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Optically generated pseudo-Stark effect in ruby

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We report observations of an optically produced splitting of the luminescence lines of concentrated ruby samples for optical intensities of approximately 200 W/cm^2. This splitting is attributed to optical generation of a large, uniform electric field (10^6 V/cm). At high intensities ($I > 2$ kW/cm^2) high photoconductivity causes the splitting to decrease and disappear. It is suggested that the field-generation mechanism is directional charge transfer via two-step excitation of Cr^{3+} ion or ion clusters. The required electrical asymmetry is shown to be due to a growth-induced anisotropy of the Cr^{3+} ion distribution.

I. INTRODUCTION

The optical properties of ruby have been studied extensively for many years and continue to be the subject of current investigations in several areas of physics.[1,2] It therefore intrigued us to discover a new optical effect in this material: namely, illumination of crystals, having a Cr^{3+} ion concentration between 0.2 and 0.9 wt.%, with 514.5-nm laser radiation causing the *R*-line luminescence to exhibit a splitting of up to 5 cm^{-1}. Furthermore, the splitting persisted for at least several hours even though the illumination was removed in the meantime.

In this report we will describe the various properties of this optically induced splitting and present a possible explanation in terms of an optically generated, macroscopic, internal electric field in excess of 10^6 V/cm. This interpretation is consistent with the observation at high intensities of large photoconductivity which causes the splitting to decrease, and disappear. The generation of a field of this magnitude is possible via a directional charge transfer mechanism, equivalent to the bulk photovoltaic effect in pyroelectric crystals.[3] In ruby the electrical asymmetry is shown to arise from a growth-induced anisotropy of the Cr^{3+} ion distribution.

II. EXPERIMENTAL SETUP

The fluorescence spectra of several ruby samples varying in Cr^{3+} concentration from 0.05 to 0.9 wt.% were obtained at 10 K.[4] In each case, the sample was a thin (~ 0.1 mm) slice which was illuminated with an argon laser loosely focused to an area of about 1.5×10^{-3} cm^2 at the sample. The fluorescence was imaged on a 0.5-mm-diam aperture, mounted before the slit of a half-meter grating spectrometer. The aperature assured that only light from the center of the illuminated spot entered the spectrometer. In some cases, the fluorescence was also analyzed with a Fabry-Perot interferometer, having a free spectral range of 5.36 cm^{-1}, which was placed before the spectrometer. In these cases the exit slit width of the spectrometer was increased so that it acted as a coarse filter to allow examination of a single emission line.

III. OBSERVATIONS

The spectroscopy of ruby is now well known. The fluorescence spectra consist primarily of transitions from the long-lived ($\tau \sim 3.6$ msec) ${}^2E(\bar{E})$ and ${}^2E(\bar{A})$ states to the ${}^4A_2$ ground state. These transitions in isolated Cr^{3+} ions are known as the R_1 and R_2 emission lines. For lightly doped crystals each of these lines exhibits a 0.38-cm^{-1} splitting due to a small crystal-field splitting of the ground state. However, in samples having greater than 0.3 wt.% Cr^{3+} ion concentration, this small splitting is generally not resolved. Also seen in emission are several lines, labeled "*N*" lines corresponding to transitions of exchange-coupled Cr^{3+} ion pairs. The relative density of these pairs of course increases with increasing Cr^{3+} ion concentration.

The emission spectrum at 10 K in the region near the *R* lines, of a sample containing 0.9 wt.% chromium excited with 514.5-nm radiation, is shown in Fig. 1. To obtain the spectra shown in Fig. 1(a), the incident laser intensity was adjusted to 6 kW/cm^2. Each emission line appears as a single line with a width determined by the resolution of the spectrometer. However, as the intensity of the exciting Ar-ion laser beam is decreased, both of the *R* lines and some of the *N* lines are observed to split. Figure 1(b) shows a well-resolved splitting of the *R* lines obtained after a few minutes of irradation at 150 W/cm^2. The sequence of events after the light is turned on is shown by the Fabry-Perot scans of the R_1 line in Fig. 2. Each scan covers a range including two maxima of the Fabry-Perot bandpass. Initially (Fig. 2, line 1), the spectrum appears as a single line

