Thermalizational mechanism of photoinduced electric domain structure formation in ruby

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Abstract. A model explaining the formation of electric domain structure in heavily doped ruby under intensive laser irradiation is suggested. The model is based on the following facts: thermalization of metastable level $\bar{\text{E}}$ of Cr^{3+}; distribution in the A and B sublattices during crystal growth; hopping conductivity in a system of Cr^{3+} ions excited into a metastable level. It is demonstrated experimentally that the number of Cr^{3+} ions decreases during the formation of internal photoelectrical structure in ruby, the distribution of Cr^{3+} ions in the A and B sublattices is inhomogeneous in the sample, and the rate of formation of the domain structure depends on the irradiation prehistory of the sample. Observing the dynamics of the electric domain structure in ruby, conclusions on the microscopic nature of the formation of internal electric fields and the close arrangement of the excess charged chromium ions in domain walls are drawn. The suggested thermalizational model describes a starting mechanism for the formation of internal electric fields in domains and explains qualitatively most of the known experimental results.

1. Introduction

It was demonstrated experimentally (Liao *et al* 1980, Basun *et al* 1984) that if one irradiates heavily doped ruby at a temperature lower than about 150 K by laser light with frequency resonant with the transition into the absorption bands, then a long-lived strong electric field (up to some hundreds of kV cm^{-1}) is formed in the sample. The formation of internal electric fields under intensive laser irradiation is well known for ferroelectrics (Lines and Glass 1977). Ruby is not a polar crystal and does not have spontaneous polarization at any temperature. Nevertheless the photoinduced electric field in ruby forms a regular electric domain structure. The fields in the domains are parallel to the optical axis of the crystal and are equal in intensity. They are antiparallel to each other in different domains (Basun *et al* 1984). Both this fact and the obvious low-temperature nature of the effect make it different from the known photoelectric phenomena in dielectrics.

A qualitative explanation of this effect was given within a phenomenological theory (Dyakonov and Furman 1984) in which the presence of an absolute negative photo-conductivity in the irradiated sample was supposed. Later the experimental observation of the mentioned photoconductivity (Basun *et al* 1984) supported this theory. The first microscopic model of this effect (Liao *et al* 1980) was based on the supposition that for some unknown reason associated with ruby crystal growth the concentration of Cr^{3+}

ions of sublattice A (c_A) differs from that of sublattice B (c_B), and the balance $c_A > c_B$ or $c_A < c_B$ is constant in the sample†. The authors believed that the difference in concentrations under irradiation led to a photovoltaic current in the sample and photovoltaic charges on its surfaces and, hence, to a homogeneous electric field in the bulk of the sample.

Basun *et al* (1984) and Dyakonov and Furman (1984) showed that this model did not correspond to experimental data concerning the domain structure of the photoinduced electric field. They explained the negative photocurrent by the difference in the populations of metastable levels $\bar{E}$ of the Cr^{3+} ions belonging to A and B sublattices but not by the difference in the concentrations.

Other attempts to construct a microscopic model of this effect known in the relevant literature (Malinovskii *et al* 1986, Novikov and Sturman 1988, Emel'yanov 1985) do not seem to be convincing because only some experimental aspects of the effect were analysed. The main aim was to explain the mechanism of the negative photoconductivity in ruby but not to analyse the process of electric domain structure formation. Besides, these models did not explain the intrinsic significance of the low temperature in this process.

At the same time a number of experiments on the low-temperature spectral energy migration in ruby (Kurkin 1983, Monteil *et al* 1985, Duval and Monteil 1984), on the mechanisms of photoconductivity in ruby (Basun *et al* 1986, Kaplyanskii *et al* 1987) and our observations of the dynamics of the formation of electric domain structure led us to the conclusion that the 'domain growing asymmetry' of Cr^{3+} distribution in the A and B sublattices may be the physical reason for the considered effects. This supposition and the microscopic mechanism of sign-changing photostimulated hopping conductivity via chromium ions in ruby allow us to formulate the thermalizational starting mechanism for the formation of photoinduced electric domain structure.

2. Microscopic model

Three basic assumptions are used in the suggested microscopic model.

(i) The domain structure of ruby is formed during crystal growth. We suppose that the concentrations of Cr^{3+} ions from different sublattices in some parts—domains of the sample—is unequal $(c_A/c_B = \gamma \neq 1)$. We call the domains with $\gamma > 1$ and $\gamma < 1$ A domains and B domains, respectively. This idea was first proposed by Monteil *et al* (1985) on the basis of their experimental observation of differences in the energy transfer rate between the chromium ions from different sublattices.

(ii) The thermalization of a metastable level $\bar{E}$ of heavily doped ruby at low temperatures (Kurkin 1983) exists and is manifested in rapid spectral migration along the contour of the inhomogeneously broadened $\bar{E}$ level. This migration results in a more populated low-energy part of the inhomogeneous contour of the $\bar{E}$ level under stationary excitation of luminescence through the absorption bands. It is observed experimentally as the long-wave displacement of the maximum of R_1 luminescence line with respect to R_1 absorption line.

