INFLUENCE OF ELECTRIC FIELD ON THE LUMINESCENCE SPECTRA OF EXCHANGE-LINKED CHROMIUM ION PAIRS IN RUBY

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Submitted 29 April 1967
ZhETF Pis'ma 5, No. 12, 427-430 (15 June 1967)

We have investigated experimentally the influence of an external electric field on the long-wave ruby luminescence spectrum belonging to different pairs of Cr^{3+} - Cr^{3+} ion pairs coupled by exchange interaction.

We used in our esperiments thin single-crystal ruby plates (Cr concentrations 0.05 and 1.6%) on which transparent electrodes (SnO_2) were deposited. The experiments were carried out at 77 and 4.2°K. The ruby luminescence spectrum in the 690 - 705 nm region, observed along the field, was photographed with a diffraction spectrograph with ∿ 2.1 Å/mm dispersion.

A field applied perpendicular to the crystal axis ($E_0 \perp C$) and of intensity up to 200 kV/cm had no noticeable influence on the ruby spectrum in the investigated region. When the field was directed along the axis ($E_0 \parallel C$), a symmetric doublet splitting of a large number of luminescence lines of chromium pairs was observed, but some other pair lines showed no noticeable influence (Fig. 1).

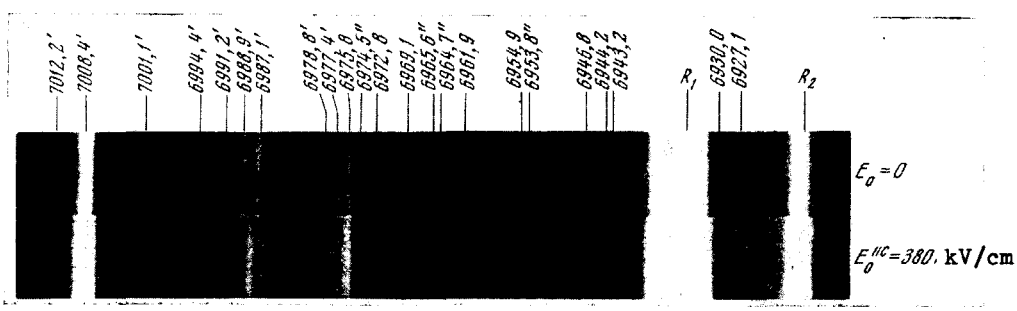

Fig. 1

The lines of the so-called N_2 series, 7013, 7009 (N_2), 7002, and 6992 Å, which correspond [1, 2] to transitions from the lowest excited state $Cr^{3+}(^4A_2)$ -$Cr^{3+}(^2E)$ of the "ferromagnetic" N_2 pair to the levels of its neighboring state $Cr^{3+}(^4A_2)$ - $Cr^{3+}(^4A_2)$ with S = 0, 1, 2, 3 exhibit a doublet splitting when $E_0 \parallel C$ (Figs. 1, 2). The dependence of the doublet width Δ^{7009} on the field E_0, measured for the most intense line 7009 Å (N_2), turned out to be practically linear (see Fig. 3, where Δ^{7009} is shown as a function of the width of the pseudo-Stark doublet of the R_2 line, which has been obtained under the same conditions and is proportional to E_0 [3,4]. The splitting differs somewhat for the different members of the N_2 series; thus, $\Delta^{7002}:\Delta^{7009} \approx 0.85$. The doublet splitting has been established also for many other lines belonging [2] to radiative transitions in the ferromagnetic N_2 pair from its upper excited states

(these lines are marked with primes in Fig. 1).* Doublet splitting is observed also in certain unclassified lines (Fig. 1).