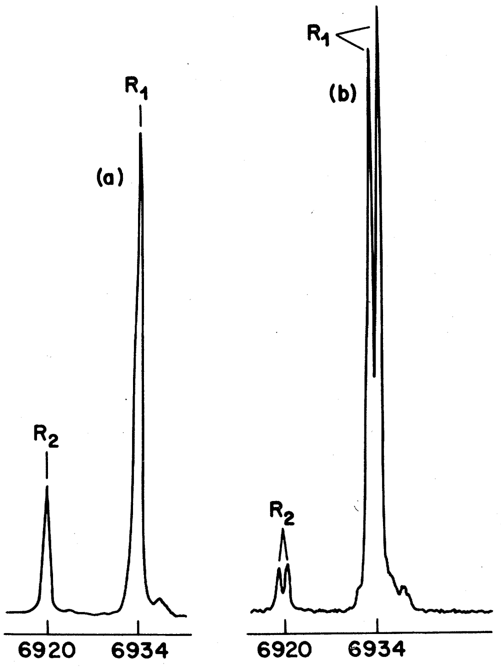

FIG. 1. Emission spectrum of 0.9-wt.% ruby sample at 10 K with 514.5-nm excitation of (a) 6 kW/cm^2 and (b) 150 W/cm^2.

about 1 cm^{-1} wide. Upon continued illumination (Fig. 2, line 2 through line 6), this line broadens and then splits into two components, each as narrow as the initial line, with the splitting increasing to a maximum steady-state value of 3.8 cm^{-1} in this case. The behavior of the splitting in several crystals can be characterized by the following observations:

(i) The rate at which the splitting develops, as well as the final steady-state value of splitting, depends on the incident laser intensity and varies from crystal to crystal.

(ii) The splitting is observed in all samples having a Cr^{3+} ion concentration greater than 0.25 wt.%. No splitting could be resolved in samples having below 0.1 wt.% chromium. In samples having Cr^{3+} concentrations of 0.25, 0.47, 0.55, and 0.90 wt.%, the measured steady-state splitting at 200 W/cm^2 of 514.5-nm light was 2.64, 3.27, 3.79, and 5.06 cm^{-1}, respectively.

(iii) The splitting rate is observed to vary quadratically with intensity at least up to 100 W/cm^2. The intensity dependence of the splitting rate of the most heavily doped sample is shown in Fig. 3 and the steady-state value of the splitting for long times is shown in Fig. 4. Above 100 W/cm^2 the splitting rate is too rapid for accurate measurement. The steady-state value is observed to decrease for intensities above 2 kW/cm^2, and above 10 kW/cm^2 all splitting was erased and the sample returned to its initial state [Fig. 1(a)].

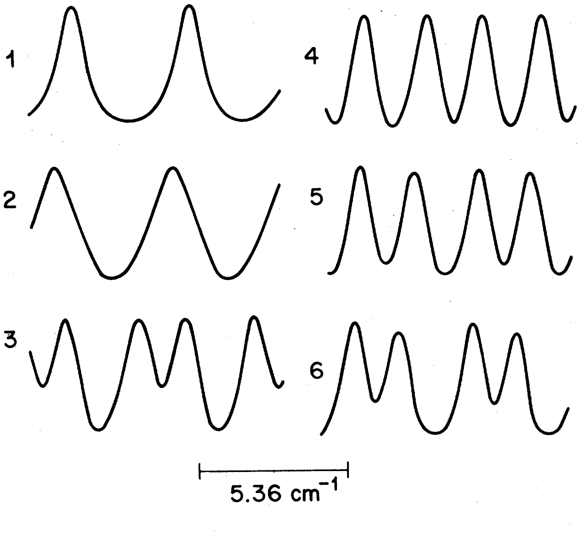

FIG. 2. Sequence of Fabry-Perot scans of the R_1 line. Each scan covers a range including two maxima of the Fabry-Perot bandpass. A slow drift of the Fabry-Perot spacing causes the positions of peaks in successive scans to drift toward the left.

