Photoelectric domain structure in ruby crystals

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It is shown experimentally that intense laser illumination of concentrated ruby at low temperatures transforms it into a new, steady, spatially inhomogeneous state that persists indefinitely after the pumping is stopped and the sample is allowed to warm up to room temperature. This new state is characterized by the presence of polar regions (domains) of strong electric field E_s (≈ 350 kV/cm) directed along the trigonal axis of the crystal and having opposite signs in different domains ($\pm E_s$). The domain structure arises on illumination in external fields $0 \leqslant E_0 < E_s$; on illumination in fields $E_0 > E_s$ the homogeneous state is stable. The critical field E_s depends on the temperature T at which the illumination is carried out and on the power density P of the optical pumping. Reversible "phase" transitions of a critical character from the homogeneous to the domain state are observed in the illuminated ruby upon changes in the external conditions—E_0, T, P. The transitions brought on by changing E_0 are accompanied by hysteresis. The observed effects are explained in terms of the phenomenological theory of the photoelectric instability of centrosymmetric crystals.[4,5] It is assumed that the photovoltaic current arising in ruby in the presence of a field is opposite in sign to the field and thus gives rise to spontaneous space charges and an electric field E_s in the illuminated crystal. A photocurrent flowing counter to the field has been observed directly in measurements of the volt-ampere characteristics. We conclude with a discussion of the microscopic mechanism for the effect; this mechanism is intimately connected with the axial polar symmetry of the impurity centers in ruby.

In 1980 Liao, Glass, and Humphrey[1] described an interesting effect during intense laser illumination of crystals of concentrated ruby Al_2O_3:Cr^{3+}. They established that illumination of ruby at $T = 10$ K gives rise to a strong (up to 10^6 V/cm) inhomogeneous internal electric field; this field is directed along the trigonal axis C of the crystal and persists in the sample for a long time after the illumination is turned off and the sample warms up to room temperature. This effect is unusual because the Al_2O_3 crystal has a center of inversion (class D_{3d}), and so for reasons of symmetry ruby should not exhibit photovoltaic effects. It was assumed[1] that the illumination-induced field was due to the bulk photovoltaic effect, with the requisite asymmetry of the crystals being due to the chromium impurity—specifically, to a dissimilar distribution of the Cr^{3+} ions (which replace Al^{3+}) over two polar crystallographic positions (differing by inversion) in the lattice.

In the present study (see also Refs. 2 and 3) it is established by experiment that laser illumination of concentrated ruby crystals in fact causes a transition to a steady, spatially inhomogeneous state containing regions (domains) in which the internal electric fields directed along the C axis are equal in magnitude but of opposite sign. Illumination of the crystals in an external electric field causes the domain structure to undergo a characteristic rearrangement, which is accompanied by hysteresis. The appearance of these photoinduced electrical domains in ruby can be explained qualitatively on the basis of a phenomenological theory[4,5] which attributes the effect to an electrical instability of the crystal under illumination. The instability occurs because the photovoltaic current which arises in the centrosymmetric ruby crystal in the presence of a field flows (according to the hypothesis[4,5])

in the direction counter to the field. In the present study a photocurrent flowing in the crystal in the direction counter to an applied external electric field was observed directly by measuring the volt-ampere characteristics of optically excited ruby. In addition, we observed reversible "phase" transitions between the homogeneous and inhomogeneous (domain) states of the optically excited ruby upon changes in the external conditions—the temperature, the external electric field, and the intensity of the optical excitation. These transitions are found to exhibit characteristic critical behavior.

§1. OBSERVATION OF PHOTOINDUCED ELECTRICAL DOMAINS IN RUBY

a. Experimental techniques

To study the electric fields in ruby we made use of the so-called pseudo-Stark line splitting in the optical spectra of this crystal.[6] The splitting arises because the Cr^{3+} (Al^{3+}) ions are located in the Al_2O_3 lattice in an inversionless crystalline field (point group C_3) with polar axis C_3 parallel to the trigonal axis C of the crystal. There are thus two Cr^{3+} positions in the lattice (A and B), which differ in the direction of the polar axis of the local crystalline field. The application of an external electric field $E_0 \| C$ causes the electric levels of the Cr^{3+} ion to undergo a Stark shift which is linear in th field. There is a corresponding shift in the energy of the transition between Cr^{3+} levels: $\delta(h\nu) = \mathbf{d} - \mathbf{d}^0 | E_0$, where $\mathbf{d}^0$ and $\mathbf{d}$ are the dipole moments along C_3 of the Cr^{3+} ions in the ground and excited states; for ions in positions A and B the shifts are identical in size but of opposite sign. As a result, all the lines in the luminescence (and absorption) spectra of the Cr^{3+} ions in ruby are split in an external field $E_0 \| C$ into symmetric doublets of width

$$\Delta\nu = 2\beta E_0, \tag{1}$$

where $\beta = |\mathbf{d} - \mathbf{d}^0|/hc$. The individual components of the doublet correspond to transitons in ions A and B. Being symmetric, the pattern of the spectral splitting is not affected by changes in the sign of E_0.

The appearance of a photoinduced electric field along C in ruby under laser ilumination is detected[1] by the onset of a pseudo-Stark doublet splitting (in the absence of external field) of the luminescence lines R_1 and R_2, which correspond to transitions to the ground state from the two sublevels of the metastable ^2E state of Cr^{3+} ($\bar{E}\to{}^4A_2$, $2\bar{A}\to{}^4A_2$). The strength of the photoinduced field is found according to (1) from the value $\Delta\nu$ of the doublet splitting of the R lines [for which $\beta = 0.39{\cdot}10^{-5}$ cm^{-1}/(V/cm)].[7]

The majority of our experiments have been done on Al_2O_3 single crystals grown by the Verneuil method, with chromium concentrations $c\simeq 0.4\%$. The samples were in the form of thin slabs $\sim 10\times 10\times 0.1$ mm in size, cut along the basal plane of the crystal ($\perp C$). Transparent SnO_2 electrodes were deposited on both sides of the slabs; the centers of the slabs were illuminated through the electrodes by a Spectra-Physics cw Ar laser. The area of the illuminated region, defined by the diameter of the laser beam (~ 0.1 mm), was a small fraction of the total area of the slab. A voltage V was applied to the electrodes from an external source, producing in the crystal an average field $E_0 = Vl^{-1}$ ($E_0\|C$), where $l\approx 0.1$ mm is the thickness of the slab. The samples were placed in liquid (or gaseous) nitrogen. The R lines in the luminescence spectrum of the samples (at $T = 77$ K) had a half-width of $\Delta \approx 1$ cm^{-1} due to inhomogeneous broadening of predominantly concentrational origin.[8]

