

# Kinetics of self-induced rotation of the plane of polarization of resonant radiation in a $\text{KCl}:\text{Li}^+$ crystal

M. Ya. Valakh, M. I. Dykman, M. P. Lisitsa, E. V. Pidlisnyi, G. Yu. Rud'ko, and G. G. Tarasov

*Institute of Semiconductors, Academy of Sciences of the Ukrainian SSR, Kiev*

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A theoretical and experimental study was made of the kinetics of rotation of the plane of polarization of radiation exciting resonantly reorientable  $F_A(\text{Li})$  centers in a KCl crystal. A good agreement was achieved between the calculated and experimental dependences of the angle of rotation on time and illumination intensity. The parameters representing the reduction in the local symmetry of an impurity center and the associated absorption were determined.

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Earlier investigations of two of the present authors<sup>1,2</sup> demonstrated that the propagation of resonant radiation in cubic crystals containing impurities may be accompanied by self-induced rotation of the plane of polarization (SRPP). In particular, such rotation can result<sup>2</sup> from optical orientation of nonspherical tunnel centers, i.e., impurities with several equivalent equilibrium positions (orientations) in one unit cell. The local symmetry of such impurities in any one equilibrium position is lower than cubic and, therefore, the absorption coefficient of a single impurity is anisotropic (for a uniform distribution of the tunnel centers over the orientations the absorption coefficient of the whole crystal is clearly isotropic). Since the overlap integrals of the wave functions corresponding to different orientations of the centers are considerably greater in the excited state than in the ground one, excitation with resonant radiation increases reorientation probability. If the radiation is linearly polarized, then excitation and reorientation affects primarily centers of that orientation for which the projection of the dipole moment of a transition along the direction of  $E$  is maximal. This produces a nonequilibrium distribution of the orientations of the impurity centers. Such optical alignment results in bleaching of a crystal at the relevant frequencies and in an anisotropy of the absorption of the orienting resonant radiation. Therefore, the problem of propagation of radiation should be solved in a self-consistent manner: the polarization of the medium, calculated allowing for the impurity orientation by the radiation itself, should be substituted in the Maxwell equation. This is done for the steady-state conditions in Ref. 2, where it is shown that self-induced anisotropy of the impurity absorption gives rise to SRPP.

Experimentally, SRPP was first observed by Valakh et al.<sup>3</sup> in the region of resonant absorption of  $F_A(\text{Li})$  centers in KCl. These centers are complexes each of which consists of an F center and an  $\text{Li}^+$  ion replacing a cation. Their spectrum consists of two bands, one of which ( $F_{A1}$ ) corresponds to a nondegenerate transition (its dipole moment is parallel to the axis of the center) and the other ( $F_{A2}$ ) to a doubly degenerate one. The former transition was excited in Ref. 3.

Clearly, an  $F_A$  center has six equivalent orientations out of which only three are optically distinguishable. At

sufficiently low temperatures ( $T < 100^\circ\text{K}$ ) the probability of reorientation of the  $F_A(\text{Li})$  centers in KCl is negligible in the ground state, whereas it is close to  $1/2$  in an excited state.<sup>4</sup> Therefore, even relatively weak polarized resonant radiation can ensure a fairly high degree of optical orientation of these centers.

## 1. EQUATIONS DESCRIBING KINETICS OF SELF-INDUCED ROTATION OF THE PLANE OF POLARIZATION

Optical orientations of tunnel centers is described by the rate equations<sup>2</sup>

$$\frac{d\rho_n}{dt} = - \sum_m (C_{nm}\rho_n - C_{mn}\rho_m), \quad \sum_n \rho_n = 1, \quad (1)$$

where  $\rho_n$  is the population of the  $n$ -th equilibrium position.

If the field is sufficiently weak so that the population of the excited level is low, the coefficients  $C_{nm}$  are

$$C_{nm} = A_{nm} + B_{nm} |d_n E|^2, \quad (2)$$

where  $d_n$  is the dipole moment of a nondegenerate transition in the  $n$ -th well (degenerate transitions will not be considered here) and  $E$  is the field intensity of a light wave. The parameters  $A_{nm}$  and  $B_{nm}$  govern the probabilities of reorientation in the ground and excited states of an impurity. In Ref. 2 they are determined for various models of impurities.

The system (1) is valid in a wide range of radiation intensities for strongly and weakly coupled tunnel centers at moderately low temperatures when the reorientation process (at least in the ground state) is of the hopping type.

