Theory of an absolute negative photoconductivity of ruby

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Microscopic mechanisms of an absolute negative photoconductivity (ANP) of ruby subjected to resonant and nonresonant action of light are proposed and investigated. In the case of the resonant excitation the negative current is associated with a selective intracenter filling of metastable ^2E levels of active Cr^{3+} ions and subsequent symmetric intercenter hopping recombination, as proposed by Basun, Kaplyanskiĭ, and Feofilov [JETP Lett. **43**, 445 (1986)]. In the case of nonresonant excitation via U or Y bands the ANP is due to a field-induced reduction in the lifetime of the ^2E excitations at active centers and resonant energy transfer. In high fields an important role is played by the asymmetry of the intracenter recombination in short-lived $^4T_2$ levels of Cr^{3+}. The theory accounts for all the experimental data on the field, spectral, kinetic, concentration, and temperature dependences of the ANP. The theoretical predictions are discussed.

INTRODUCTION

Liao, Glass, and Humphrey[1] discovered in 1980 a spontaneous appearance of an electric field of $E_0 \approx 10^6$ V/cm in concentrated ruby under the action of blue-green light of moderate intensity. More extensive studies of this effect were made[2–4] and it was found that it was due to the existence of a current directed against the field, i.e., due to an absolute negative photoconductivity (ANP) in fairly low fields $E < E_0$.

The interest in the ANP is not simply due to the high intensity of the photoinduced field, but also to the novel and unusual nature of the effect itself that has no other analogs in semiconductors or insulators.

Many important relationships and manifestations of the ANP in ruby have now been established reliably. They include critical temperature and concentration dependences of the field E_0, its high value and unusual range of changes at low illumination intensities, as well as formation and modification of electrical domains.[1–5] Discovery of a resonant ANP, characterized by a change of the sign of the current when the frequency of light ω is scanned in the vicinity of the R line of ruby,[6,7] has been important for the understanding of the nature of the effect. Finally, experimental data on the kinetics of the current observed in response to light pulses have been published recently[8] and they supplement significantly the picture of the phenomena occurring in ruby.

Theoretical investigations of the mechanisms of the ANP have been lagging considerably behind the experimental studies.[1)] Although a microscopic description of the ANP proposed in Refs. 11 and 12 provides useful general ideas (hopping transport of charge, active centers, asymmetry of intercenter transitions), the investigated mechanisms do not apply directly to ruby. An important but far from complete interpretation of the resonant ANP, based on the idea of selective intracenter excitation of active Cr^{3+} ions, can be found in Refs. 6 and 7. The treatment given in Ref. 13 is internally inconsistent and does not describe the physical situation in ruby.

In the present paper we shall develop a theory of the ANP in ruby at low illumination intensities and we shall show that this theory provides a qualitative (and in some cases a semiquantitative) description of the experimental results and also makes certain predictions. The aim will be to tackle two main tasks. The first is the explanation of the negative nature of the current and determination of the current-voltage characteristic $j(E)$ in low fields. The second is finding the mechanism of the change of the sign of the current at high values of E and determination of the photoinduced field E_0.

The paper is organized as follows. In §1 we shall give the necessary spectroscopic data on Cr^{3+} ions in ruby, introduce the concept of active centers responsible for the transfer of charge, and discuss the expressions for the probabilities of the main electron transitions. We shall derive a general expression for the current allowing for the selectivity of the intracenter excitation and recombination and for the asymmetry of the intercenter recombination processes.

The resonant ANP is discussed in §2. In weak fields, $E \lesssim E_0$, the negative current is due to selective intracenter excitation of the active Cr^{3+} ions[6] and the subsequent intercenter recombination. An increase in E increases strongly the positive contribution of the current, associated with jumps between metastable ^2E levels of chromium, and the total current changes its sign. The qualitative ideas put forward in Refs. 6 and 7 are used to obtain expressions describing the main features of the spectral dependence of the current and also the dependence $j(E)$ in low and high fields. The photoinduced field E_0 and the critical temperature T_c are determined.

Mechanisms of the nonresonant ANP are discussed in §3. In the case of nonresonant excitation there is a characteristic weakening of the selectivity of filling of metastable levels of the active centers. This is accompanied by a corresponding reduction of the current normalized to the absorbed energy. Competing negative and positive contributions to j are then due to different processes. The negative contributions include firstly the field-induced reduction in the lifetime of the metastable states and the resonant transfer of the energy of ^2E excitations. The most important among the positive contributions observed in low and moderate fields E is related to the intercenter recombination of highly

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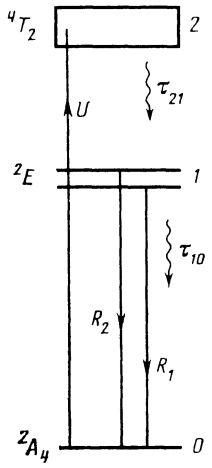

FIG. 1. Main levels and transitions involving Cr^{3+} in ruby.

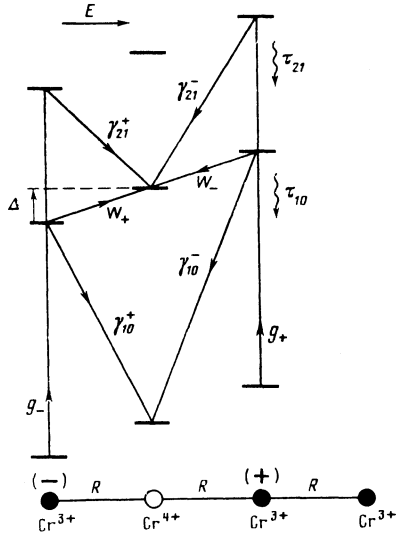

FIG. 2. Working levels in main transitions in active centers in the presence of an electric field.

excited short-lived $^4T_2$ states of Cr^{3+}. This instantaneous reponse accounts in particular for the fast kinetics of the current in the case of pulsed excitation[8] and for the change in the sign of j in the range of fields $(3–5)\times 10^5$ V/cm. In view of the different Cr^{3+} concentration dependences of the positive and negative contributions of the current and ANP disappears at a sufficiently low concentration of chromium. This accounts for the critical chromium concentration dependence of E_0 reported in Ref. 3. The critical temperature dependence of the ANP can be explained by a steep rise of the probability of jumps between the ^2E levels. The value of T_c then decreases slightly compared with the value in the resonance excitation case.