The photoinduced electric field in the sample was produced as in Ref. 1. The sample, at a temperature $T = 77$ K, was subjected to intense laser radiation ($\lambda = 514.5$ nm, beam power density $P\approx 100$ V/cm^2) in the absence of external field ($E_0 = 0$). As in the experiment of Ref. 1, the luminescence spectrum from the excited region of the sample in time began to exhibit a symmetric doublet splitting of the R_1 line, indicating that a photoinduced nonuniform electric field was arising in this region. After ~ 10 min the splitting reached a maximum value $\Delta\nu_s$ (Fig. 1a), ranging from 2.5 to 2.9 cm^{-1} in different samples. This indicates that the field saturates at a level $E_s = \Delta\nu_s/2\beta = 330$–370 kV/cm. The photoinduced field E_s persists indefinitely in the sample after the optical pumping is stopped, both at 77 K and when the sample is warmed to room temperature.

b. Influence of external electric field on the optical spectrum of samples containing a photoinduced field

The influence of an external electric field $E_0\|C$ on the luminescence spectrum of a sample in which a photoinduced field $E_s = 370$ kV/cm had been produced by the method described in §1a was studied at 77 K and 1.8 K. For this purpose a voltage V producing an average field E_0 was applied to the sample from an external source. It is important to note that the luminescence in these experiments was excited by a "probe" beam from an Ar laser (wavelength 514.5 nm) with a very low power density (~ 1 W/cm^2), at which the
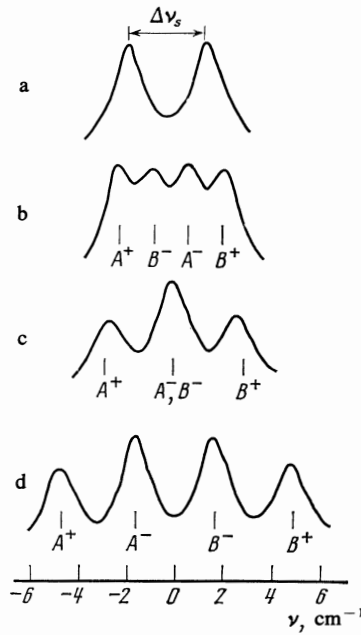

FIG. 1. a) Photoinduced doublet R_1 in the luminescence spectrum (a) $E_0 = 0$) and its splitting in an external electric field $E_0\|C$: b) $E_0 = 185$ kV/cm, c) $E_0 = 370$ kV/cm, d) $E_0 = 740$ kV/cm.

beam only excited ruby emission but did not of itself have a noticeable effect on the state of the illuminated region.

It was found that each of the components of the initial "photoinduced" doublet of the R_1 line (Fig. 1a) in the external field undergoes a practically symmetric reversible doublet splitting (see the spectrograms in Figs. 1 and 2). As a result, R_1 becomes a quartet in an external field. It is seen in Fig. 2 that the shift of the components in the field E_0 is linear and that it corresponds in size to the shift in an external field (the dashed lines in Fig. 2) of the components of the "ordinary" pseudo-Stark doublet splitting of the homogeneous R_1 line in a sample with no internal field ($\delta\nu = \pm\beta E_0$).

The observation of a reversible pseudo-Stark quartet splitting of R_1 implies directly that the photoinduced field makes the sample inhomogeneous; it contains regions (do-
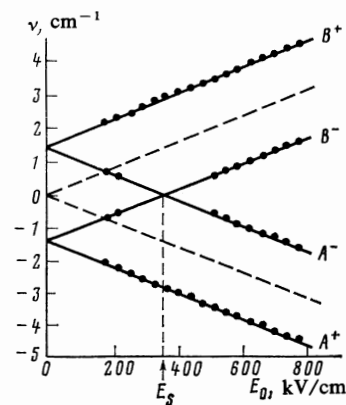

FIG. 2. Shift of the components of the splitting of the photoinduced doublet R_1 versus the field $E_0\|C$. The dashed line is the pseudo-Stark splitting of R_1 in a sample without a photoinduced field, and the points are experimental data.

mains) in which the field parallel to the C axis is equal in magnitude but of opposite sign ($\pm E_s$). In fact, in the absence of external field ($E_0 = 0$) the domains with $\pm E_s$ give identical (and hence indistinguishable) doublets Δv_s in the R_1 luminescence spectrum, since the symmetric pseudo-Stark doublet splitting depends only on the magnitude of the field. However, the application of an external field $E_0 \| C$ causes the field which acts on the Cr^{3+} ions in the domains of different sign to become different: in the " + " domains the external field E_0 adds to the photoinduced field ($E_s + E_0$) and in the " − " domains it subtracts from it ($E_s - E_0$). As a result, the luminescence spectra of the " + " and " − " domains have different-sized splittings of the pseudo-Stark doublets ($\Delta v^{\pm} = \Delta v_s \pm 2\beta E_0$), and a quartet appears in the combined spectrum. Figures 1 and 2 identify the quartet components belonging to the Cr^{3+} ions in the A and B positions in the domains of different sign. It is clear that when the external field becomes equal to the photoinduced field ($E_0 = E_s$) there is a complete compensation of the field in the " − " domains, and the pseudo-Stark doublet in the spectrum of these domains degenerates into a singlet (and the combined quartet spectrum degenerates into a triplet, Fig. 1c). We also note that all the components of the R_1 quartet are of approximately equal intensity (Fig. 1b). This indicates both that the volumes of the " + " and " − " domains are equal and that the average concentrations of the Cr^{3+} ions in A and B positions in these domains are close.

c. Selective excitation of the luminescence in photoinduced electrical domains of different sign

At $T = 77$ K the luminescence of a sample with a previously produced (Sec. 1a) photoinduced field $E_s = 370$ kV/cm was excited by the 476.5 nm line of the Ar laser at a low power density ~ 1 W/cm^2. The proximity of the 476.5 nm line to the intense, narrow B_1 absorption line of ruby at 476.2 nm (due to the transition $^4A_2 \rightarrow {}^2T_2$ in the Cr^{3+} ions) prompted the idea of the experiments.

