SPLITTING OF THE EMISSION LINES OF RUBY BY AN EXTERNAL ELECTRIC FIELD

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The fluorescence emission of ruby ($Al_2O_3 + Cr^{3+}$) has been investigated in great detail in recent years and it is now well understood.[1] In highly diluted pink ruby with chromium concentrations below 0.05%, the emission consists essentially of two lines at $R_1 = 14\,421$ cm^{-1} and $R_2 = 14\,450$ cm^{-1} corresponding to transitions from the split components of the $t_2^3\ ^2E$ state to the ground state $^4A_2$, respectively. Since the ground state is split by 0.38 cm^{-1},[2] both emission lines are actually doublets, which can easily be observed at 77°K with a high-resolution grating instrument.

We have superimposed an external electric field upon the internal crystal field and observed a new additional splitting of the emission lines, which is much larger than expected from a superficial consideration of the Stark effect. Ruby plates of 1-mm thickness with a chromium concentration of approximately 0.01% were cut from a large single crystal parallel and perpendicular to the optic axis. The samples were immersed in liquid nitrogen and illuminated with a 100-watt Hg lamp. The emission of the crystal was focused on the entrance slit of a Bausch and Lomb grating spectrometer with a 50 000-line/in. grating. With this system the ground-state splitting of the R_1 and R_2 lines was clearly visible (see Fig. 1 top). Upon application of an external electric field parallel to the optic axis of the ruby, a surprisingly strong effect on the emission pattern was observed. Both components of the R_1 and R_2 lines exhibit a distinct splitting which is shown in Fig. 1 for the R_1 line for several electric fields. On the top (no field) and the bottom ($E_0 = 1.58\times10^5$ v/cm) of this figure, actual microphotometer traces of the photographic plate are presented; at intermediate fields, only the positions of the individual components are indicated. The frequency shift is so large that the two center lines pass the midpoint between the two original R_1 components at a field of about 65 kv/cm and cross over at still higher fields. It is interesting to note that the center of the split lines does not shift with applied electric field; furthermore, both components of the R_1 (see Fig. 1) and R_2 lines split by the same amount. It can be seen from Fig. 2 that the splitting $\Delta\nu$ is directly proportional to the electric field. At a field of 1.7×10^5 v/cm, $\Delta\nu$ reaches a value of one wave number (3×10^{10} cps). With increasing electric field, the emission lines slightly broaden. No detailed study was made of this effect. Polarizers in the light beam indicated that the polarization is unaltered by the electric field. In specimens with the electric fields perpendicular to the optic axis, no change in the emission pattern could be observed for fields as high as 1.7×10^5 v/cm.

The observed splittings of the R_1 and R_2 fluorescence lines in the presence of an electric field are not normal Stark splittings. This is because both the initial and final states of the fluorescence are Kramers doublets whose degeneracies may not be removed in the presence of any electric field. In what follows, we shall show that the apparent splittings are due to the opposite Stark shifts of the energy levels of chro-

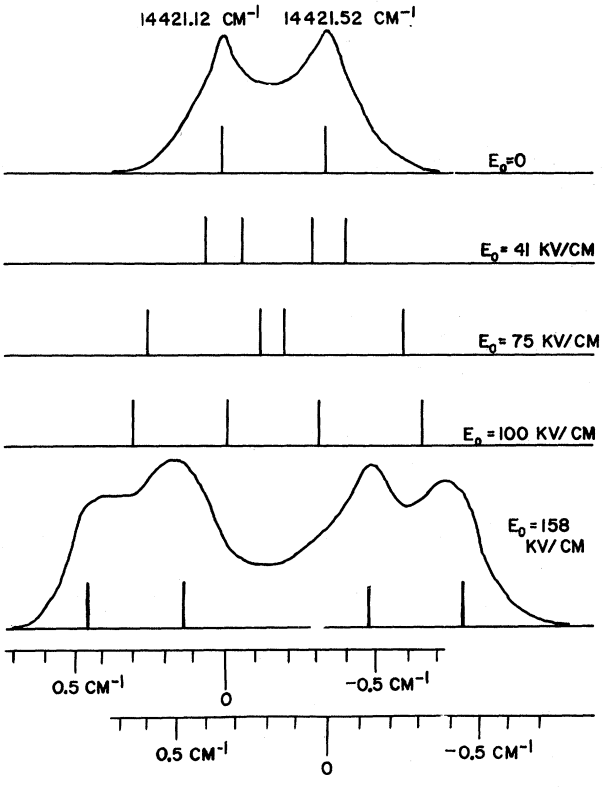

FIG. 1. Splitting of the R_1 line in an electric field parallel to the optical axis.