(iii) There is hopping conductivity through the Cr^{3+} ions excited into the metastable state (Basun *et al* 1986, Kaplyanskii *et al* 1987). The mechanism of this conductivity is

† The A and B sites of Cr^{3+} ions in the corundum lattice (Al_2O_3) have opposite displacements of Cr^{3+} ions along the optical axis of the crystal relative to the oxygen planes (Kaiser *et al* 1961).
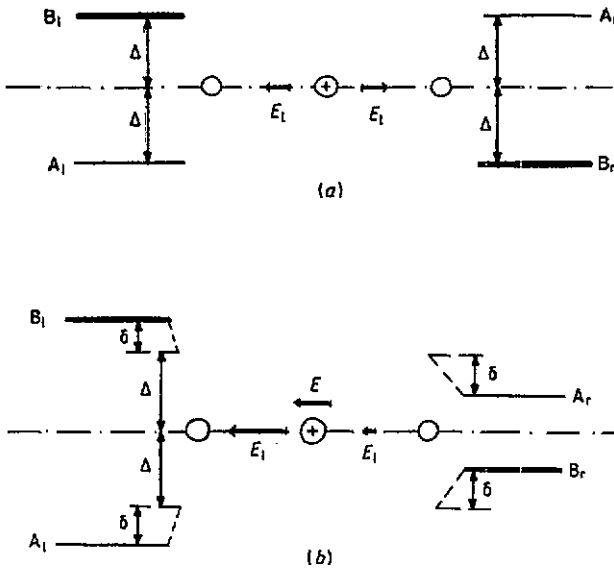
Figure 1. The scheme of the energy levels $\bar{E}$ of the photoelectric active Cr^{3+} ions in a three-atom chain. E_l is the local electric field of the excess charged central ion, E is the internal electric field of the domain, Δ is the shift of the $\bar{E}$ level of PAI in the local field E_l and δ is the shift of the $\bar{E}$ level of the sublattice in the field E.

that the electron tunnel-hops from excited Cr^{3+} ions onto neighbouring excess charged Cr^{4+} ions or from Cr^{2+} ions onto excited Cr^{3+} ions. That is, the excess charge carriers (CC) Cr^{4+}, Cr^{2+} (excited or existing in the sample) are hopping in optically irradiated ruby.

To give a simple model of the thermalizational mechanism, let us consider a chain of three chromium ions at distance r from each other along an optical axis in some domain of the crystal (figure 1). Here the central ion is CC ('+' for definiteness, i.e. Cr^{4+}), and we call the neighbouring Cr^{3+} ions photoelectric active ions (PAI) according to Basun *et al* (1986). In figure 1, close to the PAI, illustrations of the metastable levels E of these ions in the electric field of the central CC are presented. We assume that the energy of the $\bar{E}$ level of the Cr^{3+} ion of the A sublattice decreases if the ion resides on the left side of CC and increases if the ion is on the right side (for the B sublattice it is vice versa). We suppose that there is an ensemble of such chains in a domain. The probability of PAI belonging to any sublattice (W_A, W_B) is determined by the concentration of this sublattice in the domain. Using $W_A/W_B = c_A/c_B = \gamma$ and $W_A + W_B = 1$ we obtain

$$W_A = \gamma/(\gamma + 1) \qquad W_B = 1/(\gamma + 1). \qquad (1)$$

Neglecting the inhomogeneous width of the $\bar{E}$ level in the model, we conclude that the $\bar{E}$ levels of PAI produce a two-level system with energy splitting 2Δ determined by the electric field of the CC on the PAI: $\Delta = e\beta/4\pi\varepsilon_0\varepsilon r^2$, where e is the charge of the electron, $\varepsilon_0 = 8.85 \times 10^{-14}\,C\,V^{-1}\,cm^{-1}$ is the electric constant, $\varepsilon = 11.3$ is the dielectric constant of corundum and $\beta = 0.39 \times 10^{-5}\,cm^{-1}/(V\,cm^{-1})$ is the constant defining the splitting of the $\bar{E}$ level (Basun *et al* 1986). The degeneracy of the levels is determined by the ion locations: an ion occupying a definite sublattice and an ion located to the right side

(A_r, B_r) or the left side (A_l, B_l) of CC. The statistical weight (g) of different states is determined by the probability of the ion in a given site occupying a definite sublattice (1). For the higher energy level in figure 1, $g(B_l) = 1/2(\gamma + 1)$, $g(A_r) = \gamma/2(\gamma + 1)$; and for the level of lower energy, $g(A_l) = \gamma/2(\gamma + 1)$, $g(B_r) = 1/2(\gamma + 1)$.

Taking into account the thermalization of a metastable level, we suppose that in the two-level system, when stationary optical pumping into the absorption band takes place, thermodynamic equilibrium with the lattice temperature T is established. Then the populations of sublevels of this two-level system are the following:

$$n(B_l)/n(A_l) = (1/\gamma)\chi \qquad n(A_r)/n(B_r) = \gamma\chi \qquad n(B_l)/n(B_r) = n(A_r)/n(A_l) = \chi \tag{2}$$

where $\chi = \exp(-2\Delta/kT)$ and k is Boltzmann's constant. Taking the total population of the two-level system equal to $n_0 = n(A_l) + n(A_r) + n(B_l) + n(B_r)$, the populations of PAI on the left (n_l) and on the right (n_r) side from the CC and their difference are calculated:

