

Alternating-sign photostimulated resonant electrical conductivity of chromium ions in ruby

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A current observed during the excitation of $\text{Al}_2\text{O}_3:0.4\% \text{Cr}$ in the R lines changes sign as the frequency is scanned over the lines. This photocurrent results from a hopping of excess charge along Cr^{3+} ions excited into the 2E state. The sign of the current changes because of a spectrally dependent, spatially asymmetric excitation of Cr^{3+} ions in the Coulomb field of the charge carriers (Cr^{2+} or Cr^{4+}).

Concentrated ruby crystals exhibit some unusual photoelectric properties.^{1,2} The current-voltage characteristic of the photocurrent, $j''(E)$, in a field $\mathbf{E}||C$ (C is the trigonal axis of the crystal) has an N -shaped structural feature with regions of negative absolute and differential conductivity. As a result, an electrical instability occurs in optically excited ruby, and domains of a strong electric field $\pm E_s$ ($|E_s| \approx 5 \times 10^5$ V/cm form spontaneously). In the present letter we report the first study of the spectrum of the photocurrent in concentrated ruby. We have observed, and we offer an interpretation of, an *alternating-sign resonant photoconductivity*. The elementary mechanism which determines the direction of the charge transport in the field is determined; this information is important for understanding the nature of all the photoelectric anomalies of ruby.

The measurements were carried out at 77 and 4.2 K with thin (0.2 mm) single-crystal wafers of $\text{Al}_2\text{O}_3:0.4 \text{ wt.}\% \text{Cr}_2\text{O}_3$ in the orientation $1C$. A static voltage which produces a uniform field $\mathbf{E}_0||C$ is applied to transparent electrodes deposited on the faces of the wafer. The wafer is illuminated through the electrodes by the beam from a tunable pulsed laser (LZhI-504; $\Delta t_p = 20$ ns, $f_{\text{rep}} = 10$ kHz, $P_{\text{av}} = 100$ mW). The steady-state photocurrent $j''(\nu)$ is measured; it is a linear function of P_{av} . To avoid the formation of electrical domains,^{1,2} we carry out the measurements in fields E_0 near the critical field $E_s = 475$ kV/cm, at which the sign of the photocurrent changes on the I - V characteristics during excitation in the Ar line at 514.5 nm.

Figure 1 shows the results of the measurements of $j''(\nu)$ in the vicinity of the U band (the transition ${}^4A_2 \rightarrow {}^4T_2$ in Cr^{3+} ions) and the R_1 line (${}^4A_2 \rightarrow \bar{E}$) of the absorption of ruby for two fields $\mathbf{E}_0||C$: $E_0 > E_s$ and $E_0 < E_s$. Also shown here are spectra characterizing the absorption of ruby, $k(\nu)$: in the U band, the excitation spectrum of the $R_1 + R_2$ luminescence; in the R_1 line, the luminescence line during excitation through 4T_2 . In external field $\mathbf{E}_0||C$ there is a "pseudo-Stark" doublet splitting of all the spectral bands, caused by an opposite shift of the levels of the Cr^{3+} ions, which occupy polar positions A and B in the lattice, which differ by an inversion.³

For the U band, the behavior $j(\nu)$ corresponds closely to the course of the absorption $k(\nu)$ both at $E_0 > E_s$, and when we have $j > 0$, and at $E_0 < E_s$, at which the