The concluding section provides theoretical predictions, deals with the unsolved problems, and outlines future investigations.

§1. MAIN MODEL

The experimentally observed spectral dependences of the photocurrents[1,3,6,7] demonstrate unambiguously that the transport of charge is associated with the intracenter excitation of the Cr^{3+} ions. The main levels and transitions exhibited by the Cr^{3+} ions in ruby are shown in Fig. 1. The nonresonant ANP is excited by pumping of the wavelength of the U (or the shorter-wavelength Y) absorption band. An electron at the T level relaxes rapidly, in a time $\tau_{21}=10^{-7}–10^{-9}$ s, and nonradiatively to the metastable E level.[14,15] The lifetime at this metastable level is governed by radiative processes and at temperatures $T\lesssim 150$ K amounts to $\tau_{10}\approx(3–4)\times 10^{-3}$ s. Luminescence from the crystal-field-split ^2E level gives rise to the familiar R_1 and R_2 lines of ruby. This splitting is not relevant to our discussion.

It is important to note that the Cr^{3+} ions in the corundum lattice are equally likely to be at two polar positions A and B. At these positions the frequency shifts of the transitions caused by an electric field are equal and opposite $\pm\omega_d=\pm\hbar^{-1}\mathbf{d}\cdot\mathbf{E}$, where $\mathbf{d}$ is the effective dipole moment parallel to the trigonal axis of a ruby crystal.[3,16] In the case of the R lines[2)] we have $\hbar^{-1}d\approx 0.4\times 10^{-5}$ cm^{-1}/(V·cm^{-1}). The opposite shifts of the levels at the A and B positions are manifested experimentally as the splitting of the lines by an amount $2\omega_d$, which represents the pseudo-Stark splitting.

The intracenter excitation of the Cr^{3+} ions does not of itself result in charge transport. However, it facilitates the subsequent participation of electrons in the creation of an electric current. At low illumination intensities, when the lux-ampere characteristic of ruby can be regarded as linear, an electric current can only be created as a result of intercenter hopping of excited electrons to neighboring centers, which have close or lower energies. Hopping of electrons from one Cr^{3+} ion to a neighboring Cr^{3+} ion is then impossible, because it would have created Cr^{2+}, Cr^{4+} pairs and this would have increased the energy significantly. We can regard it as generally established that only those Cr^{3+} ions participate directly in charge transport which are the nearest neighbors of Cr^{4+} (or Cr^{2+}, see Ref. 6). Following Refs. 6 and 12, we shall refer to them as the active Cr^{3+} ions. The current j is then due to electron hopping from excited Cr^{3+} states to Cr^{4+}, i.e., it is due to a charge-transfer reaction. It can be regarded as the motion of a Cr^{4+} hole along a crystal.

A scheme of the operating levels of the active centers and of the actual transitions in the presence of an electric field is given in Fig. 2. The relative shfit of the levels of the neighboring centers is $\Delta=\hbar^{-2}eER$, where R is the average distance between the Cr^{3+} ions. The difference between the probabilities of jumps along the field (W_+, γ^+) and against the field (W, γ^-) is related to this shift.

If we use $n_{1,2}^+$ and $n_{1,2}^-$ to denote the electron densities at the levels 1 and 2 of positive and negative active centers (Fig. 2), we obtain the following expression for the current j:

$$j=-eR[n_1^-(W_++\gamma_{10}^+)-n_1^+(W_-+\gamma_{10}^-)+n_2^-\gamma_{21}^+-n_2^+\gamma_{21}^-]. \quad (1)$$

The field E, unless otherwise stated, will be regarded as parallel to the trigonal axis of a crystal.

Equation (1) allows for two different ANP mechanisms: a "selective" mechanism associated with the difference between the values of n^+ and n^- due to the intracenter transitions, and an "asymmetry" mechanism associated with the influence of the field on the intercenter processes. These two mechanisms are important for the description of the ANP. However, we shall ignore hopping between the upper T levels. This will be justified later.

We shall discuss the probabilities of the intercenter pro-

cesses γ and W. It follows from general considerations that all of them contain an exponentially small hopping parameter $\exp(-R/a)$, where a is the corresponding localization radius of an excited electron, i.e., the radius of the square of the wave function. Obviously, the probabilities W_+ and W_- of the intercenter hopping between the metastable ^2E levels (Fig. 2) are related by the general expression

$$W_+ = W_- \exp(-\hbar\Delta/T). \quad (2)$$

There is no similar relationship between the rates of intercenter recombination processes γ_{21}^+, γ_{10}^+ and γ_{21}^-, γ_{10}^-. In fields of hundreds of kilovolts per centimeter, typical of experiments on ruby, the argument of the exponential function in Eq. (2) is $\hbar\Delta/T \gg 1$. For example, if $E = 5\times 10^5$ V/cm and $T = 4$ K (which corresponds to the results in Refs. 3 and 6), we find that $\Delta \approx 800$ cm^{-1} and $\hbar\Delta/T \approx 2.7\cdot 10^2$. Consequently, with the exception of very low fields, we have $W_+ \ll W_-$. Hence, it follows that hopping between the metastable ^2E levels makes a positive contribution to the current and the ANP is impossible without sufficiently fast intercenter recombination.

We shall now discuss the expressions for W_- and $\gamma^\pm$. It should be pointed out straightaway that we shall not be concerned with the absolute values of these quantities but with their dependences on the field shift Δ.