The absorption spectrum of a sample with a photoinduced field $E_s \approx 370$ kV/cm has a B_1 line which is split into a doublet of width 10.5 cm^{-1} [the value of β in (1) for the B_1 line, $\beta_B = 1.44 \cdot 10^{-5}$ cm^{-1}/(V/cm), is 3.7 times larger than β_R for the R lines[7]]. The application of an external field causes a reversible splitting of the "photoinduced" doublet of B_1 into a quartet, in a manner analogous to that discussed in §1b for the R lines. The outer components of the B_1 splitting correspond to transitions in the " + " domains, in which E_s adds with E_0, and when the latter has the value $E_0 = 370$ kV/cm the longest-wavelength component of B_1 coincides with the position of the laser line at 476.5 nm. (The field E_0 at which the coincidence occurs is accidentally close in value to E_s. Therefore, in the " − " domains, which have "difference" combined field, the net field is close to zero, and the inner components of the quartet merge. Thus B_1, like all the other Cr^{3+} lines (Fig. 1c), has a triplet shape in the field $E_0 = 370$ kV/cm.) In this situation the 476.5 nm line excites predominantly the Cr^{3+} ions of the A + type, which are located in a definite polar position (A) in domains of a definite sign (" + "). Accordingly, at $E_0 = 370$ kV/cm the lumines-

cence spectrum of a sample excited by the 476.5 nm line exhibits a substantial intensification of the long-wavelength A + component of the R_1 triplet (Fig. 3a), i.e., of the component which corresponds to the transitions $\bar{E} \rightarrow {}^4A_2$ is selectively excited Cr^{3+} ions (for comparison, the dashed line in Fig. 3a shows the R_1 triplet under nonselective excitation by the 514.5 nm line).[1]

The most important result comes from studying the 700.9-nm luminescence line N_2, which is due[9] to exchange-coupled ion pairs Cr^{3+}–Cr^{3+}. The luminescence of these pairs is excited mainly through a migration of the optically produced $\bar{E}$ excitation via isolated Cr^{3+} ions, with a subsequent transfer of the excitation to the pairs.[9] Since the pairs have a constant dipole moment, the N_2 line exhibits a pseudo-Stark splitting in both external[10] and photoinduced[1,2] electric fields.

It was found that under conditions of selective excitation of the Cr^{3+} ions in the " + " domains by the 476.5 nm line, the outer components of the "triplet" luminescence line N_2 are noticeably intensified in comparison with the central component (see Fig. 3b, where the dashed line shows the N_2 triplet under nonselective excitation by the 514.5 nm line). Thus, under selective excitation of the isolated Cr^{3+} ions found at the A position in the " + " domains, there is a predominant transfer of excitation energy to the N_2 pairs located in the same " + " domains. This clearly demonstrates a localization of the corresponding isolated Cr^{3+} ions and N_2 pairs within domains of the same sign and also indicates that the " + " and " − " domains are separated in space, preventing the excitation from migrating between domains.[2] The conclusion that the photoinduced electrical domains exist as spatially separate regions in ruby is thus confirmed by direct experimental evidence.

§2. RESTRUCTURING OF PHOTOINDUCED ELECTRICAL DOMAINS IN AN EXTERNAL FIELD

In §1 the external electric field was used only as a factor causing an additional Stark shift of the levels and spectral lines of the Cr^{3+} ions in the photoinduced domains. Let us now turn to a study of the influence of an external electric field on the domain structure itself. The characteristic feature of these experiments is that the external field E_0 is applied under conditions of intense laser illumination ($P \approx 100$
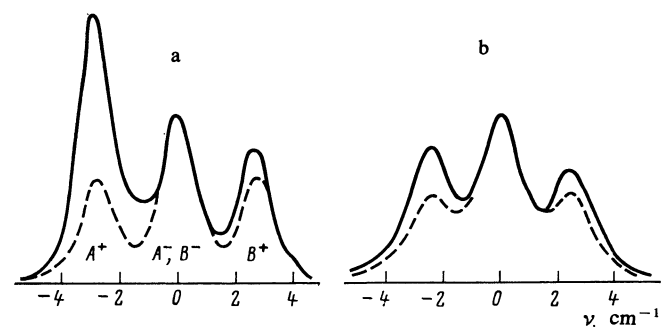

FIG. 3. Spectra of R_1 (a) and N_2 (b) in an external field $E_0 = 370$ kV/cm with the luminescence excited by the 476.5 nm line (solid curves) and by the 514.5 nm line (dashed curves).

W/cm²), where it is possible to have a rearrangement of the domain structure.

In experiments carried out at $T = 77$ K the sample was subjected simultaneously to intense laser illumination (514.4 nm, $P \approx 100$ W/cm²) and an external voltage V. We studied the R_1 line shape, which was mainly a steady pattern that evolved into a spectrum. We found that the steady spectrum R_1 depends most importantly on the relationship between the strengths of the applied external field E_0 and of the photoinduced saturation field E_s characteristic of the particular sample (see Sec. 1; in the samples studied $E_s = 370$ kV/cm).

a. Illumination in an external field $E_0 < E_s$

For $E_0 > E_s = 370$ kV/cm the R_1 spectrum measured under an applied voltage V evolves, as a result of intense illumination, into a steady shape which is practically independent of E_0. The spectrum is a symmetric doublet with a constant splitting $\Delta \nu_s \approx 2.9$ cm^{-1}, identical to the doublet induced by illumination in zero external field (Sec. 1; Fig. 1a). This shape of the final steady spectrum does not depend on the initial state of the sample prior to its intense illumination in the external field E_0. The initial state of the sample could be either the "ordinary" homogeneous state or a spatially inhomogeneous domain state produced, for example, by preliminary illumination in zero external field (Sec. 1).

Steady doublet R_1 spectra identical to that shown in Fig. 1a are observed when the external field E_0 is applied to the illuminated sample. Now suppose that the external voltage V and the intense illumination of the sample are turned off simultaneously. Then the spectrum of the R_1 luminescence (excited now by a probe beam of low intensity $P \approx 1$ W/cm²) is a quartet with intense inner and weak outer components, with the difference in the intensities of the components being greater the higher the field E_0 in which the illumination took place (see Fig. 2 in Ref. 2). The splittings of the inner and outer doublets of the quartet correspond to fields $E_s - E_0$ and $E_s + E_0$, respectively. This spectrum persists indefinitely in the crystal at $T = 77$ K and also when the crystal is warmed to $T = 300$ K.