The contribution of tunnel centers to the polarization of a crystal in the region of resonant impurity absorption is given by

$$P = C_0 q \sum_m d_m (d_m E) \rho_m \left( \sum_m d_m^2 \right)^{-1}. \quad (3)$$

Here,  $C_0$  is the impurity concentration,  $q$  is the complex

polarizability, and  $d_{mx}$  is the projection of  $d_m$  along the direction  $x$ . If the impurity concentration is sufficiently low so that  $C_0/q \ll 1$ , we find that the Maxwell equation yields the following expression for a slowly varying (in space and time) envelope of the intensity  $E$  of a light wave traveling in the direction  $s$ :

$$(sV)E = \frac{2\pi i\omega}{c\sqrt{\epsilon}} (P - s(sP)), \quad (4)$$

where  $\epsilon$  is the permittivity of the crystal matrix.

The system of partial derivatives (1)-(4) describes the propagation of radiation under conditions of generally nonstationary optical orientation and, in particular, it describes the kinetics of SRPP. In addition to the self-evident condition  $\omega \gg C_{nm}$ , the system is derived assuming implicitly also the condition  $l\sqrt{\epsilon}/c \ll C_{nm}^{-1}$ , where  $l$  is the thickness of the crystal. This means that in the transit time across a crystal the polarizability in Eq. (3) does not change. Only then we are justified by dropping the time derivatives of the field amplitude  $E$  in Eq. (4).

In analyzing the optical orientation of the  $F_A(Li)$  centers in KCl we have to allow for the fact that an  $Li^+$  ion is noncentral.<sup>6</sup> Even at liquid nitrogen temperatures such an ion rotates rapidly about the axis of the  $F_A$  center. We shall assume that  $\omega \gg \omega_0 \gg \bar{C}_{nm}$ , where  $\omega_0$  is the characteristic frequency of rotation or jumps between the equilibrium positions of a noncentral ion about the axis of the center and  $\bar{C}_{nm}$  is the probability of reorientation. In this case the system (1) can be approximated for a time scale of  $\sim \omega_0^{-1}$  and  $\rho_n$  can be regarded as the probability of orientation of a center about one of the crystallographic directions of the  $\langle 100 \rangle$  type, which are used to label the index  $n$  ( $n = x, y, z$ ).

The coefficients  $\bar{C}_{nm}$  are given by Eq. (2) and, if we neglect the reorientation of the axis of a center, we find that  $A_{nm} = 0$  in the ground electronic state and the field term should be averaged over the rotation of  $Li^+$ , i.e.,  $\bar{C}_{nm} \propto \langle |d_n E|^2 \rangle$ . Since the noncentral nature of the  $Li^+$  ions violates the selection rules, the projection of the vector  $d_n$  for the  $F_A$  band along the direction perpendicular to the axis of a center  $n$  is finite (for a fixed position of the lithium ion).

Introducing  $d_{n1}^2/d_{n0}^2 = 2\chi$  ( $\chi \ll 1$ ) and allowing for the optical equivalence of the orientations  $n$  and  $-n$ , we obtain

$$C_{nm} = Bd^2 [|E_n|^2 + \chi(E^2 - |E_n|^2)], \quad E_n = (En), \quad d^2 = d_{n1}^2, \quad E^2 = \sum_n E_n^2, \quad (5)$$

$$P = C_0 q \sum_n \rho_n (nE_n + \chi |E - nE_n|)/(1 + 2\chi). \quad (6)$$

(The unit vector  $n$  is parallel to the positive direction of one of the axes  $x, y$ , or  $z$ .)

It should be noted that without allowance for the violation of the selection rules, i.e., for  $\chi = 0$ , it follows from Eqs. (1) and (5) that the use of polarized radiation would have resulted in 100% optical orientation, since there would have been no mechanism impeding it. Consequently, in the stationary case the radiation for which the projection of  $E$  vanishes at least along one of the direc-

tions of the  $\langle 100 \rangle$  type would not have been absorbed at all, because all the centers would have been oriented along this direction. Such radiation could not have produced SRPP, contrary to the experimental evidence.

In the case of a wave traveling along the  $z$  axis  $[001]$ , it follows from Eq. (1), (4), and (6) that

$$\frac{\partial E_n}{\partial z} = \frac{ixE_n}{1 + 2\chi} [\rho_n(1 - \chi) + \chi]; \quad n = x, y; \quad z = z' + ix'' = \frac{2\pi\omega C_0 q}{c\sqrt{\epsilon}}. \quad (7)$$

This means that in the absence of optical orientation ( $\rho_n = 1/3$ ) the value of  $2\chi''$  is the impurity-absorption coefficient of a cubic crystal.