The probability W_- represents the low-temperature limit of the exothermal reaction of electron tunneling. Theoretical and experimental investigations of the tunneling over long distances have been pursued vigorously in the last two decades.[17–19] The accumulated data demonstrate that the process is common and that it is sensitive to the parameters of the centers and of the medium. A theory of multiphonon processes used in the tunneling calculations makes it possible to express W_- in terms of a small number of parameters which have reasonable meanings and magnitudes.

One of the main parameters of an intercenter transition is the "reorganization" energy $\hbar\omega_r$, which is analogous in meaning to the polaron shift of levels. It represents the shift of ions due to a change in the electron configuration. In the case of Cr^{3+} in ruby the polaron shifts are large. For example, in the case of the U and Y absorption bands of Cr^{3+} we have $\omega_r \approx (3\text{–}4)\times 10^3$ cm^{-1} (Ref. 15). Intercenter transitions correspond to a major change in the electron configuration. We can therefore expect $\omega_r \gtrsim 5\cdot 10^3$ cm^{-1}. Another important characteristic of a crystal is its phonon spectrum. At low temperatures when $\Delta \ll \omega_r$, we can estimate W best using the Debye model.[18,19] This model yields the following expression:

$$W_- \approx \nu_0 (\Delta/\omega_r)^N \exp(-R/a_1); \quad NT \ll \hbar\Delta \ll \hbar\omega_r, \quad (3a)$$

$$W_- \approx \nu_0' (T/\hbar\Omega)^N \exp(\hbar\Delta/2T)\exp(-R/a_1); \quad \hbar\Delta \ll NT. \quad (3b)$$

Here, Ω is a frequency of the order of the Debye value, which should be regarded as a fitting parameter; $N = \omega_r/\Omega \gg 1$ is a number representing the strength of coupling to phonons; $\nu_0 \sim \nu_0' \approx 10^4\text{–}10^5$ cm^{-1} are typical electronic frequencies. The relationships between NT and $h\Delta$, governing the limiting cases described by Eqs. (3a) and (3b), is the relationship between the heats evolved during a reaction and the energies of reorganization of the classical degrees of freedom.

It is worth noting a strong dependence of W_- on Δ and T. If $\Delta \to 0$ and $T \to 0$, then $W_- \to 0$. Hence it follows that the positive contribution, associated with W_-, to the current may be significant only in high fields[3)] in the range $E \gtrsim E_0$. If the fields obey $E \lesssim E_0$, the ANP is associated with intercenter recombination processes.

The rates of intercenter recombination processes generally include nonradiative and radiative contributions: $\gamma = \gamma^n + \gamma^r$. The nonradiative recombination, characterized by an energy change $\hbar\bar\delta \gtrsim \hbar\omega_r$, is accompanied mainly by the emission of high frequency (Debye acoustic and optical) phonons. We can estimate γ^n using a single-mode model[18,20]

$$\gamma^n = \bar\nu \exp\left(-\frac{R}{a}\right)\exp\left[\frac{\bar\delta}{\Omega}\left(1 - \ln\frac{\bar\delta}{\omega_r}\right) - \frac{\omega_r}{\Omega}\right]. \quad (4)$$

The above expression is valid at temperatures much lower than the Debye value ($T_D \approx 10^3$ K). It demonstrates the familiar relationship: γ^n is a rapidly rising function of $\bar\delta$ right up to $\bar\delta \approx \omega_r$; if $\bar\delta > \omega_r$, then $\gamma^n(\bar\delta)$ shows a steep fall. This fall is responsible for the predominance of radiative recombination in the case of optical transitions.

The expressions for $\gamma_{21}^{n\pm}$ are obtained from Eq. (4) by substituting $a = a_2$, which is the radius of localization in the $^4T_2$ state, $\bar\delta = \omega_{21} \pm \Delta$, and the frequency factor $\bar\nu \approx \nu_0$. The expressions for $\gamma_{10}^{n\pm}$ are obtained by substituting $a = a_1$, $\bar\delta = \omega_{10} \pm \Delta$, and $\bar\nu \sim 10^{-3}\nu_0$. The factor 10^{-3} reflects the change in the spin as a result of the $1 \to 0$ transition. It follows from Eq. (4) and the data on the intracenter $1 \to 0$ and $2 \to 1$ transitions[14,15] that $\gamma_{21} \approx \gamma_{21}^n \gg \gamma_{21}^r$ and $\gamma_{10}^r \gtrsim \gamma_{10}^n$.

We must point out that the dependence $\gamma^n(\Delta)$ is fairly weak compared with $W_-(\Delta)$ and that right up to $\Delta \approx \Omega \approx 10^3$ cm^{-1} it can be allowed for by linear terms of the expansion. It should also be pointed out that the formal transition to Eq. (4) in the limit $\bar\delta \to 0$ would have given the value $W_-(0) \approx \bar\nu \exp(-R/a)\exp(-\omega_r/\Omega)$. For any reasonable parameters this quantity exceeds γ_{10}. In other words, use of the single-mode model in the calculation of W_- predicts the absence of the ANP.

We shall now estimate the radiative contribution γ_{10}^r. We shall do this bearing in mind the rate of the intracenter radiative recombination is $\tau_{10}^{-1} \approx 3\times 10^2$ s^{-1}, which is 6–7 orders of magnitude less than typical rates of dipole-allowed processes. This is due to the double forbiddenness on the $1 \to 0$ intracenter transition: in respect of the parity and in respect of the spin.[15,21] On the other hand, intercenter recombination is only spin-forbidden. Therefore, we can write down

$$\gamma_{10}^r = c\tau_{10}^{-1}\exp(-R/a_1); \quad c = 10^3\text{–}10^4. \quad (5)$$

To within terms of the order of Δ/ω_{10}, we have $\gamma_{10}^{r+} = \gamma_{10}^{r-}$.

We shall conclude this section by going back to the general expression for the current given by Eq. (1). If we allow for the properties of W and γ, we can see that the neglect of the jumps between short-lived T levels is permissible and that we must allow for intercenter recombination from the levels 2. Hopping between the levels 2 makes a contribution to the current which is small compared with that allowed for by means of the parameter $\tau_{21}/\tau_{10} \lesssim 10^{-4}$. In the case of the $2 \to 1$ intercenter transitions the smallness of τ_{21} is fully compensated by the high value of γ_{21}^n [Eqs. (4) and (5)].