Analysis of these results shows that intense laser illumination of a sample in an external field $E_0 < E_s$ gives rise to a steady spatial structure consisting of domains having electric fields of different sign, with the absolute value of the effective field E in the domains remaining at the level $E = E_s$ regardless of the value of the external field E_0. The combined volume of the " + " domains (with field E_s parallel to the external field) is larger than the volume of the " − " domains (with field $− E_s$ antiparallel to E_0), and the grater E_0, the larger the difference in the volume of the " + " and " − " domains. This last conclusion follows from the fact that the components of the R_1 quartets in the luminescence spectrum measured after removal of the external voltage V are of unequal intensity. In fact, when V is removed the turned-off external field E_0 is "subtracted" from the field $\pm E_s$ that has been established in the domains, and the fields in domains of different sign become different in absolute value: $E_s − E_0$ in the " + " domains and $E_s + E_0$ in the " − " domains. In the resulting R_1 quartet the inner components (the " + " do-

mains) are more intense than the outer components (the " − " domains); see Fig. 2 of Ref. 2.

b. Illumination in an external field $E_0 > E_s$

Under intense illumination of an initially homogeneous sample in an external field $E_0 > E_s = 370$ kV/cm, the R_1 spectrum measured under an applied voltage V does not change over time and is an "ordinary" pseudo-Stark doublet with a splitting determined by the external field $\Delta \nu(E_0) = 2\beta E_0$. When the external voltage V is removed (and the illumination is simultaneously stopped) the R_1 luminescence spectrum returns reversibly to the original unsplit (singlet) spectrum of ruby in the absence of field. The ruby sample thus remains homogeneous under intense laser illumination in a field $E_0 > E_s$.

Let now the initial state of the sample be the inhomogeneous (domain) state. Immediately after application of an external field $E_0 > E_s = 370$ kV/cm under conditions of intense illumination, the R_1 line is a pseudo-Stark quartet (see §1); then the quartet is transformed over time into a pseudo-Stark doublet with a splitting $\Delta \nu = 2\beta E_0$ corresponding to the external field E_0. Subsequent removal of the external voltage V (with a simultaneous shutoff of the illumination) restores the R_1 spectrum to the singlet spectrum of a homogeneous sample in the absence of field. Illumination in an external field $E_0 > E_s$ thus destroys the existing domain structure and renders the sample homogeneous.

c. Steady homogeneous and domain states of ruby under laser illumination in an external field

The experimental facts adduced in §§2a and 2b show that intense laser illumination ($P = 100$ W/cm² at 514.5 nm) of ruby at $T = 77$ K in an external field E_0 transforms the crystal into a new steady state which does not depend on the original state of the crystal but is determined by the strength of the external field E_0 in which the illumination was carried out. If the field E_0 is less than the characteristic critical field E_s for the sample ($0 \leqslant E_0 \leqslant E_s$), then the steady state is the spatially inhomogeneous domain state with fields $\pm E_s$ in the domains and with the relative volumes of the " + " and " − " domains depending on the strength of E_0. If the external field E_0 is greater than the critical value ($E_0 > E_s$), the steady state of ruby is the ordinary spatially homogeneous state in which the effective field is equal to the applied external field E_0. As the external field E_0 at which the crystal is subjected to the optical pumping is changed, a transition between the homogeneous and domain states occurs at the critical point $E_0 = E_s$.

The above picture of the formation of photoinduced domains[2] has recently found a theoretical explanation in terms of a phenomenological model[4,5] which attributes the effect to a photoelectric instability. The instability is assumed[4,5] to occur because the photovoltaic current $J(E)$ rising in the centrosymmetric ruby crystal in the presence of an electric field E is directed counter to the field. The total current density is

$$j = J(E) + \sigma E, \qquad (2)$$

where σ is the conductivity of the crystal under illumination.[3] If the absolute value of $J(E)$ at low fields is greater than

the photoconductivity current, the state with $E = 0$ will be unstable. A space charge and an internal field will arise spontaneously in the crystal. The steady-state value of the internal field is determined from the condition of zero total current (2): $E_s = -J(E_s)/\sigma$. For the present experimental situation (a slab with faces, $\perp C$, an external field $E_0 \| C$) it has been shown that in the absence of external voltage, domains of two signs ($\pm E_s$) form, occupying identical volumes and separated by plane ($\perp C$) charged walls. Upon illumination in an external field $E_0 < E_s$ the volumes with fields $\pm E_s$ are redistributed in favor of the domains having the same sign as E_0. Under illumination in field $E_0 > E_s$ the homogeneous state is stable.

For the case $E_0 = 0$ let us estimate the domain-wall surface charge density ρ_{surf} that would produce the observed field $E_s = 330$ kV/cm in the domains. In the version considered in Ref. 4, where the sample was divided into two electrical domains of different sign with a plane charged domain boundary at the center of the sample, the field E_s is given by $\rho_{surf}/\varepsilon_0\varepsilon$, where $\varepsilon = 11.4$ is the dielectric constant of Al_2O_3. A field $E_s = 330$ kV/cm corresponds to $\rho_{surf} 3.3 \cdot 10^{-7}$ C/cm$^2 \approx 2 \cdot 10^{12}$ electron charges per cm^2.

§3. VOLT-AMPERE CHARACTERISTIC AND HYSTERESIS EFFECTS IN OPTICALLY EXCITED RUBY

Analysis[3] of the steady-state field distributions in the illuminated sample at different applied external fields E_0 on the basis of the phenomenological model[4] gives the volt-ampere characteristic shown schematically in the inset in Fig. 4. On segment 1–2 ($0 < E_0 < E_s$), which corresponds to stable domain states of the crystal with fields of $\pm E_s$ in the domains (Sec. 2a), no current flows through the sample ($j = 0$).[4] Segment 3–4 corresponds to a homogeneous state of the sample, with the field in the sample determined by the external field $E_0 = Vl^{-1}$. In this case a current $j(E_0)$ flows through the homogeneous sample, and for $E_0 < E_s$ it is directed counter to the field. Thus, in the interval $E_t < E_0 < E_s$ there are two steady states of the sample—a homogeneous state and a domain state—which differ in the strcutre and size of the field in the sample and in the values of the current flowing through it. This circumstance makes it possible in principle to have hysteresis in the E_0 dependence of the current and field.