In Eqs. (1), (5), and (7) we can adopt the dimensionless time  $\tau = Bd^2 E^2(0)t$  [ $E^2(0)$  is the intensity of the incident radiation and the dimensionless coordinate  $\bar{z} = \chi''z/(1 + 2\chi)$ ]. Consequently, in the case of exact resonance ( $\chi' = 0$ ) the kinetics of SRPP is governed by two dimensionless parameters:  $\chi$  and  $l = \chi''l/(1 + 2\chi)$ . The phenomenon of SRPP can be treated analytically in the stationary case. If  $\chi' = 0$ , in the case of linearly polarized radiation, we obtain

$$\left( \frac{\lg 2\varphi}{\lg 2\varphi_0} \right)^{\left(1 + \frac{\chi}{2}\right)} \left( \frac{\cos 2\varphi}{\cos 2\varphi_0} \right)^{-(1-\chi)^{2/3}\chi} = \exp \left[ -\frac{1}{8}(1-\chi)^2 l \right], \quad (8)$$

where  $\varphi$  is the angle between the vector  $E$  and the closest  $\langle 100 \rangle$  axis for the transmitted radiation, whereas  $\varphi_0$  is the corresponding angle for incident radiation. We can see that  $\varphi \rightarrow 0$  in the limit  $l \rightarrow \infty$ , i.e., the plane of polarization does indeed rotate to the nearest  $\langle 100 \rangle$  direction. On the other hand, if  $\chi \rightarrow 0$ , then  $\varphi \rightarrow \varphi_0$ , i.e., SRPP appears only because of violation of the selection rules.

In general, the dependence of SRPP on  $\chi$ ,  $l$ , and dimensionless time  $\tau$  can be analyzed by solving Eqs. (1), (5), and (7) numerically. However, it is important to note that there is a characteristic similarity: the time  $t$  in which the polarization is rotated through a certain angle corresponding to a given value of  $\tau$  is inversely proportional to the intensity  $E^2(0)$ . This similarity appears because  $\bar{C}_{nm} \propto E^2$  and it is retained if allowance is made for the absorption and scattering in the matrix crystal. If such similarity is observed, it can be regarded as an important argument in support of the proposed reorientation model.

## 2. EXPERIMENTAL METHOD

We investigated experimentally the kinetics of SRPP in KCl single crystals containing  $F_A(Li)$  centers created by a method described in Ref. 3.

The apparatus used is shown schematically in Fig. 1. A linearly polarized beam from an He-Ne laser of the LG-56 type (1) passed through a Fresnel rhomb (2) and became circularly polarized. A Glan polarization prism (3) was used to set the required direction of crystallographic axes of a crystal (4) attached to a heat sink of a nitrogen cryostat (5). The direction of polarization of the radiation transmitted by the crystal was measured using a second Glan prism (6) and a signal produced by the load of a photomultiplier of the FEU-51 type (7) and recorded with a V2-11 microvoltmeter (8). The photomultiplier was

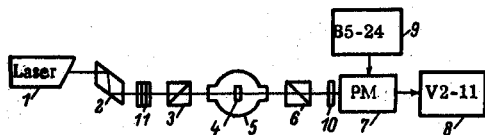


FIG. 1. Schematic diagram of the apparatus for investigating SRPP (PM represents a photomultiplier).

supplied from a V5-24 stabilized source (9). The influence of possible background radiation was reduced by placing a narrow-band interference filter (10) with  $\lambda_{\max} = 633 \text{ nm}$  in front of the photomultiplier. The intensity of the incident radiation was varied by a set of calibrated neutral gray filters (11). The error in the determination of the angles of rotation did not exceed  $\pm 1^\circ$ .

The time dependences of the angle of rotation of the plane of polarization (Fig. 2) were obtained as follows. A sample was illuminated for 2 min with the unattenuated laser beam traveling along the [001] axis of the crystal with the polarization parallel to the [100] axis. This aligned the impurity centers preferentially along the [010] and [001] directions. The Glan prism (3) was then rotated by  $45^\circ$ , time measurements were started, and additional measurements were made of the direction of the plane of polarization of the light transmitted by the crystal relative to the polarization of the incident light.