Finally, Eq. (1) describes, strictly speaking, a one-dimensional model with the same distances between the centers. In reality, jumps may occur at an angle to the field

and there is a scatter of states between the chromium ions. An allowance for these factors should result in the substitution of $R \to (0.7\text{–}0.8)R$ in the arguments of the exponential functions (see, for example, Ref. 22). We shall draw attention to the cases when such renormalization may be significant.

§2. RESONANT ABSOLUTE NEGATIVE PHOTOCONDUCTIVITY

We shall assume that the frequency of light ω is close to the transition frequency ω_{10}. In this case the T levels of Cr^{3+} are not populated: $n_2^{\pm} = 0$. We can find the current if we know $n_1^{\pm} = n_{1A} + n_{1B}^{\pm}$, where the subscripts A and B represent the positions of Cr^{3+}. Following Refs. 6 and 7 we shall allow for the fact that in the case of the positive active centers the pseudo-Stark splitting is governed by the sum of the external electric field E and the excess Coulomb field of Cr^{4+}, which is $E_c \approx e/\varepsilon R^2$ (ε is the permittivity), whereas in the case of the negative centers it is determined by the difference between these fields (Fig. 2). Therefore, the rates of photoexcitation ($\pm$) of the centers at the positions A and B are given by

$$g_A^{\pm} = \frac{\sigma_{10} J}{\hbar\omega} f(\delta - \omega_d \mp \omega_c); \qquad g_B^{\pm} = \frac{\sigma_{10} J}{\hbar\omega} f(\delta + \omega_d \pm \omega_c). \tag{6}$$

Here, σ_{10} is the absorption cross section of Cr^{3+} at the center of the R line; J is the intensity of light; $\delta = \omega - \omega_{10}$ is the detuning; $\omega_c = dE_c/\hbar$; $f(\delta)$ is the dimensionless line profile factor such that $f(0) = 1$.

The excitation selectivity is particularly strong if the width of the R line obeys $\Gamma \ll \omega_c, \omega_d$. In this case there is a quartet of frequencies in which the outer peaks $\delta = \pm(\omega_c + \omega_d)$ correspond to the excitation of the positive active centers and the inner peaks $\delta = \pm(\omega_c - \omega_d)$ correspond to the excitation of the negative active centers. Preferential excitation of the negative centers makes a negative contribution to the current and the excitation of the positive centers makes a positive contribution (Fig. 2).

The knowledge of $g_{A,B}^{\pm}$ is insufficient for the determination of $n_1^{\pm}$ because we do not know the distribution of the active centers between the positions A and B. This distribution depends on the illumination conditions.

A self-consistent description is provided as follows. We shall use $N_4^{A,B}$ to denote the concentration of Cr^{4+} at the positions of A and B and these concentrations are related by $N_4^A + N_4^B = N_4$. We shall bear in mind that the probability of encountering a Cr^{4+} ion at a position A (or B) alongside a Cr^{3+} ion at a position B (or A) is higher than that of finding a Cr^{3+} ion at a position A (or B). Since the ratio of these probabilities obeys $\alpha < 1$ (in the case of a one-dimensional model with alternate positions A, B, A, . . ., we have $\alpha = 0$). Then, apart from a shared factor of the order of unity, we can write down

$$n_{1A}^{\pm} = g_A^{\pm}\tau_{10}(N_4^B + \alpha N_4^A), \quad n_{1B}^{\pm} = g_B^{\pm}\tau_{10}(N_4^A + \alpha N_4^B). \tag{7}$$

The system (7) is closed by the steady-state condition N_4^{AB}:

$$n_{1A}^{-} + \lambda n_{1A}^{+} = n_{1B}^{-} + \lambda n_{1B}^{+}; \quad \lambda = (\gamma_{10}^{-} + W_-)/\gamma_{10}^{+}. \tag{8}$$

Solving Eqs. (7) and (8), we find the current from Eq. (1):

$$j \approx 2eRN_4\tau_{10}\gamma_{10}^{r}\frac{\sigma_{10}J}{\hbar\omega}G(\delta, E), \tag{9}$$

where

$$G = \frac{\lambda^2 f(\delta-\omega_d-\omega_c) f(\delta+\omega_c+\omega_d) - f(\delta-\omega_d+\omega_c) f(\delta+\omega_d-\omega_c)}{\lambda f(\delta-\omega_d-\omega_c) + \lambda f(\delta+\omega_d+\omega_c) + f(\delta-\omega_d+\omega_c) + f(\delta+\omega_d-\omega_c)}. \tag{10}$$

The function $G(\delta, E) = G(-\delta, E)$ determines the field and spectral dependences of the current. Its nature is not related to the model ideas and the properties of $\gamma_{10}^{\pm}$ and W_-. It is worth noting the relationship between the spectral properties of the current and the parameter λ representing intercenter transitions. It follows directly from Eq. (10) that the ANP is possible if we include only one type of resonance (involving A or B centers). This is in full agreement with the ideas put forward in Refs. 6 and 7 that the excitation of just one type of active centers should increase the length of a jump by a factor of $2^{1/3}$ and reduce strongly the current.

We shall now investigate in detail the properties of G. If we assume that $\lambda = 1$, then G has a clear minimum at $\delta = 0$,

$$G(0, E) = -1/2[f(\omega_c - \omega_d) - f(\omega_c + \omega_d)],$$

and weak positive tails. The range where j is negative always lies within the interval $\pm|\omega_c \pm \omega_d|$ and it becomes wider on increase in E. Figure 3a shows a family of the $G(\delta)$ curves for several values of E plotted on the assumption of a Lorentzian profile $f(\delta)$ and that the values of Γ and ω_c are those found experimentally. The spectral dependences are in good agreement with the experimental data obtained in fields $E = 210$ and 280 kV/cm (Refs. 6 and 7). The dependence of the spectral minimum of G on the field is characterized in the range $E \ll E_c$ by a linear region $G(0, E) = f'(\omega_c)\omega_d$, by a minimum $G(0, E) \approx -1/2$ at $E \approx E_c$, and by a tendency to approach zero in the range $E \gg E_c$ in accordance with the expression $G(0, E) = f'(\omega_d)\omega_c$. This dependence is in good agreement with the experimental data reported in Refs. 6 and 7 for fields up to $E \approx 400$ kV/cm.