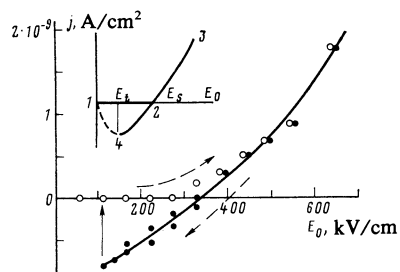The measurements were made on samples with a saturation photoinduced field $E_s = 330$ kV/cm. Under steady illumination at $P = 100$ W/cm^2 (514.5 nm) two parallel measurements were made at different values of the applied external field $E_0 = Vl^{-1}$: the steady current $j(E_0)$ flowing through the sample (the volt-ampere characteristic), and the doublet splitting $\Delta\nu(E_0)$ of the R_1 luminescence line (a measure of the effective field E in the sample).

As E_0 is increased in the interval $0 < E_0 < E_s$ the domain state of the crystal is stable, and the splitting $\Delta\nu$ remains unchanged at the level $\Delta\nu_s = 2\beta E_s$ (Sec. 2a). In the experiments the field E_0 was increased gradually in small steps. In this case the time required for the steady splitting $\Delta\nu$ to become established is very long (many hours), and therefore the values $\Delta\nu(E_0)$ measured over realistic time periods after E_0 had become established (see Fig. 5) are somewhat different from $\Delta\nu_s = 2.5$ cm^{-1} (the dash-dot line in Fig. 5). For external fields in the interval $0 < E_0 < E_s$ the measured volt-ampere characteristics (Fig. 4) show that the current j flowing through the illuminated sample is zero. This result agrees completely with the theoretical conclusion (segment 1–2 in the inset in Fig. 4).

As E_0 is increased further above the point $E_0 = E_s$ and on up to $E_0 = E_0^{max} = 650$ kV/cm, the splitting $\Delta\nu$ increases linearly with the field and corresponds to a pseudo-Stark splitting $\Delta\nu = 2\beta E_0$ in the field of a homogeneous sample (see Fig. 5 and Sec. 2b). At $E_0 > E_s$ a current begins to flow through the sample; the current increases with increasing E_0 (Fig. 4), corresponding to segment 2–3 on the volt-ampere characteristic for the homogeneous sample (inset in Fig. 4).

On the reverse path, as the external field E_0 decreases from E_0^{max} to $E_0 = E_s$ the curves of $\Delta\nu(E_0)$ and $j(E_0)$ coincide with the curves for increasing E_0 in the interval $E_s < E_0 < E_0^{max}$ (see Figs. 4 and 5). However, as E_0 is decreased below the point $E_0 = E_s$ there is a pronounced hysteresis in the behavior of the splitting $\Delta\nu(E_0)$ and current $j(E_0)$. In a certain interval $E_0 < E_s$ the splitting $\Delta\nu(E_0)$ continues to follow the pseudo-Stark splitting $\Delta\nu(E_0)$ in a uniform external field (see Fig. 5). This result is a direct indication that the homogeneous state of the illuminated sample persists in a certain region $E_0 < E_s$ (approximately to $E_0 = 100$ kV/cm) on the reverse path of the applied voltage. Further evidence of the persistance of the homogeneous state under these conditions is the "inertialess" conversion of the R_1 spectrum into a singlet when the external voltage is turned off.
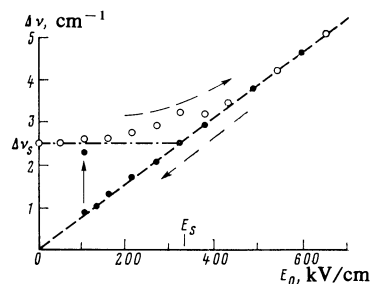

FIG. 4. Current through a sample illuminated at a power of 100 W/cm^2 versus the external field E_0; (O) increasing E_0, (●) decreasing E_0; the inset shows the theoretical volt-ampere characteristic.

FIG. 5. Steady-state doublet splitting of the R_1 line in the luminescence spectrum a sample illuminated at a power of 100 W/cm^2 versus the external field E_0: (O) increasing E_0; (●) decreasing E_0. The dashed line is the pseudo-Stark splitting $\Delta\nu = 2\beta E_0$.

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It can be seen from Fig. 4 that on the reverse path of E_0 the electric current changes sign at the point $E_0 = E_s$, and upon further decrease in E_0 it increases in absolute value, remaining negative. This corresponds to the theoretically expected behavior for a "frozen" homogeneous state of the sample on the reverse path of the external field in the region $E_0 < E_s$ (segment 2–4 on the volt-ampere characteristic in the inset in Fig. 4). An extremely important experimental observation is the negative sign of the current, which for $E_0 < E_s$ is directed coutner to the uniform electric field in the sample. This fundamental fact, by confirming the main hypothesis of the theory of Refs. 4 and 5, shows that the total photoelectric current during laser illumination of ruby in uniform fields $E_0 < E_s$ flows counter to the external field.

The photocurrents j directed counter to the field are clearly responsible for the separation of charges in the volume and the creation of the space charge that forms domain walls within the illuminated sample. Here the charge density on the wall is $\rho_{surf} \approx \bar{j}\Delta t$, where $\bar{j}$ is the average value of the current and Δt is the formation time of the wall. The value of $\bar{j}$ can be estimated from measurements of the negative currents on the volt-ampere characteristics in a homogeneous sample, when the charges are not "held back" in the volume $(\bar{j} \approx 10^{-9}$ A/cm^2 at $P + 100$ W/cm^2, Fig. 4). There is fair order-of-magnitude agreement among the value of this current, the value $\rho_{surf} = 3.3 \cdot 10^{-7}$ C/cm^2 (§2c), and the time of formation of the domain structure during illumination at the same power $(P = 100$ W/cm$^2)$ in zero external field $(\Delta t \approx 10$ min, §1a).

For $E_0 < E_s$ the homogeneous state is found to be unstable on the reverse branch of the experimental hysteresis. Over a certain time after the application of a field $E_0 < E_s$ the negative current falls (in absolute value) to zero (the arrow in Fig. 4). The splitting $\Delta v(E_0)$ increases from the pseudo-Stark splitting corresponding to the homogeneous state to the value Δv_s corresponding to the domain state with fields $\pm E_s$ (the arrow in Fig. 5). These observations are evidence of a spontaneous transition of the sample from the reverse branch of the hysteresis (the homogeneous state) to the forward branch (domain state). The smaller the field E_0, the faster the transition between branches occurs; at $E_0 = 110$ kV/cm it takes about an hour. Moreover, upon sufficiently fast changes in the external field E_0 the region 100 kV/cm $< E_0 < E_s$ of the lower branch of the volt-ampere characteristic can be traversed many times and in both directions (this region, 2–4 in the inset of Fig. 4, is characterized by a negative current through the sample).