$$n_l = n(A_l) + n(B_l) = n_0'(\gamma + \chi) \qquad n_r = n_0'(1 + \gamma\chi)$$
$$R_0 = n_l - n_r = n_0'(1 - \chi)(\gamma - 1) \tag{3}$$

where $n_0' = n_0/(1 + \chi)(1 + \gamma)$. These populations are equal $(R_0 = 0)$ in two limiting cases: (i) $\gamma = 1$, i.e. when the sublattice concentrations are equal; (ii) $T \to \infty$. If $\gamma \neq 1$ and $T \neq \infty$ there is always an asymmetry in the space distribution of the populations of chromium PAI in the metastable state. The sign of the asymmetry will be discussed below, but now we note that the absolute value of the difference of populations in the high-temperature approximation $(2\Delta < kT)$ is inversely proportional to the temperature

$$R_0 \simeq n_0(\gamma - 1)\Delta/(\gamma + 1)kT. \tag{4}$$

Let us take into consideration the hopping conductivity in ruby (Basun *et al* 1986). Let V designate the probability of tunnel-hopping of a CC on the neighbouring PAI, which is in the $\bar{E}$ state. In the model it is supposed that V does not depend on the sublattice that the ions of the chain occupy and also does not depend on the sign of the CC. Then for the considered ensemble of three-atom chains the hopping probability of CC in a definite direction (to the right or to the left) is proportional to V and to the density of the final states, i.e. to population n_l or n_r:

$$W_{l(r)} = \eta V n_{l(r)} \tag{5}$$

where η is a numerical factor.

The current density caused by the thermalizationally oriented hopping conductivity is proportional to the difference of probabilities of the left hoppings and right hoppings:

$$I_h = eN(W_l - W_r) = \eta e N V R_0 \tag{6}$$

where N is the density of CC (the density of chains).

The current direction is determined by the sign of R_0, i.e. by the relationship between γ and 1. Let us consider the motion of CC '+' in the B domain. It is seen from (3) that $R < 0$, i.e. the number of excited PAI on the right side of CC is larger than that on the left side. Then in accordance with the scheme in figure 1, CC '+' hops to the right. Similar analysis of the motion of negative CC in the same domain shows that it hops to the left. It is supposed that CC of the same sign concentrate near the domain walls, and form the space charges and the electric field in the domain. Consequently, the internal electric

field of the B domain is directed from the right to the left. As we assumed, this electric field increases the energy of sublattice B and decreases the energy of sublattice A. In the A domain ($\gamma > 1$) the electric field that is formed similarly is of the opposite direction, i.e. it increases the energy of sublattice A and decreases the energy of sublattice B.

The following law may be formulated: the photoinduced electric field formed in a domain due to the thermalizationally oriented hopping current of cc is directed in such a way that it increases the energy of the sublattice with larger concentration. So it is established that at $\gamma \neq 1$ the thermalizational asymmetry of the population of chromium PAI in the metastable state $\bar{E}$ may be the initial reason for the internal electric field photoexcitation in the domain and the direction of this field is shown. It should be emphasized that at equal sublattice concentrations ($\gamma = 1$) the hopping photocurrent is equal to zero ($R_0 = 0$ in (6)) and hence no photoinduced electric structure is formed.

When an electric field (E) is generated in a domain, the levels of the two-level system split as shown in figure 1(b). The electric field removes the degeneracy and forms the four-level system of metastable $\bar{E}$ levels of Cr^{3+} PAI. Taking into consideration the thermalization of this system, the population of the levels can be calculated similarly to (2):

$$n(B_l)/n(A_l) = \chi\lambda/\gamma \qquad n(B_r)/n(A_r) = \lambda/\gamma\chi \qquad n(B_l)/n(B_r) = n(A_r)/n(A_l) = \chi \tag{7}$$

where $\lambda = \exp(-2\delta/kT)$ and $\delta = \beta E$ is the shift of $\bar{E}$ levels in the electric field of a domain. The space asymmetry of the population in the electric field is deduced similarly to (3):

$$R(E) = n_l(E) - n_r(E) = n_0(\gamma - \lambda)(1 - \chi)/(\gamma + \lambda)(1 + \chi). \tag{8}$$

It follows from (8) that, together with the increase of the photoinduced electric field in the domain (i.e. the decrease of λ), the initial excess population of $\bar{E}$ levels of PAI in one of the sublattices (B in our example) decreases and simultaneously the absolute value of the space asymmetry of population decreases.

Thus thermalization of the system of metastable $\bar{E}$ levels of chromium PAI leads to two competing processes in each domain: (i) the photoinduced hopping current of cc to the domain walls, which results in the formation of the electric field in the domain; and (ii) the redistribution of the population of metastable levels of PAI in sublattices in the formed field preventing the increase of this field.

