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Dielectric Relaxation Changes Due to Optical Conversion "$F \to Z_1$" in KCl:SrCl$_2$ Crystals*

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Optical-absorption and dielectric-loss measurements have been carried out and correlated in additively colored KCl:SrCl$_2$ single crystals, in order to discern whether the impurity-vacancy dipolar complexes are involved in the optical conversion of F centers to Z_1 centers. The Z_1 centers were created by irradiating samples containing only F centers at 40°C by means of high-intensity light absorbed by the F band; a concentration of $\simeq 10^{17}$ Z_1 centers was obtained in about 30 sec. In the meantime the concentration of impurity-vacancy complexes n_{IV} was measured by means of dielectric losses. The results show that n_{IV} is not instantaneously affected by the growth of Z_1 centers but rather decreases slowly thereafter in a time of about 20 min after the F-light illumination. The total change of n_{IV} was approximately 10% of the initial value ($\simeq 10^{18}$ dipole cm^{-3}), i.e., $\simeq 10^{17}$ dipoles. Similar measurements have been carried out by irradiating at 0°C and by determining n_{IV} by measuring the discharge of the induced polarization at increasing temperature (method of the ionic thermoconductivity): the results obtained thus are consistent with the ones at 40°C. This experiment rules out the possibility that the impurity-vacancy dipoles take part directly in the Z_1-center formation; the proposed models are discussed in view of these results.

I. INTRODUCTION

SOME properties of Z_1 centers, obtained in alkali halide crystals doped with divalent metallic impurities, are known from optical-absorption and paramagnetic-resonance measurements. It is however difficult to connect the results in a unified scheme and consequently any interpretation of these centers in terms of physical models is not yet unequivocal. The proposed models describe the Z_1 center as an electron localized into complexes containing the divalent impurity: however, it is not clear whether these are the free impurity (Seitz[1]), the impurity associated with a cation vacancy (Pick[2]) or the impurity associated with a vacancy pair (Kleefstra,[3] Lüty[4]). See Fig. 1. Even the theoretical calculations[5–7] did not contribute to making a clearer picture, but rather they introduced new contradictions.

In this work the problem has been investigated from a new viewpoint, by correlating optical-absorption and dielectric-relaxation measurements. For this purpose we studied how the concentration of impurity-vacancy dipolar complexes (I. V. dipoles, which give place to dielectric absorption[8]) is influenced by the optical conversion $F \to Z_1$ at different temperatures. By means of this kind of analysis it is possible to establish whether the I. V. dipoles are involved in the formation of Z_1 centers.

II. EXPERIMENTAL DETAILS

The samples used were cleaved from crystals grown in our laboratory by means of the Kyropoulos method in a N$_2$ atmosphere. The pure KCl crystals were obtained from Merck ultrapure powders which contain less than 10^{-5} divalent metal impurities in weight. The doped crystals, chosen for the experiment contained $\simeq 10^{-3}$ SrCl$_2$ by weight. Crystals containing a higher concentration of SrCl$_2$ have been ruled out because of the precipitation phenomena, occurring after the quenching, which make the concentration of I.V. dipoles by itself not constant with time and therefore disturb the experiment under way. The additive coloration was performed at 540°C in potassium vapor for 20 min.

The $F \to Z_1$ conversion was studied by means of dielectric losses, ionic thermocurrents[9] (I.T.C.) and optical-absorption measurements. The dielectric-losses measurements were carried out in the frequency range from 80 to 10^5 cps by means of a General Radio 716 C capacitance bridge. A sample container was designed in order to carry out the measurements in controlled atmosphere at temperatures above room temperature and to irradiate the samples with visible light. The sample holder can accept two samples, one of which is irradiated and the other is used as a reference. We used ferrite electrodes, each coated with thin silver foil or fine mesh; one of them was pierced to allow the light to pass through.