These results demonstrate the possibility of measuring the current $j(E_0)$ on the "homogeneous" branch 3–4 of the volt-ampere characteristic (Fig. 4) over a wide range of fields E_0, including the critical point $E_0 = E_s$. In the region $E_0 > E_s$ (the region of positive photoelectric current) the maximum values of the field are limited by breakdown effects. In the region $E_0 < E_s$, corresponding to negative current, the minimum values of the field $(E_0^{min} \approx \frac{1}{3}E_s)$ are limited by the instability of the lower branch and the transition of the system to the upper (domain) branch. The point of zero current $j(E_s) = 0$ on the volt-ampere characteristic can be

used to determine a most important parameter—the critical field E_s.

§4. INFLUENCE OF ILLUMINATION INTENSITY ON THE BEHAVIOR OF THE DOMAIN STRUCTURE

Using the technique described in Sec. 3, we measured the dependence of the current density j on the external field E_0 for various illumination power densities P (see Fig. 6). The value of P was varied by regulating the laser power at a constant diameter of the laser beam illuminating the sample. The current density $j(E_0)$ was measured as E_0 was decreased from large values so that the crystal remained homogeneous (see §3), lying on branch 3–4 of the volt-ampere characteristic $j(E_0)$ (inset in Fig. 4). It is seen in Fig. 6 that the $j(E_0)$ curves intersect the abscissa progressively closer to the origin with increasing P, i.e., the saturation value of the photoinduced field E_s (corresponding to the point $j = 0$) falls off as the pumping P is increased.

The dependence of the fields E_s on the pumping density P as obtained from the position of the zero-current point $j(E_s) = 0$ on the volt-ampere characteristic (Fig. 6) is shown in Fig. 7. For comparison we also show the results of a direct measurement of the saturation field E_s in ruby as a function of the illumination intensity; these results were obtained from the value of the steady-state splitting $\Delta v_s = 2\beta E_s$ of the R_1 luminescence line when the sample was illuminated in zero external field (Sec. 1a). The $E_s(P)$ curves obtained by the two different methods are in good agreement. The descending $E_s(P)$ curve has a charcteristic bend at $P = 1$ kW/cm^2, and at large $P > 2$ kW/cm^2 the value of E_s decreases very slowly with increasing P. These results are in general agreement with the data of Ref. 1, which show a decrease in the photoinduced splitting Δv_s with increasing P. It is seen from Fig. 7 that the maximum value E_s^{max}, which is observed at small P is about 330 kV/cm.

Figure 8 shows the measured lux—ampere characteristics—the photocurrent j through a homogeneous sample versus the poewr density P at several fixed values of the external field E_0. In large fields $E_0 > E_s^{max}$, at which the photocurrent is positive (Fig. 4), the $j(P)$ curve is clearly faster than linear.[4] When $E_0 < E_s^{max}$ and the sample is originally in a homogeneous state, an increase in P gives rise to a negative photocurrent, which then changes sign and increases in the
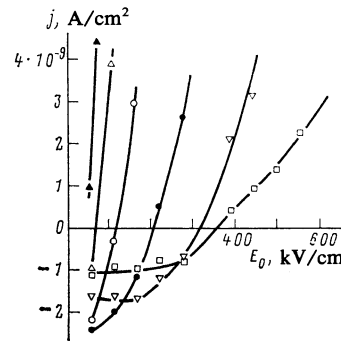

FIG. 6. Volt-ampere characteristics of a homogeneous sample at different power levels P of the optical excitation: (▲) 3.9; (△) 3.1; (○) 2.3; (●) 1.5; (▽) 0.8; (□) 0.4 kW/cm^2.
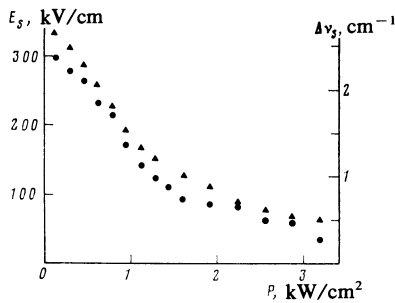
FIG. 7. Critical photoinduced field E_s versus the power of optical excitation, as inferred from the zero-current points on the volt-ampere characteristics (▲) and from the splitting of R_1 under illumination of the sample in zero external field (●).

positive direciton. This behavior of $j(P)$ clearly corresponds to a "vertical" transition ($E_0 = $ const) on the volt-ampere characteristics corresponding to different P (see Fig. 6).

Because the saturation field E_s depends on the illumination power P, one can observe a reversible transition between the domain and homogeneous steady states upon change in P. Suppose the sample is in an external field E_0 ($\lessdot E_s^{max}$) and is illuminated at a certain intensity P_0, producing the corresponding domain structure in the sample (§2); no current j flows through the sample (cf. §3). When the illumination intensity P is increased above a certain value $P_c > P_0$, a positive current begins to flow through the sample (see the inset in Fig. 8). This is a direct indication that when the pumping is increased above $P = P_c$ the sample undergoes a transition from the domain state into the homogeneous state (cf. §3, Fig. 4). This phenomenon occurs because E_s is shifted to lower values with increasing P (see Fig. 7). Because of this, the external field E_0 in which the domain sample is located turns out to be larger for $P > P_c$ than the saturation field $E_s(P_c)$ which corresponds to this intensity. The steady state for $E_0 > E_s(P_c)$ is already the homogeneous state (see §2) to which the transition occurs. Thus, the transition from the domain state to the homogeneous state on increasing optical pumping P in an external field E_0 has a critical character and is realized at a definite value of the intensity P_c (which depends on E_0).
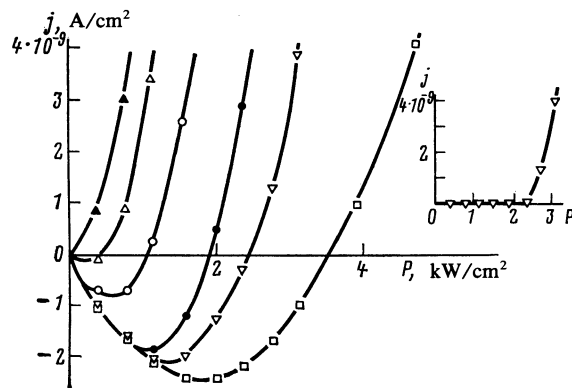