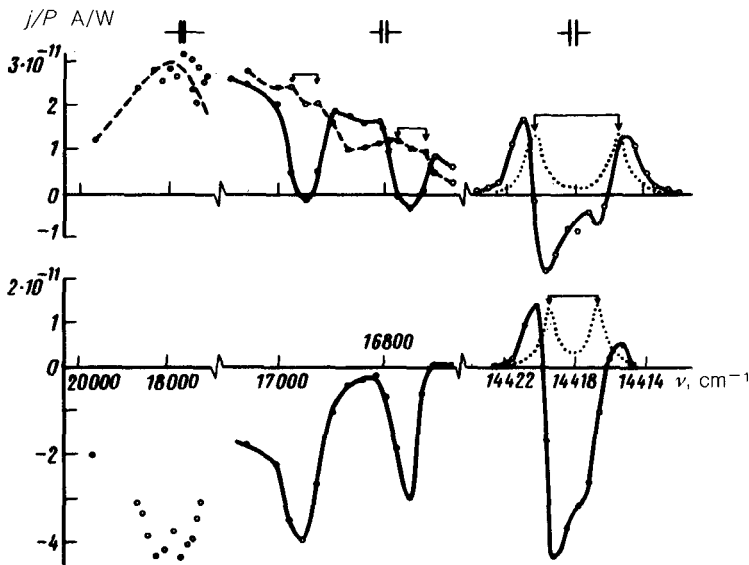


FIG. 1. Dashed line—Absorption spectrum; points and solid lines—photocurrent spectrum in the cases $E_0 > E_s$ (top) and $E_0 < E_s$ (bottom). Shown here are the pseudo-Stark doublets (arrows) and the spectral widths of the laser excitation (+ +). $T = 77$ K (U band) and $T = 4.2$ K (R_1). For the R_1 line, the value of j has been reduced by a factor of two.

photocurrent is directed opposite the field ($j < 0$). On the long-wave slope of the U band, in the middle of the pseudo-Stark doublet of the zero-phonon line (597 nm) of the U band and its first vibrational repetition, we observe narrow surges in $j''(\nu)$ in the direction of a negative photocurrent. Near the R_1 absorption line, the photocurrent is excited primarily on the wings of the components of the pseudo-Stark doublet. The photoconductivity changes sign in the spectrum: We have $j''(\nu) > 0$ on the "outer" wings of the doublet and $j''(\nu) < 0$ on the "inner" wings. As E_0 is increased, the amplitude of the positive current increases, while that of the negative current decreases. The spectra $j(\nu)$ at $T = 77$ K and $T = 4.2$ K are slightly different.

The photocurrent thus arises during the direct resonant excitation (${}^4A_2 \rightarrow {}^2E$) or during the nonresonant excitation (through 4T_2) of Cr^{3+} into the 2E metastable state. This is an unexpected result, since the excitation energy of 2E ($14\,400\text{ cm}^{-1}$) is far lower than the ionization potential of Cr^{3+} in the Al_2O_3 lattice.⁴ We are left with the conclusion that the charge transport occurs through an impurity system of Cr^{3+} ions through photostimulated hops of an anomalous charge state of the ions (different from Cr^{3+}), which corresponds to Cr^{2+} and/or Cr^{4+} ions, which are either initially present in the ruby at a low concentration or are produced in it during intense illumination.⁵

In order to explain the spectrum and the change in the sign of $j''(\nu)$ during resonant excitation in the R line (Fig. 1), it is of fundamental importance to consider the effect of the Coulomb field E_c of the Cr^{2+} (or Cr^{4+}) charge carrier on the Cr^{3+}

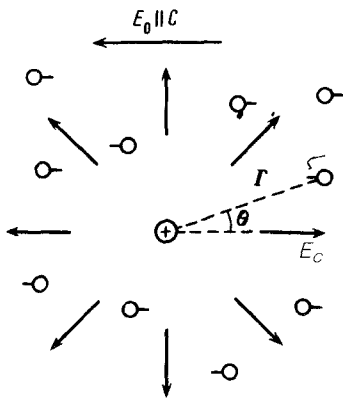


FIG. 2. Effect of the Coulomb field of the Cr^{4+} ion (at the center) on the surrounding Cr^{3+} ions in A positions (\circ) and B positions ($\text{—}\circ$).

ions around it. A photostimulated hop of an electron from a Cr^{2+} ion (or of a “hole” from a Cr^{4+} ion) occurs to these surrounding ions (Fig. 2). The field of the Cr^{4+} ion (the case we are considering here) causes in the Cr^{3+} ions a Stark shift of the R lines,

$$\Delta\nu = \frac{e \cos\theta}{4\pi\epsilon_0\epsilon r^2} \Delta d,$$

where r is the Cr^{4+} – Cr^{3+} radius vector, θ is the angle between this radius vector and the C axis, $\epsilon = 11.3$ is the dielectric constant of Al_2O_3 , and $\Delta d = 0.39 \times 10^{-5} \text{ cm}^{-1}/(\text{V}/\text{cm})$ (Ref. 3). For the characteristic distance $\bar{r} = 2 \text{ nm}$ between Cr^{3+} ions in ruby with $c = 0.04\%$, the shift (at $\theta = 0$) $\Delta\nu = 1.2 \text{ cm}^{-1}$ exceeds the half-width of the R lines. The spectrum of “photoelectrically active” Cr^{3+} ions near the charge carriers is thus shifted to the wings of the R lines (Fig. 3). Furthermore, in an external field E_0 the resultant field $E_0 + E_c$ is *different* for Cr^{3+} ions to the *right* and *left* of a Cr^{4+} ion. The corresponding arrangement of the R spectrum of the “active” ions of types A and B in the spectrum of the pseudo-Stark R doublet is shown in Fig. 3. We see that excitation to the inner wings of the R doublet leads to a selective excitation of Cr^{3+} to