The ionic thermoconductivity consists essentially in studying the discharging electric current, at linearly increasing temperatures, in a crystal polarized isothermally at higher temperatures. In our experiment the

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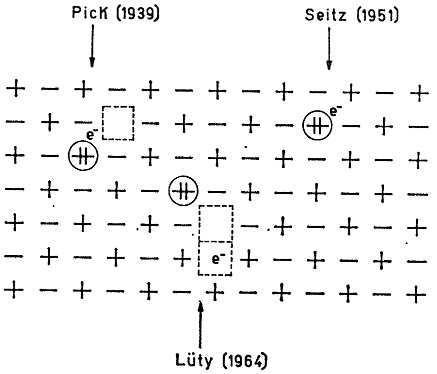

FIG. 1. Proposed models for Z_1 center.

sample was polarized in a static field of approximately 10^4 V/cm for 3 min at 235°K and quickly cooled down to $\simeq$150°K. The ionic thermocurrents were measured by a vibrating-reed electrometer able to detect currents as low as 10^{-16} A. For these measurements the assembly of electrodes was put in a stainless steel vessel, at the bottom of which a Pyrex window was sealed with Araldite to a thin annealed copper foil. This apparatus allowed the irradiation of the crystals to be accomplished at temperatures below room temperature. The contacts between samples and electrodes were improved by painting colloidal graphite on the surfaces unexposed to the light.

A CARY 14 recording spectrophotometer provided the optical absorption spectra of the samples: these measurements were always carried out at $\simeq$80°K. The irradiations were performed by means of a Philips tungsten lamp (1000 W) and a Scott interferential filter ($\lambda = 5610$ Å).

The stability of the temperature was within $\simeq$1°C. [For the electrical measurements the size of the samples was about 15 mm×15 mm×0.5 mm and for optical measurements about 8 mm×8 mm×0.2 mm.]

III. RESULTS

The concentration of I.V. dipoles can be calculated from the maximum value of the Debye peak in tanδ measurements[8] as well as from the area of the band in I.T.C. measurements.[9] As will be explained later, the former method can be employed at temperatures $\geqslant$40°C; at 0°C, where the optical conversion $F \rightarrow Z_1$ can be accomplished with the highest efficiency, we used the latter method.

A. Tanδ Measurements

The dielectric loss of KCl:SrCl$_2$, additively colored and quenched from 540°C, has been measured at 40°C as a function of the frequency: it has been ascertained that the dielectric properties of a sample containing F centers are the same as those of a noncolored one. Then the sample was irradiated, always at 40°C, with F light: with the lamp employed the saturation in the $F \rightarrow Z_1$ conversion was reached in about 1 min. The choice of the temperature was determined essentially by the following two factors: (a) 40°C is the lowest temperature at which the Debye peak in tanδ can be measured with reasonable precision; (b) it is the highest temperature at which the conversion $F \rightarrow Z_1$ can be accomplished without the formation of Z_2 centers: it is to be remembered that Z_2 centers give rise to a very high Debye peak[10] which overlaps the peak due to I.V. dipoles. It is furthermore to be noticed that Z_2 centers could not be completely eliminated after the quenching, nor could they be prevented from forming during the optical conversion $F \rightarrow Z_1$, even at 40°C.

Before and soon after the irradiation with F light, dielectric-losses measurements were carried out, as a function of time, at the frequency corresponding to the maximum of the I.V. Debye peak. As can be noticed in Fig. 2, the concentration of I.V. dipoles, soon after the $F \rightarrow Z_1$ conversion, is the same as before it: it decreases, however, slowly with time and reaches an equilibrium value in about 20 min. The total decrease represents approximately 8% of the initial concentration.

The same kind of experiment has been carried out on KCl:SrCl$_2$ not colored and on pure KCl containing only F centers. The results, as shown in Figs. 3(a) and 3(b), confirm that in such crystals no changes in the dielectric losses are induced by the optical irradiation.