The hopping photocurrent density in the presence of the electric field in the domain differs from (6) owing to the difference in tunnel-hopping probabilities of cc along and opposite to the direction of the field. From thermodynamic considerations it follows that the hopping probability along the field direction is $\exp(erE/kT)$ times larger and in the opposite direction it is $\exp(erE/kT)$ times smaller than the hopping probability in the absence of the field (V) or that in the direction perpendicular to the field (Novikov and Sturman 1988). The quantity $|erE|$ is the variation of the potential energy of charge e in the electric field E when the charge moves parallel to the field at a distance r. Allowing for this, let us represent the density of hopping photocurrent as the sum of a positive current (along the field), which corresponds to hops of cc '+' to the left, in the scheme of figure 1, and a negative current (corresponding to hops to the right):

$$I_h = \eta e N V [n_l \exp\left(\frac{\kappa\delta}{kT}\right) - n_r \exp\left(-\frac{\kappa\delta}{kT}\right)]$$

$$= \frac{\eta e N V n_0}{(1 + \chi)(\gamma + \lambda)} \left[\exp\left(\frac{\kappa\delta}{kT}\right)(\gamma + \lambda\chi) - \exp\left(-\frac{\kappa\delta}{kT}\right)(\lambda + \chi\gamma)\right] \tag{9}$$

where $\kappa = er/\beta$.

When the probabilities are equal, $W_1 = W_r$, there is no hopping current in a domain. The expression for the electric field intensity when $I_h = 0$ is easily obtained from (9) and in the high-temperature approximation ($\kappa\delta/kT < 1, 2(\Delta + \delta)/kT < 1$) it has the form

$$E'_s = \Delta(1 - \gamma)/er(1 + \gamma). \tag{10}$$

It should be noted that (i) E'_s does not depend on the temperature, (ii) $E'_s = 0$ if the concentrations of the sublattices are equal ($\gamma = 1$) and (iii) $E'_{s(\text{max})} = \Delta/er$ is maximum when all chromium ions occupy one of the sublattices ($\gamma = 0$ or ∞). The photocurrent in the domain is negative relative to the internal electric field of the domain if $E < E'_s$ as long as the stationary intensity E'_s of the domain field is reached.

As shown in phenomenological theory (Dyakonov and Furman 1984), electric equilibrium in a stationary irradiated domain may exist only if there is no total photoelectric current. In our case this includes the photocurrent due to the tunnel-hopping conductivity (I_h) and the usually considered photocurrent (I_p) due to the motion of photoelectrons in the conduction zone:

$$I = I_h + I_p \tag{11}$$

$$I_p = \sigma_p E \tag{12}$$

where σ_p is the ordinary (non-hopping) photoconductivity. Using expressions (9), (11) and (12), we obtain the condition for the equilibrium electric field photoinduced in a domain. In the high-temperature approximation it takes the form

$$E_s = \Delta(1 - \gamma)/\beta(1 + \gamma)(\kappa + \xi kT) \tag{13}$$

where $\xi = \sigma_p/\beta\eta eNV$.

One of the conditions of the high-temperature approximation ($\kappa\delta/kT < 1$) is apparently incorrect (see analysis of Novikov and Sturman (1988)). Therefore the expressions (10) and (13) can be used only for qualitative consideration of the processes described. So it follows from (10) and (13) that if a sample has excess charged chromium ions the internal electric field can be formed without ordinary photoconductivity. If the frequency of the irradiation is insufficient for two-quantum photoelectron excitation through the metastable level, then $\sigma_p = 0$. In this case the electric field in the domain produced only by the tunnel-hopping photoconductivity reaches its maximum intensity (10). If the density of ordinary photoconductivity (σ_p) increases, E_s decreases according to (13).

Another qualitative result is the weak dependence of E_s on temperature (expression (10) does not include the temperature) and at the same time the inverse proportionality to the temperature of the starting rate of field increase determined by R. It is in rather good agreement with the experimental results at temperatures lower than ≈ 90 K.

Within the suggested model it is important to consider processes that take place if the sample is placed into an external electric field E_0. Then it is not enough to consider only one domain, as was done before, but one should simulate the processes taking place in the domain wall. Let us represent this wall as a plane perpendicular to the optical axis and dividing two regions of the sample: domain A, where $c_A/c_B = \gamma_A > 1$, and domain B, where $c_A/c_B = \gamma_B < 1$ and $\gamma_A = 1/\gamma_B$. In figure 2 part of this wall is shown; the B domain is on the left side, the A domain on the right side. In accordance with the previous analysis, it is easy to conclude that without the external electric field the CC of the same sign move in the domains in opposite directions. In figure 2(a) CC '+' hops to the wall and '−' hops away from it. In the vicinity of the wall a positive space charge is formed and the photoinduced electric fields in the domains are directed in the opposite direction
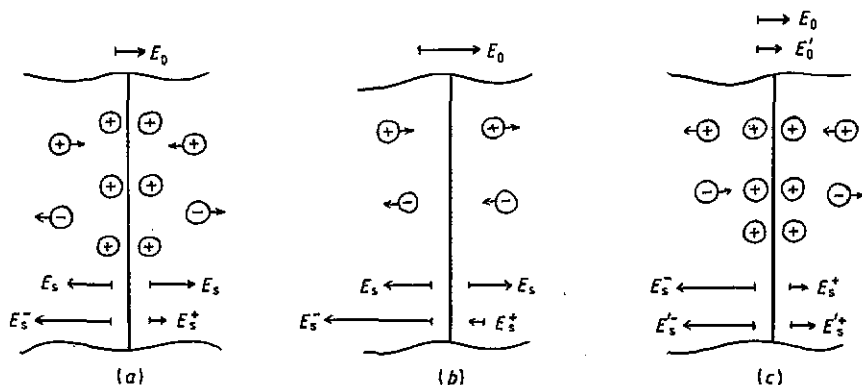
Figure 2. Sketch of the motion of CC near a domain wall in an external electric field E: (a) $E_0 < E_s$, (b) $E_0 > E_s$, (c) $E_0 \rightarrow E_0'$, $E_0' < E_0 < E_s$.