FIG. 8. Photocurrent versus the excitation power for the homogeneous state of the sample (in the inset, at the transition from the domain state to the homogeneous state) at varies E_0: (▲) 444; (△) 333; (O) 273; (●) 167; (▽) 111, (□) 56 kV/cm.
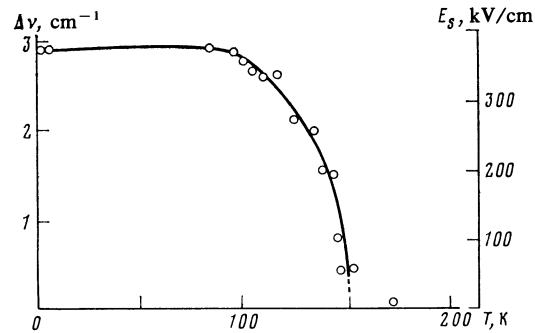

FIG. 9. Temperature dependence of the steady-state photoinduced splitting Δv_s and saturation field E_s in ruby.

§5. CRITICAL TEMPERATURE BEHAVIOR OF THE TRANSITION OF RUBY FROM THE HOMOGENEOUS TO THE SPATIALLY INHOMOGENEOUS STATE

To elucidate the temperature dependence of the saturation value of the photoinduced field $E_s(T)$ we subjected an Al_2O_3:0.4% Cr crystal to intense illumination (514.5 nm, $P = 50$ W/cm^2) at temperatures in the interval 1.8–300 K and then measured the steady-state doublet splitting Δv_s with the aid of a "weak" excitation of the luminescence ($P = 1$ W/cm^2) at sufficiently low temperatures ($T < 80$ K) that the R_1 line shape is not affected by temperature broadening.[12]

The $\Delta v_s(T)$ curve is shown in Fig. 9. It is seen that in the low-temperature interval below ~ 90 K the value of Δv_s is practically constant; as T is raised further Δv_s falls off, going to zero at $T_c = 150$ K. At $T > T_c$ there is no photoinduced splitting of the R_1 line. The values of $\Delta v_s(T)$ (and, accordingly, the values of the internal field $E_s = \Delta v_s/2\beta$) plotted in Fig. 9 are the steady-state values reached during the illumination regardless of the initial state of the crystals. In particular, if the sample had a domain structure produced by illumination at low temperature and a corresponding splitting of the R_1 line ($\Delta v_s = 2.9$ cm^{-1}), then a subsequent intense ilumination of the sample at $T > T_c$ will cause the spectral splitting of the R_1 line to vanish ($\Delta v_s \rightarrow 0$), i.e., will destroy the domain structure.

Thus, under conditions of intense optical pumping of concentrated ruby the character of its steady state depends critically on the temperature of the crystal. For $T < T_c = 150$ K the steady state is the inhomogeneous state with a domain structure. For $T > T_c$ the steady state is the "ordinary" homogeneous state. If, under conditions of intense illumination, the temperature passes through the point $T_c = 150$ K, there is a reversible transition of the crystal from the homogeneous phase ($T > T_c$) to the domain phase ($T < T_c$). the $E_s(T)$ curve is similar in shape to the characteristic temperature dependence of the order parameter for a second-order phase transition.

We stress that the temperature-induced transition between two states occurs only under intense illumination of the crystal. The temperature-induced transitions are blocked completely when the crystal is held in darkness or under weak ($P \approx 1$ W/cm^2) illumination.[5] Thus the domain state (with internal field E_s) produced by intense illumina-

tion at $T = 77$ K persists indefinitely (up to two years)[2] in darkness at 300 K. This "memory" is obviously due to the circumstance that the charges responsible for the internal field, which reside on the domain boundaries within the sample, are localized in deep traps. Experiments on the dark thermal annealing of the photoinduced (at $T = 77$ K) internal field in ruby have shown that only at $T = 700$ K is there a rather rapid destruction (in about an hour) of the field E_s and the domain structure.

§6. DISCUSSION

The main conclusion of this study—that concentrated ruby undergoes under intense illumination a transition to a spatially inhomogeneous steady state with electrical domains of different sign—is based on experiments involving spectroscopic measurements of the electric fields in the crystals (§§1b and 2), measurements of the photocurrents through the samples (§3), and the selective excitation of luminescence in domains of just one sign (§1c). The experimental data agree with the theoretical treatment[4,5] of the photoinduced formation of electrical domains as a photoelectric instability which develops because the photocurrent arising in the centrosymmetric ruby crystal in the presence of a field E is opposite in sign to the field, as we have observed directly in the experiments (Sec. 3). The fundamental quantitative characteristic is the value of the field E_s at which the total photocurrent (3) in a homogeneous sample is equal to zero. This field determines the saturation electric field in the photoinduced domains. The photoelectric domain instability of ruby under intense optical pumping is an example of the domain-type electrical instability of solid-state systems having negative differential conductivity.[13] It is interesting to note that besides having a negative differential conductivity (for $|E_0| < E_t$), ruby has a negative absolute conductivity (for $|E_0| < E_s$)—see the inset in Fig. 4.

In the present study we have focused on the steady (domain or homogeneous) states to which the illuminated sample undergoes a transition under some experimental conditions or other.[6] We have shown that the domain state is stable when the crystal is illuminated in external field E_0 lower than the critical field E_s, which itself depends on the sample temperature T and the level of optical pumping P. "Phase" transitions between the domain state and homogeneous state upon changes of one of three external factors E_0, T, and P exhibit a pronounced critical behavior. We also observed another characteristic phase-transition phenomenon—the "slowing down" of the light-induced formation of a steady domain structure as the external conditions approached critical ($T < T_c$ near T_c, $E_0 < E_s$ near E_s, Ref. 3).[7]

The critical behavior of the transitions follows from the theory for the formation of the photoinduced domains.[4,5] The condition of instability of the $E = 0$ state under illumination is $\partial j/\partial E \mid_{E=0} < 0$ (negative differential conductivity at small E). The total photocurrent j depends in general on the light intensity P, the temperature T, the concentration c of Cr^{3+} ions, and the concentrations of other impurities and defects. The specific form of this dependence depends on microscopic processes which are not yet known. However,

irrespective of the microscopic processes, the phenomenological condition $\partial j(E, P. T, c ...)/\partial E = 0$ (for small E), which determines the existence boundary for the photoelectric instability of the $E = 0$ state, yields an equation for determining the critical values of the parameters at which illuminated ruby can undergo a "phase" transition from the homogeneous state to the spatially inhomogeneous state.