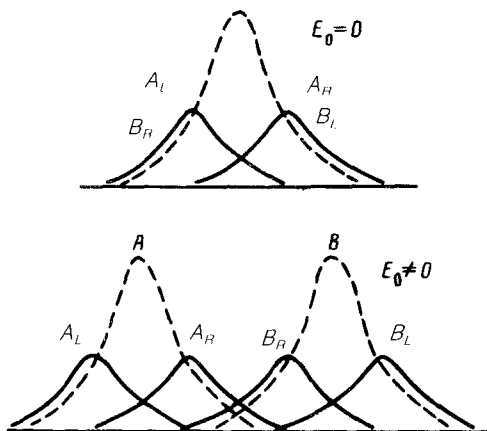


FIG. 3. Schematic representation of the R line for the bulk of the Cr^{3+} ions (dashed line) and for the photoelectrically active Cr^{3+} ions (solid line).

the right of Cr^{4+} , so that a hop of a hole from a Cr^{4+} ion to a Cr^{3+} ion is possible only to the right, i.e., in the direction opposite the external field E_0 (a current $j'' < 0$). Excitation to the outer wings of the R doublet, which selectively involves the "left-hand" Cr^{3+} ions, leads to the possibility of a transport of a hole exclusively to the left, along the direction of the field E_0 ($j'' > 0$). The shape of the spectrum of the resonant photocurrent, $j''(\nu)$ (Fig. 1), agrees with these conclusions, which—as is easily shown—are the same in the case of "negative" charge carriers¹⁾ (Cr^{2+}).

It can be seen from Fig. 3 that on the overlapping inner wings of the R doublet, where the current is $j'' < 0$, the Cr^{3+} ions of types A and B are excited simultaneously (there are the "right-hand" ions). On the outer wings, with $j'' > 0$, only the ("left-hand") ions of type A or only those of type B are excited. The average distance \bar{r} between ions, between which charge transfer is possible in principle, is smaller in the first case by a factor of $3\sqrt{2}$ than in the second. This difference is extremely important for the hopping conductivity, for which the hopping probability is $\sim \exp\left(-\frac{2r}{a}\right)$, where a is the radius of the ψ function of the impurity ion. This circumstance provides a qualitative explanation for the large absolute value of the negative current (at $E_0 = 370 \text{ kV/cm} < E_s$) and for its decrease with increasing E_0 (Fig. 1), when the overlap of the "inner" spectra of the A and B active ions decreases because of the opposite pseudo-Stark shift.

By analogy with the negative $j''(\nu)$ in the R lines, we can explain the resonant negative surges in $j''(\nu)$ near the zero-phonon line (and its first satellite) of the U band. However, during very nonresonant excitation of Cr^{3+} into 2E through the structureless part of the U band, the spatial asymmetry of the excitation of the active ions is greatly suppressed. In this case, we should take into account²⁾ the unavoidable additional "resonant" excitation of active ions into the 2E state by R -luminescence light emitted by the bulk of the Cr^{3+} ions in order to explain the negative current at $E_0 < E_s$ (Fig. 1 and the I - V characteristic for $\lambda_{\text{exc}} = 524.5 \text{ nm}$). As follows from Fig. 1, the nature of the overlap of the luminescence spectrum of the ground R doublet (dashed line) with the photoconductivity spectrum (solid line) leads at $E_0 < E_s$ (while the R doublet is poorly resolved) to an asymmetry in the spatial excitation in favor of the "right-hand" active ions. The result is a predominance of the negative current. We furthermore do not rule out the possibility that a role is being played by the effect of the field E (which is strong for the polar positions) on the energy barriers near the chromium ions which determine the probability for the hopping of a charge between these ions.

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¹⁾In the case $E_0 \perp C$, in which the R line is not split, the current satisfies $j''(\nu) > 0$ and is close to the R_1 line but significantly broader; this circumstance also suggests effective excitation in the wings. The shape of the $j''(\nu)$ curve is evidence that the mechanism of a resonant negative absolute photoconductivity discussed in Ref. 6 is not operating in the ruby.

²⁾As was pointed out by M. I. D'yakonov.

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