from the wall. The motion of CC in the domains is the same if $E_0 < E_s$, and it is important in principle that the field increase stops at the moment when according to (13) or (10) the field reaches the value E_s, since then it is a sum of the internal field and the external one. In this case for each domain the expression

$$E_s = E_0 + E_s^\pm \tag{14}$$

is correct, where $E_s^\pm$ is the equilibrium internal fields in '+' and '−' domains, respectively; in the '+' domain the internal electric field is directed along the external one, whereas in the '−' domain the external and internal fields are oppositely directed. According to the chosen direction of the external field in figure 2, domain A is a '+' domain and B is a '−' domain. Taking into account the opposite directions of the internal fields in the domain, we obtain

$$E_s^\pm = E_s \mp E_0 \tag{15}$$

which corresponds exactly to the experimental results (Basun *et al* 1984).

The picture of CC motion is qualitatively changed when $E_0 > E_s$ (figure 2(b)). If in the '−' domain the directions of the hoppings of CC are the same as in the case when $E_0 < E_s$, then in the '+' domain the directions of hoppings are changed. As a result the domain wall now does not differ from any other plane perpendicular to the optical axis, since the CC of different signs hop to the wall from different sides. Hence, in the vicinity of the domain wall (as in any other place) the process of hopping relaxation of CC, i.e. $Cr^{2+} + Cr^{4+} = 2Cr^{3+}$, takes place. It should be noted as well that in accordance with the expressions (9), (11) and (12) for $E_0 > E_s$ hoppings in all domains are directed along the external field.

Previously only the current density in one domain was discussed. It should be noted that expressions of the kind in (9) and (12) cannot be directly compared to the experimental current versus voltage characteristics of the photocurrent in ruby. The thing is that at present the arrangement of domains in the sample and their sizes are unknown. But following the suggested model, the experimentally observed photocurrent is determined to a great extent by the arrangement of the domains on the inner surfaces of the sample where they contact with conductors.

The qualitative results of (9) and (12) are the following:

(i) For $E_0 < E_s$ in a stable state the photocurrent in each domain of the sample and, consequently, in the sample must be absent.

(ii) For $E_0 > E_s$ the photocurrent in each domain and in a sample is positive independent of the arrangement of domains (we are speaking only about the photocurrent directed along the optical axis of a sample).

(iii) Particularly we should consider the case when for $E_0 < E_s$ after the formation of the stable space charges near the domain walls the external electric field is decreased $(E_0 \rightarrow E_0', E_0' < E_0)$. Then the redistribution of CC takes place in such a way that the internal fields increase in '+' domains and decrease in '−' domains (see figure 2(*b*)). In both kinds of domains during the redistribution of CC to a new stable state the hopping photocurrents are directed oppositely to the external field, and consequently the photocurrent in the sample is negative.

Finishing the consideration of the oversimplified chain model of photoexcitation of an internal electric field in ruby, we summarize the results, which are in agreement with the experiments. The model:

(i) gives the starting mechanism for the increase of internal electric fields and their limiting values;

(ii) explains the independence of the stable intensity of the field on temperature and the rate of field increase, which is inversely proportional to the temperature;

(iii) explains the dependence of the intensity of the internal field on the external one in the case of irradiation in an external electric field;

(iv) describes qualitatively the current versus voltage characteristics of the photocurrent in ruby.

To carry out quantitative estimates we use a model that is closer to reality. The random distribution of Cr^{3+} PAI in the neighbourhood of CC is considered instead of the three-atom chains and the normal form of the inhomogeneously broadened R_1 line is assumed. This calculation does not lead to qualitatively new results. Moreover, the formula determining the maximum intensity of the photoinduced electric field in the domain coincides in form with (10). But one has to replace r in (10) by the most probable distance $\bar{r} = 5r_0/9$ at the known mean distance r_0 between impurities (Hertz 1909).

Using $\bar{r} = 1$ nm (which corresponds to $\approx 0.4\%$ weight concentration of Cr_2O_3) one estimates $E_s \simeq 6.2 \times 10^3$ V cm^{-1}. It is approximately two orders of magnitude smaller than the experimentally observed electric fields in domains. One of the possible reasons for the discrepancy is the much more essential effect of PAI situated nearer to CC than the distance $\bar{r}$.