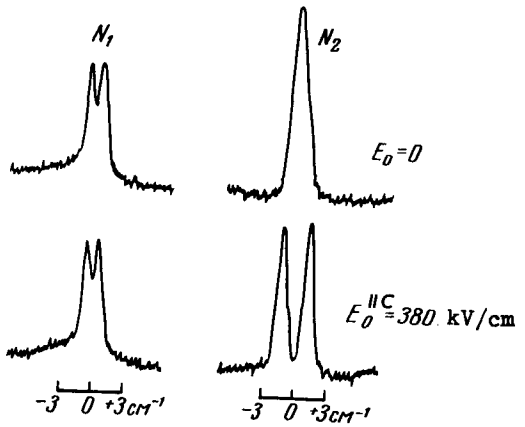

Fig. 2

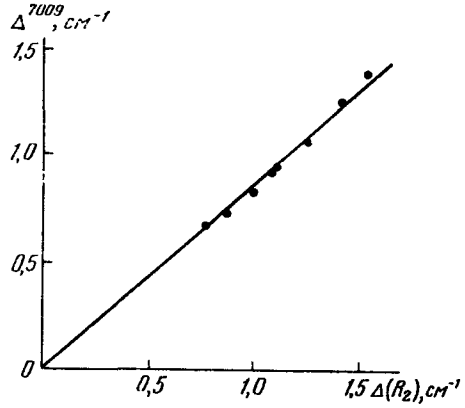

Fig. 3

The intense line 7041 Å (N_1) belonging [2] to the transition from the lowest excited state $Cr^{3+}(^4A_2)$ - $Cr^{3+}(^2E)$ of the "antiferromagnetic" N_1 pair to the level S = 2 of its ground state $Cr^{3+}(^4A_2)$ - $Cr^{3+}(^4A_2)$ exhibits no splitting in fields $E_0 \parallel C$ up to about 400 kV/cm (Fig. 2). There is likewise no splitting at $E_0 \parallel C$ in a number of other lines corresponding according to [2] to transitions from the upper radiative sublevels of the antiferromagnetic N_1 pair (double-primed in Fig. 1), and also in some unclassified lines.

It follows from the foregoing that the presence or absence of a linear Stark effect in the spectra of interacting ion pairs in ruby depends on the type of pair. The observed phenomena can be qualitatively interpreted taking [5] into account, by starting with concrete models of the N_1 and N_2 pairs proposed on the basis of their spectroscopic [1,2] and piezospectroscopic [6] properties.

The N_2 pairs are identified in [1, 2, 6] with Cr^{3+}- Cr^{3+} pairs occupying cation sites that are fourth neighbors with respect to their spacing in the lattice. Both Cr^{3+} ions of such a pair are in locations having the same sign of the odd component of the trigonal crystal field. The dipole moment of such a pair in the ground state is approximately equal to double the moment of the single $Cr^{3+}(^4A_2)$ ion. In the excited state, when one of the ions is in the ^2E state, the moment of the pair is the sum of the moments of Cr^{3+} in the $^4A_2$ and ^2E states. In this approximation, in a field $E_0 \parallel C$, the transition-frequency shift determined by the difference of the moments of the pair in the two states, is equal to the frequency shift of the transition $^4A_2$ - ^2E in the electric field (R-doublet) in the isolated Cr^{3+} ion. This shift - owing to the presence of N_2 pairs with opposite moment directions in the lattice - should lead to a pseudo-Stark [3] splitting of the lines when $E_0 \parallel C$, which is indeed observed experimentally in the spectrum of the N_2 pairs. The slight difference between the splitting of the lines of the N_2 pairs and of the R lines of isolated ions (see Fig. 3) is apparently due to electrostatic interaction of the ions in the pair [5]. The difference in the magnitude of the pseudo-Stark splitting of different lines of the N_2 series, noted above, also shows a noticeable influence of the external field on the magnitude of the exchange interaction in the pair, which

determines the relative position of its main levels S = 0, 1, 2, 3 and of the lines of the N_2 series.

In the N_1-pair model proposed in [6] (third neighbors), the Cr^{3+} ions entering into the pair occupy places with opposite signs of the odd trigonal field. This leads to cancellation of the dipole moments in both the ground state of the pair and in its excited state (owing to resonant excitation transfer between the ions). There should therefore be no linear level shift in an electric field, in agreeement with the experimentally observed absence of a noticeable influence of the field on the N_1-pair spectrum.

Thus, the results of our investigation confirm fully the classification given in [1,2] for the lines and the N_1- and N_2-pair model considered in [6].** In qualitative agreement with the theory of [5], experiment indicates that the directions of the odd trigonal field at the ion locations of the exchange-linked Cr^{3+} - Cr^{3+} pair plays a decisive role in the behavior of its spectrum in an electric field.***

The authors thank V. I. Cherepanov and A. E. Nikiforov for useful remarks.

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*The positions of all lines belonging to pairs, indicated in Fig. 1, have been measured on samples of Al_2O_3 with 1.6% Cr, and differ from the data of [2], which were obtained with samples having 0.5% Cr, by an average long-wave shift of about 0.5 Å.

**The lines 6973, 6969, and 6962 Å, which split in the field into doublets, form a sequence with intervals close to those of the N_2 series. This suggests a connection between the lines and transitions to the levels S = 0, 1, 2 of the N_2 pair from one of the higher radiative levels (14381 cm^{-1}).

*** Preliminary experiments reveal that the field has likewise no influence on the 7451 Å ruby emission line that belongs [6] to the chromium pair of second neighbors with opposite directions of the odd-field components.

STRUCTURE OF α MODIFICATION OF OXYGEN

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Submitted 30 March 1967
ZhETF Pis'ma 5, No. 12, 430-434 (15 June 1967)

Neutron-diffraction investigations of solid oxygen at 27, 20.4 and 4.2°K yielded reliable Debyegrams of the β and α modifications of O_2 [1].

A neutron-diffraction pattern obtained with α-O_2 is shown in Fig. 1 (where a small-scale Debyegram of β-O_2 is also shown). There is no corresponding analog among the hitherto published