### 3. DISCUSSION OF EXPERIMENTAL RESULTS

The kinetics of rotation of the plane of polarization is presented in Fig. 2. It is worth noting a clear similarity between the time dependences: the ratio of the times needed for rotation through a certain angle is inversely proportional to the ratio of the intensities of the incident radiation and is independent of the angle of rotation. Similarly, all the theoretical curves (shown continuous in Fig. 2) are deduced from the same curve by altering the scale. The discrepancy in the ratio of the scales of the theoretical curves for the different intensities and filter transmission coefficients did not exceed 10%. In the range of short times (inset in Fig. 2) the experimental dependence of the angle of rotation was nearly linear and, within the limits of the experimental error ( $\pm 1^\circ$ ) the maxi-

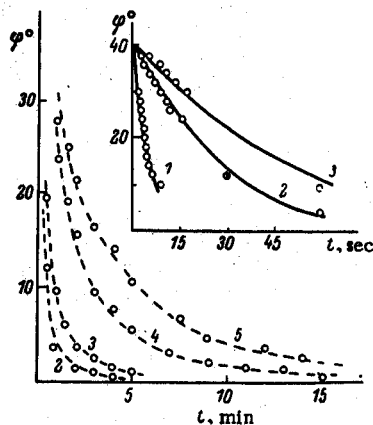


FIG. 2. Kinetics of SRPP for different intensities of resonant radiation. The points are the experimental results and the continuous curves are theoretical. Intensity of the radiation incident on a crystal (rel. units): 1) 1.00; 2) 0.20; 3) 0.10; 4) 0.04; 5) 0.02.

mum angle of rotation for  $t \rightarrow 0$  was independent of the illumination intensity and amounted to  $40.5^\circ$  for the investigated crystal. In the range of long times the angle of rotation approached zero asymptotically.

In the experimental arrangement used, the linearity of the time dependence of the angle of rotation in the range of small values of  $t$  was a direct consequence of Eqs. (1), (5), and (7). The initial angle of rotation  $\phi_1$  in the limit of  $t \rightarrow 0$  was found by solving Eq. (7) subject to the boundary condition  $E_x(0) = E_y(0)$  (the incident radiation was polarized along the [100] axis). The quantity  $\rho_n$  was taken to represent the steady-state populations created by preliminary illumination with radiation polarized along the [100] axis [ $\rho_y = \rho_z = (2 + \chi)^{-1}$ ,  $\rho_x = \chi(2 + \chi)$ ]. Consequently, it was found that

$$\varphi_t = \arctg \exp \left[ \frac{(1 - \chi)^2 I}{8(1 + \chi/2)} \right]. \quad (9)$$

According to Eq. (9), the angle of rotation  $\phi_1$  is indeed independent of the illumination intensity, but depends strongly on the thickness  $\tilde{l}$ . A comparison of Eqs. (9) and (8) and the experimental data for  $\phi_1$  and for the steady-state angle of rotation measured by the method of Ref. 3 makes it possible to determine quite accurately the parameters  $\chi$  and  $\tilde{l}$ . In particular, it is clear from the experimental data for the sample represented in Fig. 2, where the maximum value of the steady-state SRPP angle  $(\phi - \phi_0)_{\max}$  is  $\sim 16^\circ$ , that  $\chi = 1/25$  and  $\tilde{l} = 22$ . For these values of  $\chi$  and  $\tilde{l}$  it follows from Eqs. (8) and (9) that  $\phi_1 \approx 40.2^\circ$  and  $(\phi - \phi_0)_{\max} \approx 16.5^\circ$ , and that the theoretical and experimental values of  $\phi_0$  corresponding to the maximum of  $(\phi - \phi_0)$  are identical. The value  $\chi = 1/25$  seems to be more accurate than the estimate  $\chi = 1/15$  given in Ref. 3 with an accuracy of 30%, because in addition to the steady-state SRPP, we also measured  $\phi_1$  and the value of this angle was very sensitive to the parameters  $\chi$  and  $\tilde{l}$ .

A comparison of the results of a computer solution of Eqs. (1), (5), and (7) with  $\chi = 1/25$  and  $\tilde{l} = 22$  with the experimental data on the SRPP kinetics showed that the calculated long-duration tail decreased more rapidly than that found experimentally. After a long time, the kinetics was governed mainly by the region far from the front face of the crystal where the field intensity was low and the reorientation time was long.<sup>5</sup> Therefore, even in the case of relatively weak absorption or scattering of light by the matrix crystal, the time dependence of the angle of rotation became slower. Nonresonant background was indeed observed in the absorption spectra of the investigated crystals. This was partly due to the long-wavelength wing of the absorption band of the residual F centers. Therefore, in describing the kinetics the right-hand side of Eq. (7) was supplemented by the term  $-k''E_n/2$ , where  $k''$  is the reciprocal of the nonresonant absorption length. A satisfactory agreement with the experimental results was obtained for  $k''(1 + 2\chi)/\mu'' = 1/34$ . One should point out that allowance for nonresonant absorption did not affect  $\phi_1$  or the steady-state SRPP angle and, consequently, it did not influence the accuracy of the determination of  $\chi$  and  $\tilde{l}$ .