3. Experiments

Experimental investigations involved the observation of the luminescence and absorption spectra of ruby during irradiation of different samples. The scheme of the experiments was similar to that used by Liao *et al* (1980) and Basun *et al* (1984), and the sources of radiation were a steady argon laser, a pulsed garnet laser and a filament lamp. All the experiments were carried out at 77 K. Ruby plates 0.07–0.43 mm thick with a concentration of 0.45% weight Cr_2O_3 grown by Verneil's method were used as samples. The C_3 axis in most of the samples was perpendicular to the planes of plates.
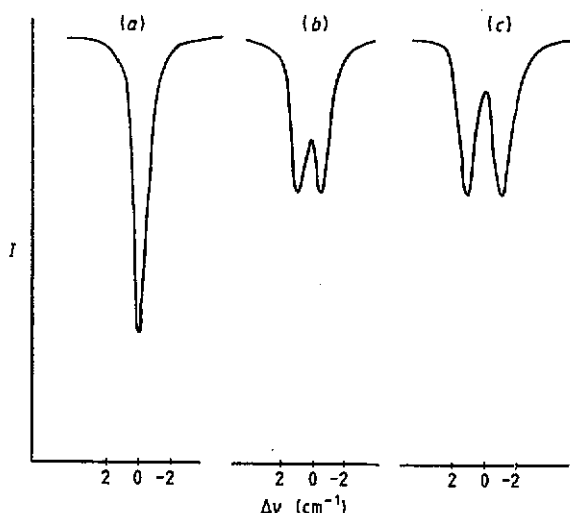
Figure 3. The form of the R_1 transmission line of ruby: (a) without an external electric field; (b) $E_0 \simeq 180\,\mathrm{kV\,cm^{-1}}$; (c) after laser irradiation.

3.1. The quantity of excess charged chromium ions in a sample

One aspect of the microscopic model is the assumption that the internal electric fields are produced by space charges placed near the domain walls. The space charges consist of excess charged chromium ions with the same sign. Consequently, during laser irradiation excess charges must be created and, hence, the quantity of Cr^{3+} ions must decrease. This quantity was tested by measuring the integral optical absorption of R lines. The principal peculiarity of these measurements is that there is an internal electric field in an irradiated sample and the absorption coefficient of R lines in ruby changes in an electric field (Neustruev 1977). Therefore it is necessary to compare the effect of the internal electric fields of domains and the effect of the external electric field on the absorption coefficient in the same sample.

Figure 3 presents the R_1 line transmission spectra of a ruby sample 0.43 mm thick without an external field (a), in an external field $E_0 \simeq 180\,\mathrm{kV\,cm^{-1}}$ (b) and after the formation of the electric domain structure with an internal field of $E_s \simeq 275\,\mathrm{kV\,cm^{-1}}$ (c). From the transmission spectra the spectral function of the absorption coefficient was obtained and the value of the integral absorption was calculated.

It turns out that the integral absorption of the R_1 line of the sample placed in an external electric field of $180\,\mathrm{kV\,cm^{-1}}$ is greater by $9.5 \pm 1.5\%$ than the integral absorption of the same line without the external field. According to Neustruev (1977) we suppose that the transition probability $^4A_2 \leftrightarrow {}^2E$ in the electric field increases by $\simeq 9.5\%$.

In the same sample with induced internal electric structure with $E_s \simeq 275\,\mathrm{kV\,cm^{-1}}$, the integral absorption was not changed within the accuracy of observation. Consequently during creation of the electric domain structure the number of Cr^{3+} ions in the irradiated part of the sample decreases by at least 9.5%.

Note the slight broadening of components of the R_1 line in figure 3(c) in comparison with the initial width (figure 3(a)). It may be explained only if the excess charged ions are assumed to be closely arranged in the sample. In the other case the homogeneous
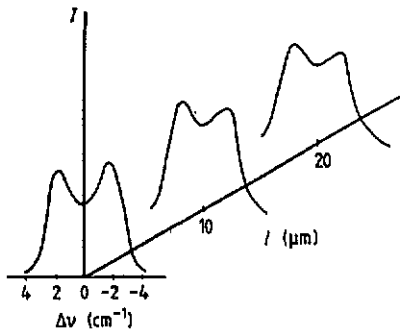
Figure 4. The space dependence of R_1 luminescence spectral line from small surface areas of the sample.
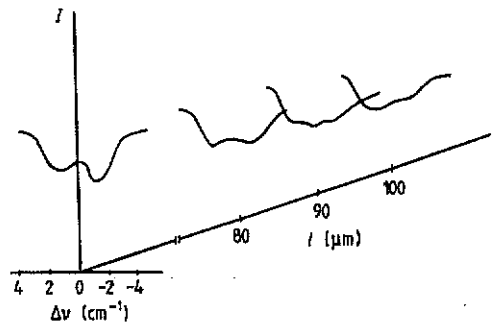

Figure 5. The space dependence of R_1 transmission spectral line of small parts of the sample.

distribution in the sample should mean that Cr^{3+} ions do not exist without the neighbouring CC, i.e. almost all Cr^{3+} ions must be PAI, and their lines must be broadened, which is not observed experimentally.

3.2. The space dependence of the relative intensities of the components of the R_1 line in irradiated samples

To investigate the inhomogeneity of the electric domain structure of the sample the R_1 line luminescence and absorption spectra obtained from small parts of the sample were studied. A ruby sample image magnified with the objective was projected onto a diaphragmed entrance slit of the monochromator. The signal was detected from the surface area of $2 \times 100\ \mu m^2$. The size of $2\ \mu m$ was made with the slit and the size of $100\ \mu m$ with the diaphragm. To observe the space dependence of spectra the sample was shifted in the direction perpendicular to the optical rays and to the monochromator slit.