The transitions on changes in T and P were discussed above. As to the parameter c, it has been established[1] that illumination at $T = 10$ K of a sample with $c < 0.1\%$ does not lead to splitting of the R_1 lines; for $c > 0.25\%$ there is always a splitting Δv_s, which increases with increasing c (at least up to $c = 0.9\%$). These results possibly indicate the presence of a critical concentration c_c lying in the region 0.1–0.2%. The dependence of the transition on other (unidentified) impurities and lattice defects is probably manifested in the fact that we observed no photoinduced domain formation in a series of rubies ($c \geqslant 0.9\%$) grown by other methods.

It should be kept in mind that concentrated ruby grown by the Verneuil method is very inhomogeneous and structurally imperfect; these factors probably determine the actual photoinduced domain structure. We observed doublet splitting of the R lines not only on illumination of oriented thin slabs but also in the spectrum of an excited volume created by a fine ($d \simeq 0.1$ mm) focused laser beam in bulk samples of arbitrary orientation and in the spectra of illuminated highly disperse ($\sim 10 \mu$m) ruby powders. These observations indicate that the domains can be extremely small (submicron size) and that the space-charge regions which create the field in the domains have a rather irregular distribution and shape. Moreover, this "self-organized" distribution[14] of space charge in the crystal should make for a rather uniform[8] field $\pm E_s$ in the domains and bring about the observed relationship of the volumes of domains of different sign in accordance with the applied external field E_0.

In the phenomenological theory[4,5] it was essential for the formation of the photovoltaic current in the centrosymmetric ruby crystal that the crystal acquire a polar asymmetry in an electric field. It was assumed in Refs. 4 and 5 that this asymmetry is due to a difference between positions A and B in the number of Cr^{3+} ions, not in the ground state,[9] but in the excited ^2E state: in an electric field the ^2E states in the A and B positions are energetically nonequivalent (see Sec. 1a), and the excitations tend toward a Boltzmann distribution.[10] The population difference leads to uncompensated photovoltaic current during photoionization from the ^2E states of the A and B ions. The sign of this current with respect to the field E, which acts only indirectly (through the population), can, in principle, be negative.

We note that in this scheme the "active" impurity ions in the polar A and B positions may not be the Cr^{3+} ions[11] but Cr^{2+} ions, which are known to be formed during intense illumination of ruby.[16] In this case the phototransport of charge in concentrated ruby will have the character of photostimulated hops of the charge state Cr^{2+} along the system of Cr^{3+} ions, whose concentration is extremely high ($\sim 10^{20}$ cm^{-3}). The linear shift of the Cr^{2+} levels in an electric field is much larger[12] than the shift of the t^3 levels of Cr^{3+}; this

larger shift would give a larger energy in the Boltzmann factor describing the distribution of the Cr^{2+} ions over the A and B positions in a field, an important consideration for explaining the high critical temperature $T_c = 150$ K.

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[1]The finite intensity of the other (besides A^+) components of R_1 (Fig. 3a) is attributed mainly to the fact that the B_1 line is located on the wings of the broad U and Y absorption bands of ruby, through which the 476.5 nm radiation excites all the Cr^{3+} ions to a certain degree. The intensification of the short-wavelength B^+ components is due to the transfer of excitation between the Cr^{3+} ions in the A and B positions in the " $+$ " domains.

[2]According to Ref. 11, the spatial migration of the $\bar{E}$ excitations is limited to distances $<0.03\,\mu$m.

[3]The dark conductivity of ruby at 77 K is too small to measure.

[4]Recall the results of photocurrent measurements for the case of photoinduced domains in a ruby slab cut along a plane containing the C axis, where the external field E_0 and the photocurrent j are perpendicular to C. The volt-ampere characteristic (for $P = 0.1$ kW/cm^2) has a linear ohmic shape.[3] Thus, the shape of the volt-ampere characteristic for $j \perp C$ is fundamentally different from that for $j \| C$.

[5]This circumstance is very important from a methodological standpoint, since it enables one, by lowering the level of illumination, to "freeze" states of the crystal at any stage of the transition and to study these states at different temperatures.

[6]The time required for the steady state to be established after the external conditions are changed depends importantly on the initial state of the sample (§§2 and 3a and also Ref. 3) and can in general be very large. The kinetics of the formation and destruction of the domain structure or of its transformation upon changes in the external conditions (for example, the rearrangement of the domain structure in an external electric field) is a question of great interest in its own right and is the subject of a separate discussion.

[7]It is of interest to analyze the properties of these transitions in illuminated ruby in terms of the general concepts of nonequilibrium phase transitions in open systems (see, e.g., Ref. 14).

[8]The nonuniformity of the field E_s indicates that there is no appreciable broadening of the components of the photoinduced pseudo-Stark doublet.

[9]The assumption in Ref. 1 that a "growth" asymmetry of the distribution of Cr^{3+} over A and B positions plays a decisive role in the formation of the photovoltaic current is obviously incorrect in view of our observation

of electrical domains having fields of different sign and especially in view of the switching of the signs of the domains in an external field.

[10]It seems to us that the unequal populations of the ^2E states of $Cr^{3+}(A)$ and $Cr^{3+}(B)$ in a field can also come about effectively on account of their different pumping under selective excitation by the laser lines through the absorption bands. In fact, since these bands suffer a pseudo-Stark splitting in a field, the absorption of the laser line is different for bands due to the A and B ions (coefficient Sec. 1c).

[11]The possibility of photoionization of isolated Cr^{3+} ions from the ^2E state by Ar-laser photons with $h\nu \approx 20\,000$ cm^{-1} is questionable in view of the data of Ref. 15 on the upper excited levels of Cr^{3+} in Al_2O_3.

[12]According to Ref. 7, even for the higher excited state $^4T_2$ (t^2e) of the Cr^{3+} ions the Stark shift is ~ 15 times larger than the shift of the ^2E state.

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