In higher fields, $E = 370$, 475, and 640 kV/cm, the experimental dependences $j(\omega)$ demonstrate clearly new relationships which are missing from Fig. 3a. Two spectral minima appear and the positive tails of the current increase. However, in a field $E = 640$ kV/cm the value of j corresponding to $\delta = 0$ is much smaller than that found by calculation (for $\lambda = 1$) and it is close to zero. These features can be explained provided we include in Eq. (10) the difference between the parameter λ and unity. Figure 3b shows the dependence $G(\delta)$ obtained for previous values of Γ and ω_c and different values of λ. We can see that an increase in λ enhances the relative contribution of the positive tails and instead of one negative minimum there are now two of them. There is also an increase in $G(0, E)$ which becomes positive. It should be pointed out that Eqs. (9) and (10) do not account for some asymmetry of the spectral dependence of the

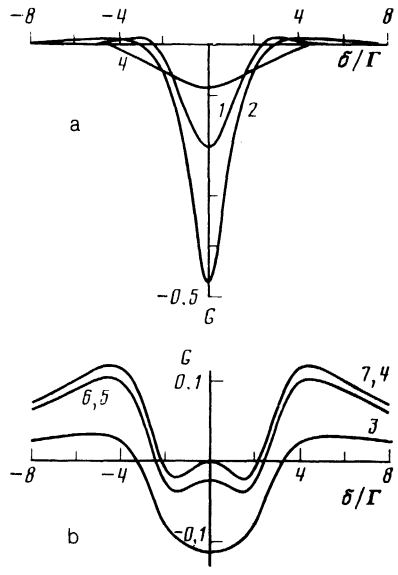

FIG. 3. Spectral properties of the current: a) dependence $G(\delta)$ for $\omega_c = 2\Gamma, \lambda = 1$, and $\omega_d/\Gamma = 1, 2$, or 4; b) dependence $G(\delta)$ for $\omega_c = 2\Gamma$, $\omega_d/\Gamma = 4, \lambda = 3$, 6 or 5, 7 and 4.

current. Such an asymmetry should be related to the inequivalence of the positions A and B at a given point in a crystal. It is not clear from Refs. 6 and 7 to what extent the asymmetry effect is important.

The condition for the vanishing of the current can be readily obtained from Eq. (10). If the detuning is $\delta = 0$, this condition is particularly simple:

$$\lambda = f(\omega_d - \omega_c)/f(\omega_d + \omega_c). \tag{11}$$

This is the equation for the photoinduced field E_0. Judging by the experimental data of Refs. 6 and 7, we may assume that the sign of the current at the center of the R line is reversed in a field $E_0 \approx 650$ kV/cm. This corresponds to $\lambda \approx 6$.

We shall now use a model representation to deal with the rates of intercenter processes. According to Eqs. (3)–(5), the values $\lambda = (\gamma_0^- + W_-)/\gamma_{10}^+$, which exceed unity quite considerably, can only be due to a field-enhanced increase in W_- (we can assume a considerable difference between the nonradiative contributions $\gamma_0^{n\pm}$ when $\Delta > \Omega$, but this would lead to $\lambda < 1$ because $\omega_r < \omega_{10}$). Using Eqs. (3a) and (5), we readily obtain the following expression for the photoinduced field at low temperatures:

$$E_0 \approx \frac{\hbar\omega_r}{eR}\left(\frac{c}{\nu_0\tau_{10}}\right)^{1/N}. \tag{12}$$

Since $N = \omega_r/\Omega \gg 1$, the field E_0 depends very little on the selected values of c and ν_0; it is determined mainly by the reorganization energy ω_r. Assuming that $R = 20$ Å, $\nu_0 = 10^5$ cm^{-1}, and $N = 10$, and allowing for the renormalization $R \to 0.7R$, we find that $E_0 = 650$ kV/cm corresponds to $\omega_r \approx 7 \times 10^3$ cm^{-1} and $\Omega \approx 700$ cm^{-1}. These values are in reasonable agreement with those expected. It follows from Eq. (12) that E_0 cannot change significantly when the ANP is excited by other narrow lines with different values of Γ. This has been found experimentally.[6,7]

If the above ideas on the role of W_- are correct, the current should exhibit a strong nonlinear rise in the range $E > E_0$. The system of equations (3) makes it possible to predict the temperature dependence $E_0(T)$. If $T \ll eE_0RN^{-1}$, it follows from Eq. (3a) that $E_0 = \text{const}$. If $T > eE_0RN^{-1}$, it is clear from Eqs. (3b) and (12) that $E_0(T)$ is given by

$$T = \frac{\hbar\Delta_0}{N}\exp\left(-\frac{eE_0R}{2NT}\right); \quad \Delta_0 = eRE_0 \quad (T=0). \tag{13}$$

The argument of the exponential function is small on the basis of the conditions in Eq. (3b), i.e., the dependence $E_0(T)$ is very steep at low values of E_0. If we assume that $E_0 = 0$, we can find the critical temperature above which there is no ANP:

$$T_c \approx \hbar\Delta_0/N. \tag{14}$$

Using the previous values of the parameters, we obtain

$$T_c \approx 160 \text{ K}. \tag{15}$$

We shall show below that the critical temperature deduced using our theory and the dependence $E_0(T)$ at $T \approx T_c$ should not differ very greatly for the resonant and nonresonant ANP. In the case of the nonresonant ANP we have $T_c = 150$ K.