B. I. T. C. Measurements

The experiment has been performed also at 0°C, where the efficiency in the optical conversion $F \rightarrow Z_1$ reaches its maximum. Since at 0°C the I.V. dipoles cannot be detected by means of tanδ measurements, ionic thermoconductivity measurements have been carried out in order to measure their concentration. As expected the concentration of dipoles is not subjected to any change immediately after the optical conversion

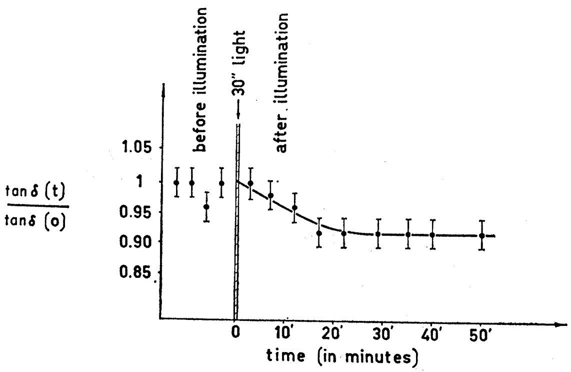

FIG. 2. Behavior of dielectric losses [tan $\delta(t)$/tan $\delta(0)$] of additivity colored KCl:SrCl$_2$ at 140 cps before and after the irradiation with F light for 30 sec at 40°C.

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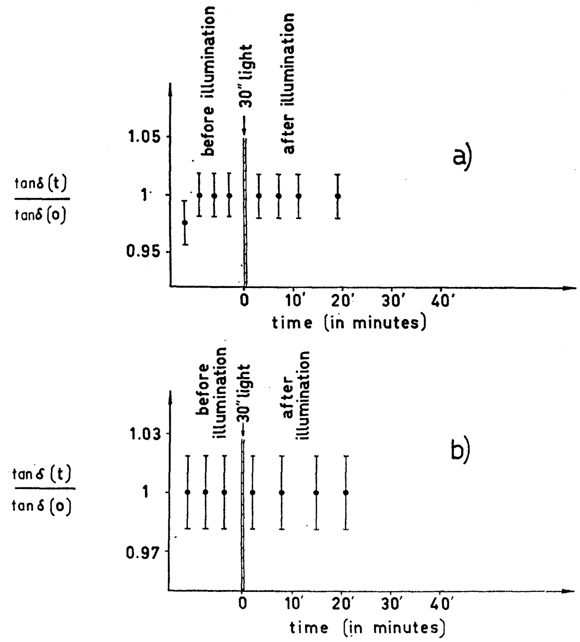

FIG. 3. Behavior of dielectric losses [tan $\delta(t)/\tan\delta(0)$] ($w=140$ cps, $T=40$°C) before and after the irradiation (F light for 30 sec) in: (a) KCl:SrCl$_2$ not colored and (b) E.L.H. pure KCl additively colored.

$F\rightarrow Z_1$ at 0°C: in Fig. 4 the thermocurrent bands before and after the conversion are compared: no variations of intensity are observed within 3%, which represents the reproducibility of I.T.C. measurements in these conditions. It must be pointed out that the I.T.C. measurements are carried out by quickly cooling the sample down to liquid-nitrogen temperature; therefore the situation originated by the optical conversion is hindered.

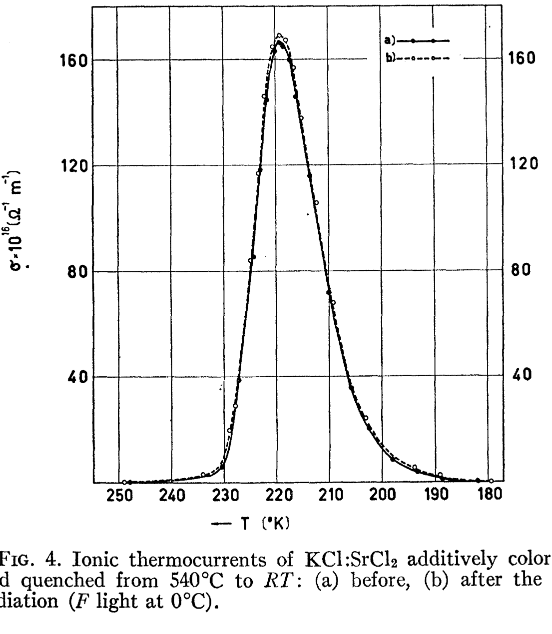

FIG. 4. Ionic thermocurrents of KCl:SrCl$_2$ additively colored and quenched from 540°C to RT: (a) before, (b) after the irradiation (F light at 0°C).