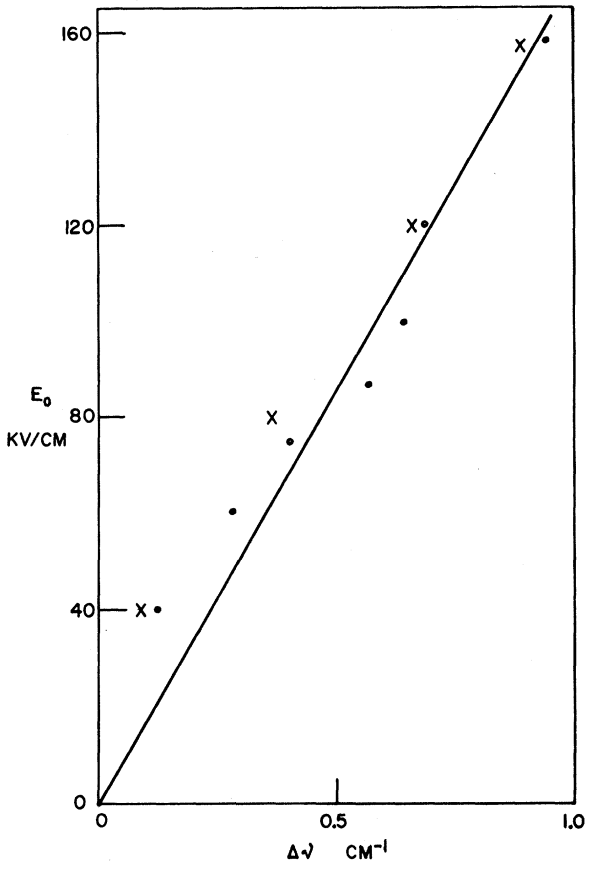

FIG. 2. Pseudo-Stark splitting $\Delta\nu$ of ruby vs applied electric field E_0. Data are obtained from the R_1 (•) and R_2 (×) lines.

mium ions at different lattice sites.

It is well known that in ruby there are two kinds of chromium sites, A and B.[3] Transformation of the A site into the B site is only possible by symmetry operations involving inversion around the chromium ion, while transformation of A to A or B to B is achieved solely by translation or by both translation and rotation around the optic axis. The A and B sites are energetically equivalent in the absence of an electric field. This circumstance may be simply expressed by the fact that the odd-parity crystal field associated with the A site, $V_u(A)$, is equal to minus the odd crystal field at the B site, $V_u(B) = -V_u(A)$.

Let us consider the local electric field acting on the chromium ions. The local field may be written in the form, $\alpha \cdot \vec{E}_0$, where $\vec{E}_0$ is the applied electric field and α is generally a tensor determined by the dielectric properties of crystals. Polarization effects due to ionic displacements and deformation of electron clouds in crystals are taken into account in the tensor α. For a uniaxial crystal such as ruby, the term in the Hamiltonian for the interaction of the chromophoric electrons with the local electric field produced by the external applied field is given by

$$V_S = \sum_i [\alpha_{\parallel} z_i E_{0z} + \alpha_{\perp}(x_i E_{0x} + y_i E_{0y})],$$

where x, y, and z are the electron coordinates and the z axis is taken along the optic axis.

Since V_S belongs to odd parity, the crystal field levels of chromium ions are perturbed by the combined action of V_u and V_S. This perturbation produces the Stark shift. Because of the opposite sign in the odd-parity crystal fields at the A and B sites, the Stark shifts for these sites are expected in opposite directions. This gives the pseudo-Stark splittings observed in our experiment. Furthermore, since V_u corresponds to the z component of the equivalent irreducible tensor,[4] a simple symmetry consideration shows that the Stark shifts are vanishing when E_0 is perpendicular to the optic axis.

The accurate calculation of this type of Stark shift is as difficult as that of the absolute intensities of the crystal field spectrum. It is, however, possible to estimate the order of magnitude of the Stark shift $\Delta\nu$ by using the relation $\Delta\nu \sim \alpha_{\parallel} \times E_{0z} \langle V_u \rangle \langle z \rangle / \Delta$, where $\langle V_u \rangle$ is the matrix element of V_u between the state relevant to the fluorescence and the high excited state of odd parity, $\langle z \rangle$ the similar matrix element of z, and Δ the energy difference between the two states appearing in the matrix elements. Putting $\alpha_{\parallel} \sim 1$, $\langle V_u \rangle \sim 1000$ cm^{-1}, $\langle z \rangle \sim 1$ A, and $\Delta \sim 50\,000$ cm^{-1}, we obtain $\Delta\nu \sim 0.1$ cm^{-1} at $E_{0z} = 10^5$ volts/cm.