We thus found that the transient nonlinear optical effect (time dependence of the angle of self-induced rotation

of the plane of polarization in impurity-doped cubic crystals) investigated by us made it possible to determine the following characteristics of impurities by relatively simple experimental methods: lowering of the local symmetry and the associated violation of the selection rules, as well as the impurity absorption length. Even a very slight departure from the selection rules could be determined reliably: the absorption of light polarized at right-angles to the axis of the  $F_A(Li)$  centers in KCl in the region of a nondegenerate transition was, according to the results given above, approximately 25 times less than that of the light polarized along the axis. Measurements of the impurity absorption by traditional methods in the case of the centers characterized by a much higher reorientation probability in an excited state than in the ground state would be difficult because of the difficulty of ensuring a uniform

distribution of the orientation of the centers in the process of measurement.

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## Effect of intrinsic conduction on the thermoelectric properties of the $Bi_2Te_{3-y-z}Se_yS_z$ system at 300 °K

B. M. Gol'tsman, G. N. Ikonnikova, and V. A. Kutasov

*A. F. Ioffe Physicotechnical Institute, Academy of Sciences of the USSR, Leningrad*

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*Fiz. Tverd. Tela (Leningrad)* **23**, 424-428 (February 1981)

The thermoelectric properties of the multicomponent solid solutions  $Bi_2Te_{3-y-z}Se_yS_z$  were studied in the range 77-300 °K. The effect of intrinsic conduction on the quantities which determine the figure of merit  $z$  of these materials was calculated with a model in which  $z$  is characterized by the reduced energy gap width  $E_g^* = E_g/kT$  and by the quantities  $\beta \sim \text{constant} \cdot T^{5/2} m_n^{3/2} u_{on}/\kappa_l$  and  $\gamma = (m_p/m_n)^{3/2} u_{op}/u_{on} (m_n, u_{on}, m_p, u_{op})$  are the effective masses and mobilities of electrons and holes,  $\kappa_l$  the thermal conductivity of the crystal lattice). The optimum values of the electrical conductivity and the thermoelectric power at 300 °K were calculated.

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The thermoelectric properties of solid solutions of certain bismuth and antimony chalcogenides ( $Bi_2Te_{3-x}Se_x$  and  $Bi_{2-y}Sb_yTe_3$ ) have been studied by many workers and a determination has been made of the compositions of solid solutions and carrier densities optimizing the characteristics of these materials in the range 200-600 °K (Ref. 1). It is of interest to investigate also the more complex multicomponent solid solutions of bismuth and antimony chalcogenides in order to assess their prospects as thermoelectric materials.

For solid solutions having a narrow ( $< 0.2$  eV) energy gap  $E_g$ , which include those based on bismuth telluride, it has been shown<sup>2</sup> that the parameter  $(m_n/m_0)^{3/2} u_0$  (where  $m_n$  is the effective density-of-states mass,  $m_0$  the free electron mass, and  $u_0$  the carrier mobility when the electron gas is not degenerate) and the thermal conductivity  $\kappa_l$  of the crystal lattice, which determine the thermoelectric figure of merit of a material, may be considerably modified by intrinsic conduction even at 300 °K. In the present investigation, this topic was studied for the solid solution systems n-type  $Bi_2Te_{3-z}S_z$  and n-type  $Bi_2Te_{3-y-z}Se_yS_z$ , the compositions used being within the range of existence of solid solutions<sup>3</sup> ( $z = 0.06, 0.12, 0.21$  in the first

system;  $y = 0.09, z = 0.045$ ;  $y = 0.15, z = 0.075$ ; and  $y = 0.30, z = 0.15$  in the second). Samples were prepared by vertical zone melting from previously synthesized material of stoichiometric composition, with the appropriate addition of dopant. The n-type samples were made by doping with cadmium chloride, and the p-type samples with lead. The temperature gradient at the crystallization front and the growth rate were chosen so as to avoid concentration supercooling during growth, which leads to microinhomogeneities.<sup>1</sup> The electrical conductivity  $\sigma$ , the thermoelectric power  $\alpha$ , and the thermal conductivity  $\kappa$  were measured with the electric current and the heat flux along the cleavage planes of the samples.

For solid solutions based on bismuth telluride, there are difficulties in determining the Hall carrier density, as we have no information about the value of the anisotropy factor, which could be determined only by a study of the galvanomagnetic coefficients in single crystals.<sup>1</sup> The problem of growing single crystals of multicomponent solid solutions based on bismuth telluride has not been fully resolved, and we therefore used in the present work the thermoelectric power to characterize the concentration. The effect of intrinsic conduction was taken into ac-