The concentration of Z_1 centers built during the optical conversion at 40°C and 0°C has been obtained from the optical absorption measurements [see Figs. 5(a) and 6]. The growth curve of Z_1 band, at 40°C, indicates that the irradiation time chosen in this experiment is long enough to obtain a large concentration of Z_1 centers [see Fig. 5(b)]. In Fig. 7 the absorption spectra of the samples are shown soon after the irradiation with F light and 20 min after it; the temperature in the meantime remaining constantly at 40°C. No substantial variations of the concentration of the color centers are observed besides a small decrease of F and Z_1 bands and consequently a small increase of the Z_2 band.

IV. DISCUSSION AND CONCLUSIONS

In principle one expects two alternative behaviors of the concentration of I.V. dipoles after the irradiation, according to whether (a) the I.V. dipoles, or (b) the isolated divalent impurities are directly involved in the process of formation of Z_1 centers.

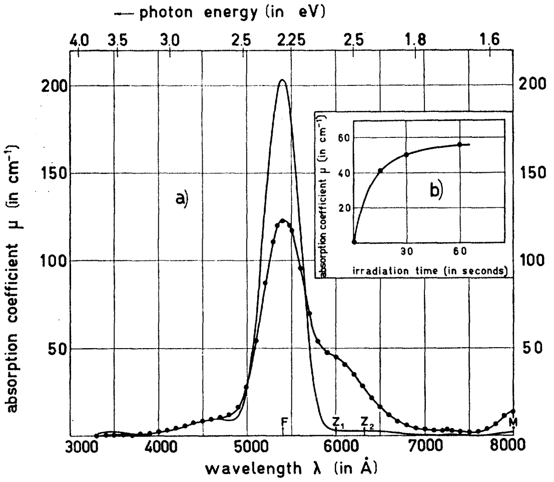

FIG. 5. (a) Optical-absorption spectra of additively colored KCl:SrCl$_2$ (———) soon after the quenching from 540°C, (•—•—•) after irradiation (1 min of F light at 40°C). (b) Growth curve of Z_1 band as a function of irradiation time (F light at 40°C).

In fact, in the former case the concentration of I.V. dipoles is expected to drop simultaneously with the growth of Z_1 centers, while in the latter case it should remain unchanged. In both cases, however, the growth of Z_1 centers destroys the thermodynamical equilibrium among free impurities, cation vacancies and I.V. dipoles, which is described symbolically by the reaction

$$\mathrm{Sr}^{++}+\oplus\rightleftarrows(\mathrm{Sr}^{++}\oplus). \qquad (1)$$

As a consequence of the optical conversion $F\rightarrow Z_1$, reaction (1) will reach a new equilibrium situation with a bimolecular kinetics. In Figs. 8(a) and 8(b) the qualitative behavior of the concentration of I.V. dipoles n_{IV} as a function of time after the irradiation is shown;

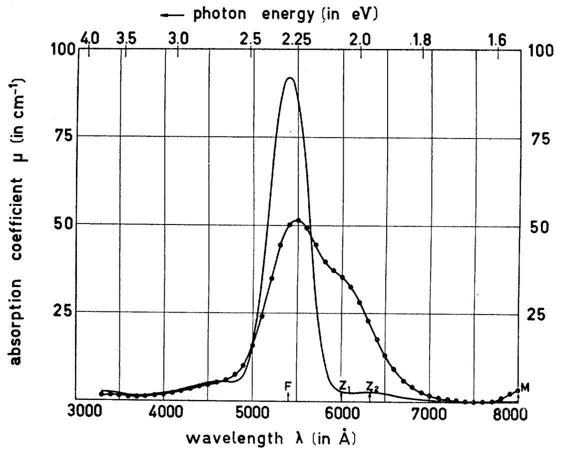

FIG. 6. Optical absorption spectra of additively colored KCl: $SrCl_2$ (——) soon after quenching from 540°C, (•—•—•) after irradiation (1 min of F light at 0°C).