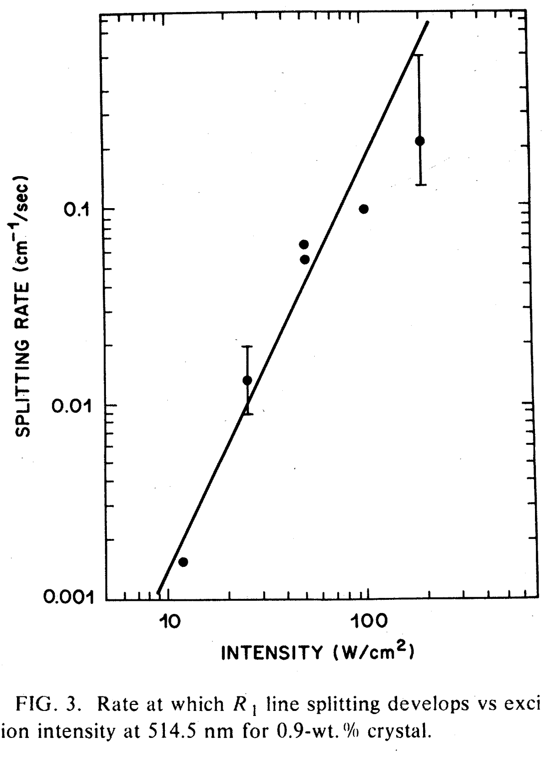

FIG. 3. Rate at which R_1 line splitting develops vs excitation intensity at 514.5 nm for 0.9-wt.% crystal.

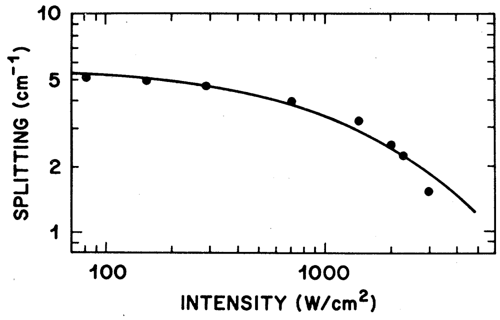

FIG. 4. Steady-state splitting of R_1 line vs excitation intensity at 514.5 nm. Solid line gives calculated dependence as discussed in text.

(iv) Once a given value of the splitting is established in a crystal, it remains, such that the next time the sample is illuminated, regardless of the intensity of the excitation light, the splitting is immediately evident and does not need to develop as in Fig. 2. The splitting persists for at least 24 h, even if the sample temperature is raised to 300 K in the meantime. Because of temperature-dependent line broadening,[5] all measurements had to be made at low temperature.

(v) The splitting rate was found to depend on wavelength according to the Cr^{3+} absorption spectrum. Excitation of $^4A_2 \rightarrow {}^4T_2$ transitions of the Cr^{3+} ion with 514.5, 496.5, and 488.0 nm, and excitation of $^4A_2 \rightarrow {}^4T_1$ transitions with 457.9 nm all produced quite rapid splitting ($\sim 10^{-1}$ to 10^{-3} cm^{-1}/sec with 60 W/cm^2). However, at excitation wavelengths of 465.5 and 476.5 nm which fall between the $^4T_1$ and $^4T_2$ absorption bands, the splitting rate was extremely small ($< 10^{-5}$ cm^{-1}/sec).

(vi) The observations did not depend on the orientation of the crystal wafer with respect to the laser, nor on the orientation of the hexagonal c axis of ruby with respect to the plane of the wafer.

(vii) The spatial distribution of the splitting could be monitored by adjusting the fluorescence imaging optics. After a few minutes of illumination at low intensities, the amplitude of the splitting was maximum in the center of the excitation spot and decreased monotonically away from the center. At high intensities, however, the splitting was found to be largest at some distance from the center. This behavior is consistent with the intensity and time dependence of the splitting described above.

IV. INTERPRETATION AND PHOTOCONDUCTIVITY MEASUREMENTS

R-line and N_2-line splitting of Cr^{3+} ion luminescence in ruby have previously been observed[6,7] only in the presence of a large external electric field applied to the ruby crystal. Cr^{3+} ions in Al$_2$O$_2$ occupy two types of sites, A and B, which are related by inversion symmetry and are hence equivalent in the unperturbed crystal. These sites become inequivalent when the center of inversion is removed by the application of a field along the hexagonal c axis resulting in a pseudo-Stark splitting of the lines.[6] It is tempting therefore to attribute the behavior observed in our experiments to the presence of an optically generated space-charge field which could persist for a long time in a highly insulating crystal even after the light is removed.