The R_1 line luminescence spectra obtained from small surface elements of a ruby sample 0.22 mm thick are shown in figure 4. The value of the sample shift is plotted on the l axis. The main feature is the change in the relative intensities of components after a small shift of the area observed. If one observes the absorption spectrum of a large volume of the sample (figure 3(b)), the intensities of components are equal, i.e. the concentrations of sublattices are equal. But it is related to the quantities averaged over the volume. If the observation volume decreases, the probability of averaging also decreases. In figure 5 the transmission spectra of small volumes of the 0.22 mm thick sample are given. The change in the relative intensities of the split components is well observed. We believe that this space variation of the relative intensities of the split components may be due to different concentrations of sublattices (c_A, c_B) in domains.

3.3. Dynamics of the production of the photoinduced domain structure

It was shown by Liao *et al* (1980) that during laser irradiation the internal electric field was smoothly increasing from 0 to E_s in the irradiated part of the sample. This field dynamics corresponds rather well to the model of the increase of photovoltaic charges
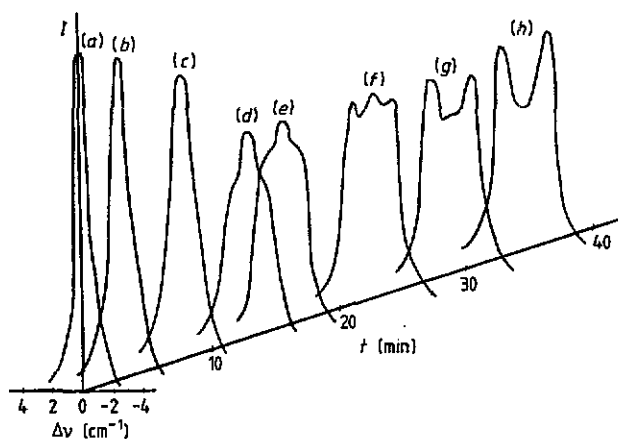
Figure 6. The form of the R_1 luminescence line during electric domain formation in ruby. The power density of the laser irradiation is $P_0 \simeq 50 \text{ W cm}^{-2}$. The thickness of the sample is 0.07 mm.

on opposite surfaces of the sample, but it is difficult to explain this dynamics in the domain model of field creation.

Here we present the results of the investigation of the dynamics of the internal electric field produced under different conditions of laser irradiation. The beam from the argon laser was directed perpendicularly to the plate. The luminescence spectra of R and N lines were observed during irradiation.

The typical dynamics of luminescence for the R_1 line is presented in figure 6. The moment of recording the centre of each R_1 line spectrum is plotted on the t axis. The *recording time of one spectrum was 2–3 min*. At the initial stage of irradiation the R_1 line broadens (figures 6(*b*), (*c*)) and then in contrast to the previously mentioned results of Liao *et al* (1980) transforms into an unresolved triplet (figures 6(*d*), (*e*), (*f*)). The side components of the triplet increase during irradiation and the central one decreases. As a result, the R_1 line turns into a doublet (figure 6(*g*)). During subsequent irradiation the lines of the doublet gradually move apart (figure 6(*h*)).

One may conclude that at the initial stage the electric field of intensity E_a ($E_a < E_s$) is produced in part of the chromium ions. Later the relative quantity of Cr^{3+} ions placed in the field E_a is increased and the transformation of the line into a doublet (figure 6(*f*)) corresponds to the moment when all Cr^{3+} ions of the irradiated part of the sample are in the field E_a.

This dynamics shows unambiguously the microscopic character of the production of the internal field E_a. It corresponds well to the representation on the domain structure of a field. One can state that the size of domains in which the field E_a is produced is much smaller than the size of the irradiated sample. This follows from the smooth change in the relative intensities of the triplet components.

This dynamics enables us to conclude that electric fields of equal intensities (in the considered case $E_a \simeq 340 \text{ kV cm}^{-1}$) are produced first in part of the domains. Then the number of domains with this internal field increases up to the filling of all the irradiated part of the sample. Later on the intensity of the electric field increases in all domains with the same rate up to E_s ($\simeq 400 \text{ kV cm}^{-1}$).
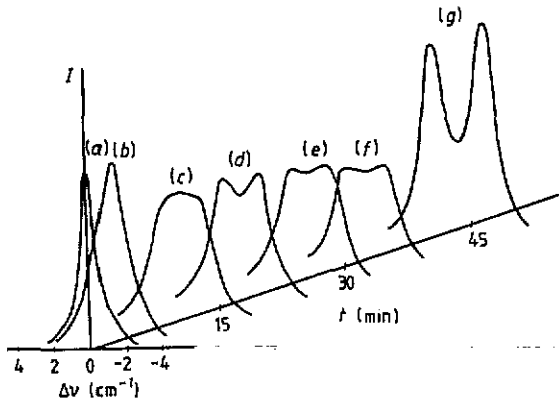
Figure 7. The form of R_1 luminescence line at the different power density of laser irradiation P: (a) P $\simeq$ 7 W cm^{-2}, irradiation during 30 min; (b–f) P $\simeq$ 200 W cm^{-2}; (g) P $\simeq$ 7 W cm^{-2}. The recorder amplification is in the cases (b–f) 15 times smaller and in the case (g) 3 times larger than in the case (a). The thickness of the sample is 0.07 mm.