in case (a) after the initial sudden drop, n_{IV} increases slowly toward an asymptotic value (which is smaller than it was before the irradiation) as a consequence of the association of impurities with vacancies; in the case (b) n_{IV} decreases gradually because of the disassociation of a fraction of them (the total change of n_{IV} should be smaller than the number of Z_1 centers). It will be, therefore, possible to distinguish between the two cases only if the growth of Z_1 centers can be accomplished with a much faster rate than the one required by the reaction (1) in order to reach its equilibrium, at the temperature of the experiment. For this purpose a high intensity and short irradiation ($\simeq$30 sec) is necessary.

The experimental results obtained by means of $\tan\delta$ measurements (Fig. 2) agree with the expectations previously formulated in the case (b) [see Fig. 8(b)]. It can be seen that the new thermodynamic equilibrium is reached in about 20 min by means of the disassociation of $\simeq 10^{17}$ dipoles. Concurrently the number of Z_1 centers created during the irradiation is $\simeq 1.5\times 10^{17}$.

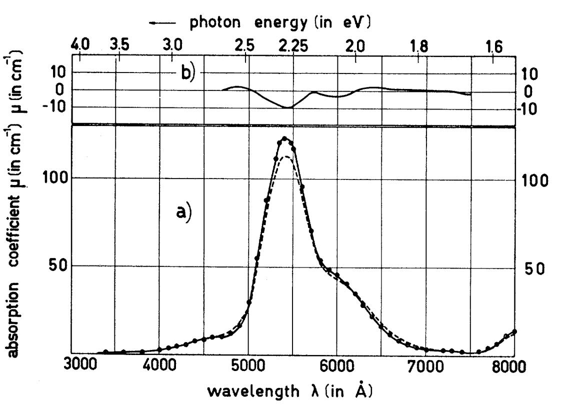

FIG. 7. (a) Optical-absorption spectra of additively colored KCl:$SrCl_2$, quenched from 540°C and irradiated with F light for 1 min at 40°C: (•—•—•) spectrum at L.N.T. soon after the irradiation, (— — —) spectrum at L.N.T. after a 20-min annealing at 40°C, (b) Difference between the two above given curves.

The observed behavior is really connected only with the formation of Z_1 centers; in fact,

(1) KCl:$SrCl_2$ crystals, in the absence of color centers, do not show any change in n_{IV} when subjected to irradiation, regardless of how long and intense [see Fig. 3(a)];

(2) in pure KCl crystals containing only F centers, $\tan\delta$ remains constant even after the irradiation [Fig. 3(b)].

The last result allows us to rule out the possibility that the decay of $\tan\delta$ shown in Fig. 2 is influenced by electronic effects connected with the ionization of the F centers or to the formation of complexes centers like M, N, or R centers. It is however to be noted that in doped crystals the concentration of such centers is much smaller than in the pure ones. Furthermore the decrease of n_{IV} during the time following the irradiation at 40°C is not to be attributed to isothermal variation of the number of color centers; the formation of a small Z_2 band, observed from absorption spectra, should produce, in any case, an increase in the $\tan\delta$ values; as previously mentioned, taking into account this possibility, the true equilibrium value of n_{IV} will be somewhat smaller than the measured one.

