF_2-Tr^{3+} crystals of the first type. In this model, one of the eight F^- neighbors of the Tr^{3+} ion in the Ca^{2+} site is replaced by an O^{2-} ion, which compensates for the excess charge of the Tr^{3+} and produces at its location an additional non-centrally-symmetrical axial field, so that the total symmetry of the local field corresponds to C_{3v} . We note that the methods hitherto used to investigate the

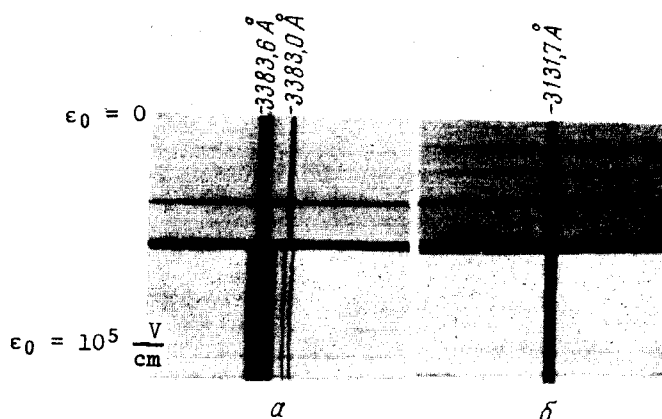


Fig. 1. Spectrograms of the line splitting of CaF_2-Ce^{3+} in the electric field: $\epsilon_0 \parallel [111]$, $L \parallel \epsilon_0$.

CaF₂-TR³⁺(I) centers, namely polarized luminescence [8], the Zeeman effect [9], the piezo-spectroscopic effect [5,10], and EPR spectra [11], all demonstrated experimentally that a trigonal field acts on the TR³⁺, but gave no information on the character of its inversion symmetry.

The complicated character of the pseudo-Stark splitting of the CaF₂-Ce³⁺ lines, compared with the 3d³ ions in Al₂O₃ [2-4], is connected with the fact that the anisotropic rare-earth centers (C_{3v}) have many orientations in the cubic lattice of CaF₂ (class O_h). These centers occupy eight positions, depending on which of the surrounding F⁻ ions is replaced by the O²⁻ ion; the trigonal axis of the TR³⁺-O²⁻ centers are parallel to the eight different [111] directions in the lattice. From symmetry considerations it follows that in an electric field the linear shift of levels (and the transition frequencies) at the center is $\Delta\nu = \alpha\epsilon_{\parallel}$ where ϵ_{\parallel} is the projection of the field of the trigonal axis of the center and α is a proportionality coefficient. In a field $\epsilon_0 \parallel [111]$, the centers C_{3v} form with respect to the field four non-equivalent groups, for which the projections of ϵ_0 on the center axes equal to $\pm\epsilon_0$ and $\pm\epsilon_0/3$. The corresponding shifts of the 4f → 5d transition frequency in these groups, namely $\Delta\nu_{1,2} = \pm\alpha\epsilon_0$ and $\Delta\nu_{3,4} = \pm\alpha\epsilon_0/3$ are indeed responsible for the symmetrical quartet splitting of the lines. The measured ratio of the distances between the outer and inner components of the quartet at 3383.6 Å is close to the calculated value ($\Delta\nu_{1/2}/\Delta\nu_{3/4} = 3$). The observed symmetry of the splitting relative to the case $\epsilon_0 = 0$ shows that the quadratic Stark shift of the levels is negligibly small.