3.4. Rate dependence of electric domain structure formation on the irradiation prehistory of the sample

We established that the rate of electric domain structure formation under irradiation of given intensity depends essentially on the prehistory of irradiation of the sample. This dependence is clearly shown in figure 7, in which the dynamics of the R_1 line luminescence is shown when the sample is irradiated by laser light with different intensities. The meaning of the t axis is the same as in figure 6. At small intensity of laser light, internal field formation is not observed or is very slow (figure 7(a)). At relatively large intensity the internal field is formed rather quickly (figures 7(b)–(f)). The line transforms into a weakly separated doublet (figure 7(f)), the components of which have much larger widths than the initial line. On subsequent irradiation with small intensity equal to that used in the case 7(a), the well separated doublet structure of the line is formed very rapidly (figure 7(g)). The width of each component of the doublet is approximately the same as the width of the initial line.

We think that a relatively large number of excess charged chromium ions appears during intensive laser irradiation and, hence, a large number of Cr^{3+} ions become the PAI. The latter lead to the broadening of the components. Simultaneously the intense irradiation leads to the usual large photoconductivity (σ_p), which, according to (13), leads to a smaller value of the stationary internal field E_s. On subsequent irradiation with light of small intensity, the rapid concentration of CC in the domain walls takes place due to the tunnel-hopping conductivity. Simultaneously E_s is increasing and the concentration of CC within domains is decreasing, which leads to the narrowing of the lines of Cr^{3+} placed inside the domains.

4. Discussion

Here we would like to discuss some experimental results, which cannot be explained using the thermalizational model only.

4.1. The directions of the photoinduced internal electric fields in domains

In the model the domain walls were supposed to be perpendicular to the optical axis. Of course, this assumption was arbitrary and we made it for simplification, taking into account that the thermalizational mechanism leads to the hopping current of excess charges only along an optical axis. If one supposes that the domain wall is a plane arbitrarily oriented with respect to the optical axis, then we inevitably come to the following conclusion. Owing to the concentration of equally charged cc in the vicinity of the wall, the electric field components perpendicular to the optical axis $(E_\perp)$ arise in the domain, and subsequently the current along the wall appears. This current redistributes the cc within the domain in such a way that $E_\perp \to 0$. The redistribution stops only when the internal field E_s becomes parallel to the optical axis in the domain. This redistribution of cc is possible in principle, since in the plane perpendicular to the optical axis the photoconductivity is isotropic. This very fact was taken into account in section 2 in the calculation of the probability of cc hopping.

·However, the total microscopic model of this redistribution of cc in domains of arbitrary form is not now obvious, especially if one considers the interaction between the space charges of many domain walls in the sample.

4.2. The temperature dependence of E_s

From (13) it follows that E_s depends weakly on the temperature. It corresponds well to experiments in the range 1.4–90 K but does not describe the rapid decrease of E_s when the temperature rises to $\simeq 150$ K. We think that this may be caused by the rapid broadening of the R lines of ruby at temperatures higher than $\simeq 90$ K (Shawlow 1961). The temperature broadening means a decrease of the inhomogeneous part of the linewidth and, consequently, the effect of thermalization of the $\bar{E}$ level decreases.

4.3. The constant value of E_s in the sample and the redistribution of the volumes of domains

To fit the theoretical calculation with experimental results concerning the constant value of E_s in all domains of the sample, one should assume in the model discussed that the balance of concentrations of sublattices is constant or that there is some additional mechanism making the intensities of the internal electric fields in different domains equal.

Novikov and Sturman (1988) noted that in an electric field there is non-resonant negative hopping photoconductivity in ruby due to the increase of the transition probability $^4A_2 \leftrightarrow \bar{E}$ of Cr^{3+} ions, i.e. due to the decrease of the lifetime of Cr^{3+} ions in the metastable state. That is why hoppings in the direction in which the electric field on the PAI (the external field + field of cc) is smaller in absolute value are more probable. A simple analysis shows that the hopping photocurrent due to this motion of excess charges is always directed oppositely to the external field.

This mechanism of non-resonant negative photoconductivity is obviously effective in a relatively high electric field (in comparison with the local electric field of cc on the PAI) and is less probable as the starting mechanism for domain structure formation. But its role in the final stationary electric field in the domain may be essential, especially because this mechanism does not depend on temperature and the sublattice of PAI.

The exact calculation of the effect of this mechanism and its effect on E_s is difficult owing to the rapid energy transfer over the E level in ruby (Duval and Monteil 1984) and the dependence of the transfer rate on the electric field.

It was noted previously that some experimental results cannot be explained without considering microscopic processes near the domain walls. We think that the variation of relative intensities of luminescence of '+' and '−' domains by domain structure formation in an external electric field $E_0 < E_s$ (Basun *et al* 1984) may be due to the distribution of excess charges near domain walls. Since the quantity of CC in the irradiated sample is rather large (see section 3.1), the excess charges forming the space charge near the domain wall occupy a considerable volume. The intensities of the electic fields are different in '+ and '−' domains; therefore different quantities of CC take part in the formation of space charges on the walls. Therefore different parts of domain volume are occupied by the CC, which is observed experimentally as the variation of intensities of luminescence of Cr^{3+} ions from '+' and '−' domains.

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