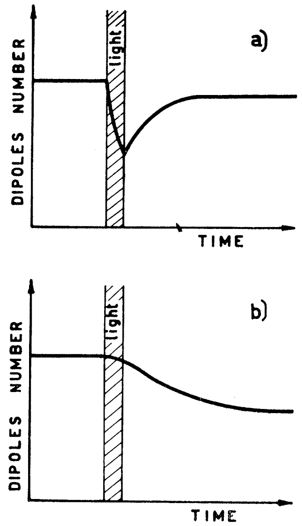

FIG. 8. Qualitative behavior of the concentration of I.V. dipoles before and after the optical conversion $F\rightarrow Z_1$ in the two following cases: (a) I.V. dipoles are involved in the Z_1 center, (b) I.V. dipoles are not involved in the Z_1 center.

The I.T.C. measurements further confirm the mechanism (b), as mentioned above, even if it has not been possible to follow the process of disassociation of I.V. dipoles. This experiment allows the following conclusions to be drawn:

(1) I.V. dipoles are not involved in Z_1 center formation from optical conversion $F\rightarrow Z_1$, and therefore the mechanisms suggested by Pick and Lüty, as well as any other mechanism requiring the direct participation of I.V. dipole are not supported by experimental evidence.

(2) The Z_1 center cannot arise from the capture of an electron by an I.V. dipole followed by a dissociation

$$(\mathrm{Sr}^{++}\oplus)+e^-\rightarrow Z_1+\oplus$$

according to one of the mechanisms suggested by Seitz. The absence of dichroism[11] and E.P.R. (electron paramagnetic resonance)[12,13] measurements support the picture of a center having a spherical symmetry, as the Seitz one does. On the other hand hyperfine structure of Z_1 center in KCl:SrCl$_2$, enriched in the magnetic isotope Sr^{87}, has not been pointed out by the latest ENDOR[14] (electron nuclear double resonance) measurements, as expected on the basis of the Seitz model. The energy absorbed by the electron in the transition from the ground state to the first excited state has been calculated by several authors on the basis of the Seitz model, and the results are very far from the experimental value of 2.06 eV in KCl:SrCl$_2$ at L.N.T. Lidiard[5] by means of thermodynamic arguments calculates an energy of 0.9 eV which would localize the Z_1 band in the infrared. Johnson and Scott,[6] by following the scheme of Simpson for the F center, obtain an energy of about 9 eV; a better agreement with the experimental measurements is encountered in calculations of Peterson and Patterson,[7] who found an energy of 3.14 and 2.59 eV, respectively, for the Seitz and Pick models.

Since Bushnell's measurements rule out the Seitz model, the Z_1 growth might be due to an ionic process, as with the one proposed by Lüty: an empty anion vacancy, resulting from the F-center optical ionization, diffuses in the lattice until it is captured close to an impurity. If this mechanism holds, however, our experimental results suggest that the impurity is an isolated divalent metal impurity not an I.V. complex.

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Self-Diffusion in Silicon Carbide*

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In available crystals, the self-diffusivity of carbon has been found to be extrinsic (experimental range 1853 to 2088°C), the carbon self-diffusivity being higher in p-type than in n-type material. The self-diffusion coefficient for Si is approximately ten times higher than that for carbon between 1927 and 2017°C.

I. INTRODUCTION

The influence of changing chemical-bond type on the disorder type, the point-defect concentration, the defect mobilities, and hence atom diffusivities in compounds, is incompletely understood. In the transition from ionic to covalently bonded materials, the criterion for maintaining electroneutrality shifts from ion vacancy to electron or hole generation to compensate for a valence difference between the host and an added impurity. This sometimes leads to different effects on self-diffusivities; in a covalent compound the defects on the respective sites may form with electron or hole compensation rather than being connected by a Schottky equilibrium. It would appear that substitutional disorder would be more important in governing self-diffusivities in covalent compounds. Such detail has not been elucidated among the Group IV semiconductors[1,2]; in germanium[3,4] the self-diffusivity has been measured, while in silicon[5–7] it has only been inferred. However, impurity diffusion in Ge and Si has been rather well documented. We report here data for some p-type and n-type SiC crystals and on p-type

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