An interpretation based on the optical generation of a macroscopic electric field is consistent with the observation of a homogeneous splitting throughout the illuminated volume, rather than a broadening of the lines which would result from a microscopic, inhomogeneous mechanism. From previous measurements[6] of the pseudo-Stark splitting $\Delta\nu$ (cm^{-1}) in an external field E (V/cm) along the c axis we have for the R lines

$$\Delta\nu = 5.6 \times 10^{-6} E \ . \tag{1}$$

Thus, from the steady-state value of the splitting we have for the 0.9-wt.% crystal

$$E_s \sim 10^6 \tag{2}$$

in units of V/cm. This field also produces a splitting of the exchange-coupled Cr ion pair line emission (Fig. 5). Due to the crystallographic orientation of the N_2 and N_1 ion pairs, the N_2 line at 700.9 nm shows a splitting while the N_1 line at 7041 Å does not as is observed for a uniform electric field of this magnitude.[7] From the splitting rate shown in Fig. 3, and Eq. (2) we can calculate the photocurrent J_{pv} (A/cm^2) (pv-photovoltaic)

$$J_{\text{pv}} = \frac{\epsilon}{4\pi}\frac{dE}{dt} = 1.6 \times 10^{-8}\frac{d(\Delta\nu)}{dt} \tag{3}$$

$$\sim (2 \times 10^{-12}) I^2 \ , \tag{4}$$

for an incident intensity $I < 100$ W/cm^2. Here ϵ is the dielectric constant of ruby. The quadratic dependence of current density on incident intensity indicates a two-step or two-photon excitation of free carriers. Since the splitting rate is seen to depend on the linear Cr^{3+} ion absorption spectrum, a two-step charge-transfer process from the Cr^{3+} ions is indicated.

Under open-circuit conditions the photocurrent generates an internal space-charge field up to a steady-state value determined by photoconductivity σ_{pc} which tends to reduce the field, i.e.,

$$J_{\text{tot}} = J_{\text{pv}} + \sigma_{\text{pc}} E \ . \tag{5}$$

In the steady state $J_{\text{tot}} = 0$ so that

$$E_s = -\frac{J_{\text{pv}}}{\sigma_{\text{pc}}} \ . \tag{6}$$

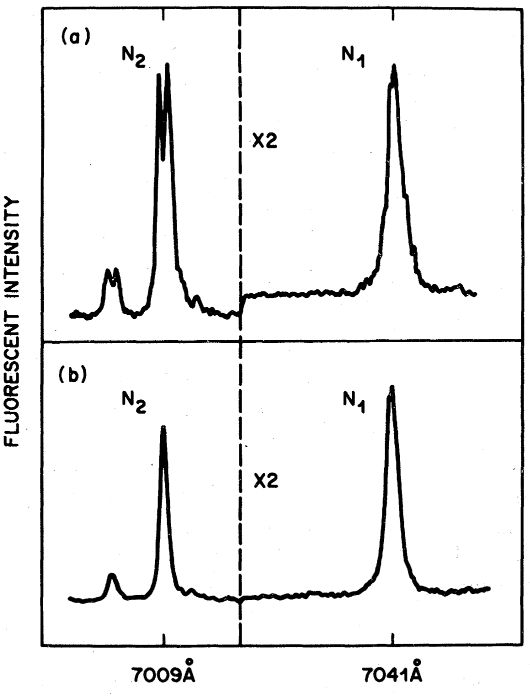

FIG. 5. Pair line-emission spectra of 0.9-wt.% ruby sample at 10 K with 514.5-nm excitation of (a) 150 W/cm² and (b) 6 kW/cm².

The observed reduction of the steady-state splitting at high intensities (Fig. 4) could be explained as the effect of increased photoconductivity. To check this hypothesis we measured the photoconductivity of several samples. Transparent conducting $InSnO_2$ films were sputtered onto opposite faces of the ruby wafers. The samples were biased with 130 V (1.3×10^4 V/cm) and the dc current was measured as a function of laser intensity. At short times after the light was turned on a rapidly decaying transient was observed which reached a steady value after a few seconds. The steady-state results are shown in Fig. 6 for the 0.9-wt.% sample. The photoconductive current increases quadratically over three decades of intensity from 10 W/cm² to 10 kW/cm² as

$$J_{pc}=1.5\times10^{-18}I^2E \ . \tag{7}$$

Linear dc conductivity at low intensities has previously been reported[8] for both ruby and sapphire and was attributed to impurity levels located about 1 eV below the conduction band. In this work the photoconductivity was found to vary from crystal to crystal and was unrelated to the Cr^{3+} ion content. In addition, the quadratic photoconductivity showed little dependence on wavelength over the range from 514.5 to 457.9 nm.