Using Eqs. (9) and (10) and the experimental value of j we can now estimate a combination of little-known parameters of ruby. If we assume that the cross section is $\sigma_{10} \approx 3 \cdot 10^{-20}$ cm^2, we find that

$$N_4N_3^{-1}\exp(-0.7R/a_1) \approx 10^{-8}. \tag{16}$$

Since in the case of ruby we have $N_4/N_3^{-1} \lesssim 10^{-2}$, Eq. (16) yields the following limit on the radius of localization of an excited electron: $a_1 \gtrsim 1$ Å. We are not aware of any estimates of the radii of localization for Cr^{3+} deduced from any other intercenter effects.

The expressions in this section are valid, strictly speaking, in the case of homogeneous broadening of the R line (at temperatures above that of liquid nitrogen). At helium temperatures, the homogeneous line width is $\Gamma_{\text{homog}} \sim \Gamma \cdot 10^{-2}$ (Refs. 15 and 24) and if the laser line width obeys $\Gamma_l \ll \Gamma$, the current should decrease because of the unavoidable intracenter excitation of nonresonant centers.[4)] This range of conditions requires a special study. However, we can expect the expressions obtained above to remain valid at low temperatures T if $\Gamma_l \gtrsim 10^{-1}\Gamma$ because of the transfer of the excitation energy to nonresonant centers from the surrounding resonant centers. The experimental results of Refs. 6 and 7 give $\Gamma_l \approx 0.3\Gamma$.

§3. MECHANISMS OF NONRESONANT ABSOLUTE NEGATIVE PHOTOCONDUCTIVITY

The main feature of the nonresonant ANP is the weakening of the selective mechanism and a corresponding reduction in the efficiency of excitation of the current. This is supported not only by the analysis given below, but also by the experimental data. It follows from Refs. 3, 6, and 7 that the difference beween the currents normalized to the absorbed energy is approximately 1.5 orders of magnitude for the resonant and nonresonant ANP. There is also a change in the mechanism of a transition from the negative to the positive current in high fields.

Weakening of the selective mechanism responsible, because of intracenter processes, for the difference between n^+

and n^- makes it necessary to allow for the asymmetry of the intercenter recombination, i.e., for the difference between γ^+ and γ^-. The number of factors responsible for the ANP now increases.

In the weak selectivity and asymmetry case, the general expression for the current of Eq. (1) can be rewritten as follows:

$$j \approx -2eR\tau_{10}\gamma_{10}{}^r N_4 \frac{\sigma_{02}J}{\hbar\omega}\left[s_1 - \xi_{10} - \frac{\tau_{21}\gamma_{21}}{\tau_{10}\gamma_{10}}\xi_{21} - \frac{W_-}{\gamma_{10}{}^r}\right], \qquad (17)$$

where

$$s_1 = (n_1^- - n_1^+)/2n_1; \quad \xi = (\gamma^- - \gamma^+)/2\gamma \qquad (18)$$

are the selectivity and asymmetry parameters, respectively. It is assumed that $s_1, \xi < 1$.

Equation (17) was simplified by dropping contributions known to be small. Firstly, in view of the large width of the U or Y absorption bands ($\gtrsim 3000\ \text{cm}^{-1}$) we ignored the difference between n_2^+ and n_2^-. Secondly, we also ignored the $2 \to 0$ recombination channel which is much weaker than the $2 \to 1$ channel. It should be pointed out that the $2 \to 1$ recombination may generally occur via the $^2T_1$ levels located between the $^4T_2$ and ^2E levels (Fig. 1).

We shall now analyze the magnitudes and signs of the parameters s_1, ξ_{10}, and ξ_{21}. One of the main factors governing the difference between n_1^+ and n_1^- is the field-induced reduction in the lifetime of metastable ^2E states associated with lifting of the parity forbiddeness of the $1 \to 0$ transition. In low fields the reduction in the lifetime is

$$\Delta\tau_{10}/\tau_{10} = (E/E_1)^2, \qquad (19)$$

where E_1 is a characteristic field. The value of E_1 can be estimated from the experimental results or can be found theoretically from the oscillator strengths. According to Ref. 23, in a field $E \approx 2.25 \times 10^5$ V/cm the reduction in τ_{10} is 15%. This gives $E_1 \approx 6 \times 10^5$ V/cm. A value of E_1 of the same order of magnitude is obtained also from theoretical estimates. The field acting on the ($\pm$) centers is $E \pm E_c$. It is then obvious that in addition to a general change E_c^2/E_1^2 applicable to the active centers, there is also a contribution $\pm 2EE_c/E_1^2$, which results in more rapid emptying of the positive (+) centers, i.e., it yields $n_1^- > n_1^+$ and $j < 0$.

In the determination of s_1 we must allow not only for Eq. (19), but also for resonant transfer of the energy of the ^2E excitation between the bulk of the Cr^{3+} ions and the active centers. It is clear from Fig. 4 that the levels of the negative (−) centers are separated from a resonance less than the levels of the positive (+) centers. Therefore, the corresponding rates of exchange of excitations satisfy the inequality $p_- > p_+$ (a similar conclusion is reached in Refs. 7 and 8). The difference between the rates $p_\pm$ does not itself result in selective population of the ($\pm$) centers. It has an effect only if we allow for the overall reduction in the lifetime of the ^2E excitations at the active centers.

In quantitative estimates of s_1 we shall assume, in accordance with Fig. 4, that

$$p_\pm = {}^1/_2 p_0 [f(\omega_c) + f(\omega_c \pm 2\omega_d)], \qquad (20)$$

where p_0 is the rate of exchange of excitations at a resonance and f represents (as in §2) the line form factor normalized to unity.

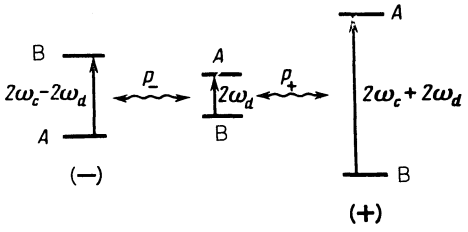

FIG. 4. Distribution of the ^2E levels of the bulk of the Cr^{3+} ions in active ($\pm$) centers, illustrating resonant transfer of excitations in low fields.