The above-mentioned Stark shifts are expected in both the initial and final states of the fluorescence. Therefore, the observed magnitude of the pseudo-Stark splitting should be compared with twice the difference of the Stark shifts in the initial and final states of the fluorescence. This would not change the estimated order of the magnitude, as the shifts are not expected to be the same in both states.

The other characteristic features expected from our theory are as follows:

(1) The center of the split components does not shift (no pseudo-Stark shift) because the crystal symmetry gives $|V_u(A)| = |V_u(B)|$. Here we neg-

lect contribution from the V_S^2 term which is very small for the fields achieved in our experiments.

(2) The magnitude of the splittings is expected to be the same for the R_1 and R_2 excited states because the Stark term is independent of spin. The same is true for the initially split ground levels having $M_S = \pm 3/2$ and $M_S = \pm 1/2$.

(3) Optical anisotropies associated with the split components are identical with each other and also with the anisotropy of the original unsplit line. All these points are in agreement with our experiments.

Although we have not given any detailed discussion on the local electric field, experiments of this type are very important because they allow a direct investigation of the local electric field. The quantitative discussion on the local field is only possible after the detailed knowledge of the odd-parity excited states is obtained.

The effect discussed here is expected to be extremely fast (comparable to the optical frequencies of the lattice), and high-frequency modulation of the ruby emission can be anticipated. The application of an ac electric field should allow frequency modulation of the output of a ruby optical maser.[5]

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ANISOTROPY OF THE MAGNETOELECTRIC EFFECT IN Cr_2O_3

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On the basis of earlier considerations of magnetic crystal symmetry effects by Landau and Lifshitz,[1] Dzyaloshinskii[2] showed that a magnetoelectric effect (i.e., a magnetic moment produced by an externally applied electric field or an electric moment produced by an externally applied magnetic field) may exist in antiferromagnetic Cr_2O_3. In his development of the thermodynamic potential which is compatible with the magnetic symmetry, Dzyaloshinskii obtained the relation[2]

$$4\pi\phi_{me} = -\alpha_{\parallel} E_z H_z - \alpha_{\perp}(E_x H_x + E_y H_y), \qquad (1)$$

where ϕ_{me} is the magnetoelectric part of the thermodynamic potential, and $\alpha_{\parallel}$ and $\alpha_{\perp}$ are the magnetoelectric parameters for the directions parallel and perpendicular to the crystallographic c axis, respectively. From this potential, one obtains (using $4\pi\partial\phi/\partial\vec{H} = -\vec{B}$) the linear relations

$$B_z = \alpha_{\parallel} E_z, \quad B_x = \alpha_{\perp} E_x, \text{ and } B_y = \alpha_{\perp} E_y. \qquad (2)$$

As a result of measurements on a nonoriented Cr_2O_3 single crystal, Astrov[3] obtained evidence that the magnetoelectric effect does exist in Cr_2O_3, and that the effect is a linear function of the electric field in accord with Eq. (2).

In this Letter, we report measurements of the magnetoelectric effect (resulting from an applied electric field) in two x-ray-oriented single-crystal disks of Cr_2O_3, and show that a large anisotropy exists both in the magnitude and temperature dependence of this effect. One of the disks was fabricated with its plane surfaces parallel to the crystallographic c axis, and the second disk with its plane surfaces perpendicular to the c axis. In the former case, the surfaces were parallel to the (110) plane. The plane surfaces were coated with silver paint to provide uniform electrical contact with the specimen. The apparatus used to measure the magnetic moment was similar to that used by Astrov.[3] However, we found it necessary to make the measurements in vacuum in order to avoid electrical breakdown in the vicinity of the electrodes. The magnetic moment was obtained by applying to the sample a 1000-cps alternating electric field and using a narrow-band amplifier of approximately 0.15-μv sensitivity to measure the voltage induced in a 10 000-turn pickup coil surrounding the sample. The largest values of $\alpha_{\perp}$ and $\alpha_{\parallel}$ correspond to induced rms voltages of