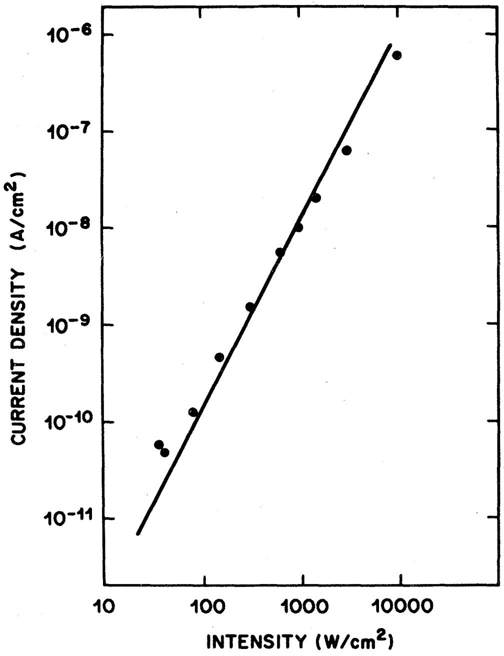

FIG. 6. Photoconductive currents vs intensity at 514.5 nm with 1.3×10^4-V/cm bias for 0.9-wt.% ruby sample.

From Eqs. (4), (6), and (7) we calculate

$$E_s=1\times10^6 \tag{8}$$

in units of V/cm for 0.9-wt.% ruby at least up to 100 W/cm² where J_{pv} depends quadratically on intensity. This value is in excellent agreement with the steady-state field calculated from the R-line splitting. At intensities above 100 W/cm² the steady-state field calculated from the splitting is observed in Fig. 4 to decrease. To attempt a quantitative fit to the data we consider saturation of the first step of the two-step excitation of the Cr^{3+} ions. With such a long-lived intermediate state as the $^2E(\bar{E})$ states of the Cr^{3+} ion, this process would be highly efficient and saturate at fairly low intensity. Then

$$J_{pv}=2\times10^{-12}(1+I/I_{sat.})^{-1}I^2 \ , \tag{9}$$

where $I_{sat}=\hbar\omega/\sigma\tau=1.5\times10^3$ W/cm² for isolated Cr^{3+} ions. (This value probably will not differ greatly for Cr^{3+} pairs.) Now with Eqs. (7) and (9) the intensity dependence of the steady-state field can be calculated over the entire intensity range and the results are shown as the solid curve in Fig. 4. The quantitative agreement is seen to be quite satisfactory and better than might be expected from the accuracy of the measurements. It lends strong support to this interpretation.

V. ORIGIN OF THE PHOTOVOLTAIC CURRENT

Up to this point we have found that the experimentally observed splitting of R and N lines can be accounted for in terms of an optically generated space-charge field of up to 10^6 V/cm, and that its magnitude is consistent with measurements of photoconductivity. We must now address the question as to what establishes the electrical sense of the crystal and how such a large electric field can be generated throughout the bulk of a 0.1-mm-thick crystal. Conventional photovoltaic effects can be ruled out since the maximum photovoltage would be limited to the value of the band gap in the crystal. Thus, high fields can only be generated in small volumes of crystal. Space-charge fields generated by diffusion of free carriers in optical intensity gradients can be ruled out by the following arguments and experimental tests. Firstly, to generate a space-charge field of 10^6 V/cm requires optical spatial frequencies of $\sim 10^7$ cm^{-1} which were not present in these experiments.[9] Varying the area of the focused laser beam while keeping the intensity constant had no influence on the results and hence ruled out diffusion perpendicular to the direction of propagation of the beam. In any case, fields generated by diffusion in this direction would be spatially nonuniform and should give rise to R-line broadening.

It appears then, that conventional mechanisms for the optical generation of the field cannot account for our observations in ruby. Large space-charge fields, in excess of 10^5 V/cm, have been generated in pyroelectric crystals,[3] for example, iron-doped $LiNbO_3$. The effect has been attributed to directional charge transfer from Fe^{2+} impurity ions along the polar axis of the crystal. In $LiNbO_3$ all impurity sites lack a center of symmetry and unlike ruby the electrical sense is the same for *all* equivalent impurities, determined by the spontaneous polarization of the host crystal. The structure of $LiNbO_3$ is quite similar to Al_2O_3 except that Al^{3+} ions in A sites are replaced by Li^+ ions and those in the B sites by Nb^{5+} ions. If the origin of the electric field in ruby is to be attributed to a similar directional charge-transfer mechanism, then the electrical sense must be established either by the intensity gradient of light in the crystal produced by simple absorption, i.e., a high-voltage Dember-like effect,[10] or else by unequal population of the A, B sites by Cr^{3+} ions.