Next, it follows from elementary considerations of the balance that

$$n_1^\pm/n_1 \approx 1 - \Delta\tau_{10}^\pm/\tau_{10}(1 + p_\pm\tau_{10}). \qquad (21)$$

Using Eqs. (19) and (20), we can now find the selectivity parameter

$$s_1 \approx \frac{2EE_c}{E_1^2}\frac{1 + p_0\tau_{10}f(\omega_c) - p_0\tau_{10}f'(\omega_c)\omega_c}{1 + p_0\tau_{10}f(\omega_c)}. \qquad (22)$$

This equation allows for two types of contribution: with and without resonance exchange of excitations. As $p_0\tau_{10}$ increases, the value of s_1 decreases. In the case of ruby we clearly have $p_0\tau_{10}f(\omega_c) \lesssim 1$ (Refs. 24 and 25). We then find that $s_1 \approx 2EE_c/E_1^2$. Compared with the case of resonant excitation, s_1 decreases by a factor which is at least $(E_c/E_1)^2 < 1$.

Equation (22) is valid if the fields are sufficiently low so that $E < E_c$. If $E \approx (1\text{–}2)E_c$, i.e., in fields of 250–500 kV/cm intensities, the dependence $s_2(E)$ tends to saturation. The nature of such saturation depends on the behavior of $\tau_{10}(E)$ and $f(\omega_c \pm \omega_d)$. The dependence of the rate of exchange of excitations on the positions of the A and B centers is also important (see Ref. 26). Since these mechanisms are not related fully to the pseudo-Stark splitting, we can expect selective excitation also in the transverse geometry $\mathbf{E} \perp \mathbf{d}$. We can go over to this case simply by substituting $f = 1$ in Eq. (22). The value of $s_1^\perp$ obtained in this way is equal to s_1 only if $p_0\tau_{10} = 0$, whereas for $p_0\tau_{10} \gtrsim 1$ (which is more likely in ruby) the value of $s_1^\perp$ is several times smaller than s_1.

We shall now investigate the asymmetry parameters ξ_{10} and ξ_{21} representing intercenter transitions. We shall do this using the results of §1. The radiative contribution $\gamma_{10}^r(\bar{\delta})$ increases in accordance with a power law. This gives $\xi_{10}^r \approx \Delta/\omega_{10}$ and the corresponding contribution to the current is positive. The value of s_1 is known to be smaller than ξ_{10}^r. The nonradiative contribution to $\gamma^n(\bar{\delta})$ increases to $\bar{\delta} \approx \omega_r$ and then decreases. Since $\omega_{21} < \omega_r$ and $\omega_{10} > \omega_r$, it follows that $\gamma_{10}^{n+} < \gamma_1^{n-}$ and $\gamma_{21}^+ > \gamma_{21}^-$. Therefore, nonradiative recombination due to the $2 \to 1$ transitions reduces the ANP, whereas similar recombination due to the $1 \to 0$ transitions enhances this effect. We consequently have

$$\xi_{21} \approx \frac{\Delta}{\Omega}, \quad \xi_{10}^n \approx -\frac{\gamma_{10}{}^n}{\gamma_{10}{}^r}\frac{\Delta}{\Omega}. \qquad (23)$$

The linear field dependence is retained up to $E \gtrsim (4\text{–}6) \times 10^5$ V/cm. It is clear from Eq. (17) that ξ_{10}^n should be added to s_1. In view of the weak nonradiative recombination due to the $1 \to 0$ transitions, the estimate of the negative current hardly changes. However, the positive contribution to the current associated with ξ_{21} is very important in the explanation of the kinetics and the chromium concentration dependences of the ANP. According to Eq. (17), this contribution

contains an additional factor $\gamma_{21}\tau_{21}/\gamma_{10}\tau_{10}$. It is not possible to estimate this factor on the basis of the model equation (4) and the published data on τ_{21}, which suffer from a considerable scatter. However, it is quite reasonable to assume that this factor cannot be much less than unity because all the small factors γ_{10}/γ_{21} (spin and phonon) affect equally τ_{21}/τ_{10}. The value $\gamma_{21}\tau_{21}/\gamma_{10}\tau_{10}$ will be refined below on the basis of the published experimental results.

We shall now compare the theory with experiments. We shall first of all consider the data on the kinetics of the current in the case of pulsed optical excitation.[8] The main results are then as follows. At the beginning of illumination a current $j>0$ appears instantaneously and it then decays slowly (with a characteristic time 2–4 ms), reverses its sign, and slowly reaches a steady-state negative value. At the end of a light pulse there is a steep negative jump of the current. This is followed by a slow disappearance of the signal. Our theory accounts for such behavior in a natural manner. The initial positive and final negative jumps of the current correspond to the appearance and disappearance of the positive contribution to the current associated with the short-lived $^4T_2$ states. The long decay time 2–4 ms is related to the establishment and relaxation of a steady state of the ^2E electrons.

The kinetic curves obtained for several values of E make it possible to estimate the field dependence of the instantaneous positive and delayed negative contributions to the current. The positive contribution fits a linear dependence on E, whereas the negative contribution shows saturation at $E\approx(3\text{–}5)\times10^5$ V/cm. This is also in good agreement with the ideas put forward above.

Under the conditions of Ref. 8 the negative contribution to j is only slightly (to the extent of 15–20%) greater than the positive contribution. This result and the data of Refs. 3, 6, and 7, together with the current-voltage characteristics obtained at low illumination intensities, make it possible to deduce the following estimates with the aid of Eqs. (9) and (17):

$$E_1=(8\text{–}10)\cdot10^5\ \text{V/cm};\quad \tau_{21}\gamma_{21}/\tau_{10}\gamma_{10}\approx{}^1/_2\text{–}2. \tag{24}$$

The value of E_1 is close to the earlier estimate of 6×10^5 V/cm.