From the polarization of the Stark components it follows, in accordance with [6], that the dipole moments of the 4f → 5d transitions in Ce³⁺ correspond to circular and linear electric oscillators σ_e , 3383.6 Å, and π_e , 3383.0 Å, oriented perpendicular and parallel to the trigonal axis of the center. According to the EPR data [11], the lowest crystal-splitting level ²F_{5/2}(4f) of Ce³⁺ in a trigonal field is the Kramers doublet E_{3/2}(±3/2) with a "crystalline" quantum number $\mu = 3/2$. Using this information and the selection rule with respect to μ in the C_{3v} group, we can establish the symmetry of the two upper 5d levels for the transitions 3383.6 Å - $\mu = \pm 1/2$, and for 3383.0 Å - $\mu = 3/2$. It is natural to assume that the close levels with $\mu = \pm 1/2$ and $\mu = 3/2$ are the components of the splitting in the trigonal field, due to the presence of the O²⁻ and of the 5d level of Ce³⁺(Γ₈⁺), which is the lower level of the crystal line splitting of the 5d state of the ion in the "ground state" cubic (O_h) lattice field ¹). Inasmuch as the level Γ₈⁺(5d) is made up of the orbital e-state of the d-electron, which is not split by a trigonal perturbation, its splitting in the trigonal field is due only to the admixture of Γ₈⁺ states and is therefore unusually small.

In conclusion we note that we have observed a doublet splitting of the purely electronic 3131.7 Å absorption line of CaF₂-Ce³⁺ crystals of the second type [5], in which the Ce³⁺ ions were situated [6,12] in a local trigonal field, also for the case when $\epsilon_0 \parallel [111]$ and L $\parallel \epsilon_0$ (Fig. 1b).

The authors are grateful to E. F. Gross for interest in the work.

- [1] N. Bloembergen, Science 133, 1363 (1961).
- [2] Kaiser, Sugano, and Wood, Phys. Rev. Lett. 6, 605 (1961).
- [3] M. D. Sturge, Phys. Rev. 133, A795 (1964).
- [4] M. G. Cohen and N. Bloembergen, Phys. Rev. 135, A950 (1964).
- [5] Kaplyanskii, Medvedev, and Feofilov, Optika i spektroskopiya 14, 664 (1963).
- [6] A. A. Kaplyanskii and V. N. Medvedev, ibid. 18, 803 (1965).
- [7] I. V. Stepanov and P. P. Feofilov, DAN SSSR 108, 615 (1956), Soviet Phys. Doklady 1, 350 (1957).
- [8] P. P. Feofilov, DAN SSSR 99, 731 and 975 (1954).
- [9] V. A. Arkhangel'skaya and P. P. Feofilov, Optika i spektroskopiya 4, 602 (1958).
- [10] A. A. Kaplyanskii, ibid. 7, 677 and 683 (1959).
- [11] M. J. Weber and R. W. Bierig, Phys. Rev. 134, A1492 (1964).
- [12] M. H. Crozier, Phys. Rev. 137, A1781 (1965).

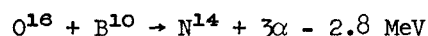
1) The orbital d-state of the electron splits in the cubic field O_h into two levels of the e and t type, of which the e level (Γ_3^+) is the lower one in the case of eightfold ($8F^-$) coordination of the ion. When the electron spin is taken into account ($D^{(1/2)}$), the symmetry of the lower level is $F_3^+(e) \times D^{(1/2)} = \Gamma_8^+$.

PICKUP OF A DEUTERON AND AN α PARTICLE IN THE INTERACTION BETWEEN B^{10} AND O^{16}

S. N. Shumilov, A. P. Klyucharev, and N. Ya. Rutkevich
 Physico-technical Institute, Ukrainian Academy of Sciences
 Submitted 5 July 1965

A rather large number of four-prong stars was observed in a study of the interaction between B^{10} ions and emulsion nuclei, three of the prongs being tracks of α particles and the fourth the track of a heavier particle.

Type NIKFI-D nuclear emulsions 400 μ thick were bombarded with B^{10} ions accelerated to 100 MeV in the linear multiply-charged-ion accelerator of the Ukrainian Physico-technical Institute. The B^{10} ions entered the emulsion in an angle of 25° to the surface. The emulsions made possible a reliable visual discrimination between tracks of singly-charged and doubly-charged particles and of heavier nuclei. Since the initial ion energy is known, it is possible to determine the energy at which the reaction took place by measuring the range of the B^{10} ion. The visual selection and subsequent detailed kinematic analysis, carried out with an "Ural-2" computer made it possible to identify 252 stars due to the reaction



The excitation function of this reaction is shown in Fig. 1. Not a single case of this reaction was found when the energy of the bombarding ions was less than 25 MeV. The cross