The first of these possibilities was ruled out experimentally: the crystal was first illuminated from one side to produce a large splitting. The direction of the laser beam was then reversed so that the sample was illuminated from the other side. This procedure reverses the direction of the optical intensity gradient produced by absorption and the splitting would be expected to decrease to zero and increase again as the field reversed sign. No such field reversal was observed.

The only remaining cause for a macroscopic electrical sense of the crystal would seem to be an unequal population of the two energetically equivalent A and B sites of Al_2O_3 by Cr^{3+} ions. Then directional charge transfers at A sites are no longer cancelled by charge transfers at B sites. Site selectivity between what are energetically equivalent sites in a grown crystal is known to occur[11] during the growth of some crystals. In fact, in Al_2O_3 doped with Gd^{3+} ions, site selectivity is such that an A/B site population ratio as large as 8:1 has been observed.[11] To determine whether such site selectivity exists in concentrated ruby, a simple ac measurement of difference between ground and excited dipole moments of the Cr^{3+} ions was made.[12]

The change of dipole moment associated with localized optical excitation (not charge transfer) of Cr^{3+} ions in acentric sites can be determined by measuring the transient displacement current if site selectivity exists.[12] In the case of $LiNbO_3$, site selectivity is of course 100% and the change of moment $\Delta\mu$ from the ${}^4A_2 \rightarrow {}^4T_2$ states was found to be 10^{-28} C cm.

Using low power (100 mW/cm^2) radiation at 514.5 nm modulated at 2 kHz the ac current response of the 0.9-wt.% ruby was monitored without an applied field. Opposite faces of the ruby platelets were electroded with $InSnO_2$ as in the photoconductivity studies. Since the modulation rate is greater than the Cr^{3+} ion relaxation rate the current response is given by

$$J\ (2\ \mathrm{kHz}) = \chi W \Delta\mu \ , \tag{10}$$

where $W = \alpha I(\omega)/\hbar\omega$ is the excitation rate of Cr^{3+} ions, α is the linear absorption coefficient of active centers, χ is the normalized difference in the populations of Cr^{3+} ions in A and B sites (due to the growth-induced anisotropy) and $\Delta\mu$ is the difference of dipole moment of the Cr^{3+} ion in the ground ${}^4A_2$ and excited ${}^2E(E)$ states in Al_2O_3. Experimentally, we measured and found, in units of A/W

$$J\ (2\ \mathrm{kHz}) = 2.5 \times 10^{-10} \ . \tag{11}$$

If we assume[12] $\Delta\mu \sim 10^{-27}$ C cm as for Cr^{3+} ions in $LiNbO_3$ (even though in this case the lowest excited state is the ${}^4T_2$ state this value should still serve as an estimate) then we find, in cm^{-1}

$$\alpha\chi \sim 10^{-1} \ . \tag{12}$$

Thus, if the active centers are isolated Cr^{3+} ions for which $\alpha \sim 20$ cm^{-1} then $\chi \sim 0.5$ wt.% or if active centers are Cr^{3+} ion pairs we estimate $\chi \sim 2$ wt.% if the ratio of the luminescence intensity of the pair lines to the R lines is taken to be a direct measure of their concentration. These results verify unambiguously that a small-site preference does indeed exist in the Cr^{3+} ion distribution.

VI. CHARGE-TRANSFER MECHANISM

The excited-state absorption spectrum of isolated Cr^{3+} ions in dilute ruby has been measured by several workers.[13] In these reports, an excited-state absorption band near 2.4 eV, is observed but has been attributed to localized transitions within the Al_2O_3 host. On the other hand, in heavily doped ruby, a band is observed[14] in the linear absorption spectrum near 5 eV which is not observed in dilute ruby. The tail of the band extends into the spectral region around 4.2 eV which is accessible by a two-step absorption via the Cr^{3+} $^2E(E)$ intermediate state, using 514.5-nm radiation. The concentration dependence of the band suggests its association with Cr^{3+} pairs or clusters. This would also be consistent with the observation that R-line splitting is only observed in concentrated ruby. In any case, the excited-state absorption cross section necessary to account for the photovoltaic current is small. Since

$$J = \frac{\chi \beta I^2 e l}{\lambda \omega} , \qquad (13)$$

where β is the nonlinear absorption coefficient $\beta = \alpha\sigma^* \tau / \hbar\omega$, σ^* is the excited-state absorption cross section, and l is the net electronic displacement per charge-transfer excitation. Using $\alpha\chi \sim 10^{-1}$ from the preceding section, $\tau \sim 3.6$ msec and in Eq. (4) we have in cm^3

$$\sigma^* l \sim 10^{-28} . \qquad (14)$$

Thus, for l as small as 10^{-8} cm, an excited-state cross section as small as 10^{-20} cm^2 is sufficient to account for the observation.