For the parameters of Eq. (24) the transition from the negative to the positive current in fields $E_0\approx(3\text{–}6)\times10^5$ V/cm can be attributed to the competition between the saturable negative "selective" contribution to j and the positive linearly rising "asymmetric" contribution. In view of the similarity of the contributions, the value of the photoinduced field E_0 in the range $(3\text{–}6)\times10^5$ V/cm may be sensitive to changes in the experimental parameters. The current-voltage characteristic recorded in fields $E\approx E_0$ is then nearly linear, which agrees with the experimental results of Ref. 3. A steep rise of $W_-(E)$ at low temperatures clearly begins in fields $E\gtrsim650$ kV/cm. On increase in temperature the value of $W_-(T)$ rises steeply in accordance with Eq. (3b). This may be the reason for the disappearance of the ANP. The corresponding critical temperature T_c is close to that deduced in §2 and to the experimental value 150 K.

We shall now consider the dependence of the ANP on the ruby concentration. According to Eqs. (17), (22), and (23), in low fields the current is negative if

$$\frac{\varepsilon R^3E_1^2}{2\hbar\Omega}\frac{\tau_{21}\gamma_{21}}{\tau_{10}\gamma_{10}}<\text{const}\approx1. \tag{25}$$

The left-hand side of Eq. (25) increases on increase in R. Therefore, when the Cr^{3+} concentration is sufficiently low, so that $N_3<N_3^c$, the nonresonant ANP should disappear. It should be pointed out that the rise of the left-hand side of Eq. (25) may be related not only to the factor R^3, but also to the parameter $\tau_{21}\gamma_{21}/\tau_{10}\gamma_{10}$. In view of the difference between the localization radii of an electron in the $^4T_2$ and ^2E states, $\Delta a=a_2-a_1>0$, this parameter includes a growing exponential function $\exp(R\Delta a/a_1^2)>1$. The experimental value $N_3^c\approx3\times10^{19}$ cm^{-3} agrees reasonably well with Eq. (25).

§4. DISCUSSION

The proposed theory makes it possible to explain the negative photocurrents and to identify the main processes responsible for the charge hopping in ruby. It explains a wide range of experimental data on the ANP, such as the field and spectral dependences, kinetics, and chromium-concentration dependences of the current, as well as the magnitudes and temperature dependences of the photoinduced fields.

This theory makes certain predictions. One of them is the lower value of the critical chromium concentration for the resonant ANF compared with the nonresonant effect. In the case of resonant excitation there should be a change in the kinetics of the current: the instantaneous positive component of j should disappear. In the case of nonresonant excitation the transition from the longitudinal to the transverse geometry should be accompanied by an increase in the fraction of the instantaneous positive current. The theory demonstrates the possibility of a steep rise of the current-voltage characteristic in the case of the resonant ANF in fields $E>E_0$.

The theory predicts the possibility of existence of a new nonresonant ANF of ruby associated with the photoexcitation asymmetry.[11,12] In view of the strong coupling to phonons, the rate of intercenter excitation of metastable states should be described by a bell-shaped curve of width $\sim(\Omega\omega_r)^{1/2}$ (Ref. 15). The ANP associated with the photoexcitation asymmetry corresponds to the fall of this curve. Its manifestation can be found also in the spectral region adjoining the U excitation band of Cr^{3+}, provided the filling of the $^4T_2$ levels is prevented.

We shall now consider some difficulties encountered in our theory. One of such difficulties is resonant excitation of the ANF at low temperatures by a narrow laser line (§2). This is a very specific case. The behavior of the current may depend strongly on the nature of the spectral migration of energy and on the spatial correlations of the energy levels of Cr^{3+}.

The second difficulty is the dependence of the current on the chromium concentration. As in any other hopping theory, the current includes a factor of the $\exp(-kN_3^{1/3}a_1^{-1})$ type, where $k=0.7\text{–}0.8$. It would therefore seem that the current should fall strongly on reduction in N_3. The results reported in Ref. 5 demonstrate a strong increase in the time taken to establish E_0 on reduction in the chromium concentration, which is in qualitative agreement with this conclusion. However, recent experiments[27] indicate that a reduction of N_3 within one order of magnitude reduces only slightly the transverse positive current in the nonresonant excitation case. One of the possible explanations of this circumstance may be the dependence of the concentration N_4, which occurs in j, on the value of N_3. The

simplest estimates based on Eq. (16) demonstrate that in this case a reduction of N_3 from 10^{20} to 10^{19} cm^{-3} should increase N_4 from 10^{15} to 10^{17} cm^{-3}, whereas the electron localization radius a_1 should remain ~ 1.5 Å. Fundamentally different treatments of these experimental results are also possible on the basis of hopping theory. Additional experiments will be decisive.

It is interesting to consider also the possibility of the appearance of the ANF in other materials. Although the pseudo-Stark splitting and the concept of the active centers in an excess Coulomb field are not specific to ruby, it is very difficult to predict the ANF in other substances. In the final analysis the sign of the current is governed by the relationship between the probabilities of different intracenter and intercenter processes. These relationships are practically unknown and they are difficult to treat by calculation or estimate. In the case of ruby the "margin" of the negative contribution to the current above the positive one may be very small. In our opinion the search for the ANF should be best conducted using the theory to predict the most promising situation.

Ruby will be used as a model material in the immediate investigations of the ANF. A continuation of systematic studies of ruby will not only refine and provide more details on the mechanisms of the effect, but also provide information on the properties of the excited chromium states and on the processes responsible for the transfer of energy and charge hopping. This applies in particular to various multiphonon intercenter processes, which are difficult to deal with by traditional methods.

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[1)]We shall not deal with the investigations carried out using the phenomenological approach.[4,9,10]

[2)]The numerical values of the energies and frequencies are all in reciprocal centimeters.

[3)]It also follows from Eq. (3a) that the low value of the dark conductivity of ruby may be related not only to the smallness of a_1, but also to the smallness of $(\Delta/\omega_r)^N$.

[4)]Our attention to this point was drawn by M. I. D'yakonov.

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