VII. CONCLUSIONS

The experimental observation and interpretation can be briefly summarized as follows: irradiation of heavily doped ruby gives rise to a splitting of the R-line luminescence. This splitting is attributed to the pseudo-Stark effect arising from the optical generation of a large uniform electric field in the bulk of the crystal. This interpretation is based on the absence of any line broadening and the consistent Stark splitting of the N_2 line. The quadratic increase of the splitting rate with intensity, and its wavelength dependence indicate a mechanism based on directional charge transfer via two-step excitation of Cr^{3+} ions or ion clusters. The electrical sense of the crystal is derived from a growth-induced anisotropy of the Cr^{3+}-ion distribution which was verified experimentally from measurements of the excited-state polarization.

Photoconductivity measurements show a two-photon excitation of free carriers by a mechanism not involving Cr^{3+} ions. The steady-state value of the R-line splitting is consistent with the measurement of photoconductivity.

While all the data are consistent with the interpretation, our understanding of the effect is not complete. The R-line splittng was not affected by extended short-circuiting of the opposite faces of the ruby crystal, nor was the magnitude of the dc photovoltaic current in the external circuit consistent with that deduced from the splitting rate. Thus, if the effect is due to an internal electric field, as suggested by all of these data, then this must arise from space charge residing close to the crystal surfaces.

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[1] See for example, J. Koo, L. R. Walker, and S. Geschwind, Phys. Rev. Lett. 35, 1669 (1975); P. M. Selzer, D. L. Huber, B. B. Barnett, and W. M. Yen, Phys. Rev. B 17, 4979 (1978); A. Szabo and M. Kroll, Opt. Lett. 2, 10 (1978); P. F. Liao and D. M. Bloom, *ibid.* 3, 4 (1978); D. S. Hamilton, D. Heiman, J. Feinberg, and R. W. Hellwarth, *ibid.* 4, 124 (1979).

[2] P. F. Liao, L. M. Humphrey, D. M. Bloom, and S. Geschwind, Phys. Rev. B 20, 4145 (1979).

[3] A. M. Glass, D. von der Linde, and T. J. Negran, Appl. Phys. Lett. 25, 233 (1974).

[4] The samples were obtained from Adolph Meller Company. The sample temperature was determined by monitoring the ratio of the R_1 to R_2 intensities.

[5] D. E. McCumber and M. D. Sturge, J. Appl. Phys. 34, 1682 (1963).

[6] W. Kaiser, S. Sugano, and D. L. Wood, Phys. Rev. Lett. 6, 605 (1961).

[7] A. A. Kaplyanskii, V. N. Medvedev, and A. K. Przhevuskii, Zh. Eksp. Teor. Fiz. Pis'ma 5, 427 (1967) [JETP Lett. 5, 347 (1967)].

[8] U. E. Hochuli, Phys. Rev. A 133, 468 (1964).

[9] J. J. Amodei, D. L. Staebler, and A. W. Steven, Appl. Phys. Lett. 18, 507 (1971).

[10] A high-voltage photovoltaic effect can in principle arise from directional charge transfer in an optical intensity gradient even when impurities are uniformly distributed between A and B sites. Such an effect would only occur with light propagating along certain crystallographic axes and in fact has never been observed experimentally.

[11] S. Geschwind and J. P. Remeika, Phys. Rev. 122, 757 (1961).

[12] A. M. Glass and D. H. Auston, Opt. Commun. 5, 45 (1972).

[13] T. Kushida, J. Phys. Soc. Jpn. 21, 1331 (1966); J. W. Huang and H. W. Moos, Phys. Rev. 173, 440 (1968); W. M. Fairbank, Jr., G. V. Klauminzer, and A. L. Schawlow, Phys. Rev. B 11, 60 (1975).

[14] D. M. Dodd (unpublished).