

STUDY OF THE CHARGE TRANSPORT IN CONTACTED AND IN INSULATED RUTIL BELOW ROOM TEMPERATURE

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To investigate the charge transport besides the overall (dc) conductivity of contacted crystals σ_{av} thermally stimulated (TS) polarization and depolarization currents of insulated crystals were obtained, a measurement frequently practiced in investigating electrolytic conductors. A detailed analysis of the data reveals that the cause of the TS currents is here a surface polarization (SP) by charge carriers thermally released from scanty occupied traps, what explains, too, how the electron SP responsible for the depolarization current is frozen in by trapping. Published TSC and TL data confirm the existence of these traps. A comparison of the results with σ_{av} then shows that the latter is caused by an enhanced occupancy of the most abundant kind of traps.

1. Introduction

Rutil is from both, the theoretical and practical point of view, an interesting crystal. It is basically an ionic crystal. Because of a high enthalpy of point defect formation and migration (see e.g. [1,2]) by comparison with the band-gap width however it is an electronic conductor [3]. At low temperatures (LT) then it is, what is called a semi-insulator. Finally it shows an unusually high and strongly anisotropic dielectric constant.

The electronic conduction and many other properties of crystals are determined by the band-gap width and by states within the gap. Consequently the most obvious technique of studying this system is a measurement of the conductivity. This requires obtaining the current passing through the crystal at a given field strength inside. The former offers no difficulty. Yet to obtain the latter presents an experimental problem, as, because of space-charge formation and other effects the potential drop between the measuring electrodes is in general nonlinear. Moreover, as far as low temperatures are concerned the special techniques device to establish it are, for many reasons, hardly feasible. Consequently the field strength is then usually calculated from the applied voltage and sample thickness. That way, however, an overall conductivity including the effect of the electrodes on the true inherent conductivity which is sought is obtained.

A simple way how to come round this difficulty is a measurement of insulated crystal as for instance employed investigating the field induced thermally stimulated relaxation (FI-TSR) in electrolytic conductors [4]. In that case displacement currents only obtained which are proportional to the dielectric displacement caused by space-charge formation and decay respectively in the investigated crystal. If then in addition the polarization of the crystal is made thick enough this polarization may be described practically as a simple surface polarization (SP) by free charge carriers [5]. As the conductivity is the only really unknown in the SP equation [6] it can, besides, be obtained from the TSR data [7, 8].

It suggests itself, hence, to consider also in the present case of an electronic conductor a SP measurement. TSR measurements can be realized either as polarization or depolarization current (TSPC, TSDC) measurements. The former are no doubt feasible in the case of a TSD it is, however, to be taken into account that electronic carriers stay mobile at low temperatures (LT) and cannot be frozen in like ionic carriers in a subsequent depolarization. They can be but trapped and so the interpretation of TSDC's presents a still unexplored field.

Consequently great care will be taken to validate the application of the SP model and, further, a confirmation of the results will be sought by comparison with the outcome of other kinds of measurements. Finally the results will be compared with measurements on contacted crystals to obtain information on the effect of the electrode on the conduction.

2. The experiments

2.1 Crystal samples: The investigated TiO_2 (rutile) crystals were grown at the Max Planck Institut Stuttgart, the doped ones with 0.5 mol% of iron oxide added to the melt. All the crystals were annealed in an oxygen atmosphere then and cut parallel (\parallel) and perpendicular (\perp) respectively to the optical axis c into about $L = 0.1$ cm thick slices of cross-section S . These were finally ground plain parallel and polished on the contact surfaces.

To check the built-in of iron, measurements at LNT between 400 and 800 nm of the optical absorption were obtained. The undoped crystal shows below 415 nm the characteristic absorption caused by excitation across the band-gap (3 eV, [3]). The doped one shows in addition a comparatively strong absorption maximum at 500 nm which corresponds with a photocurrent maximum obtained by Mizushima et al. [9] with oxidized iron group doped crystals and is attributed to a dopant-insensitive defect caused by the doping. Finally it shows a weak maximum at 750 nm, where the quoted authors found the absorption threshold of both kinds of crystals.

2.2 FI-TSR measurements of insulated crystals: There exist several reviews [10, 11], which describe techniques of measurement, evaluation and results of TSR processes. As there is described under a variety of names a multitude of more or less different techniques, it appears though inevitable to give here at least a brief description of the actually applied procedures.

Table 1. Representation of the obtained TSR currents by peaks of given $T_{m,x}$, Q/S , U obtained by a fit of eq. (1) and by $\sum Q/S$ which is compared with the value predicted by theory for a SP. 1) peak with shoulder on the LT side (Fig. 2a); 2) local maxima of HT band; 3) area of the current band above 150 K; 4) U of the separated first peak; 5) value only estimated because the peak is extremely flat.

	b	1. peak			2. peak			3. peak			Theory	
		$T_{m,x}$	Q/S $\times 10^{-11}$	U	$T_{m,x}$	Q/S $\times 10^{-11}$	U	$T_{m,x}$	Q/S $\times 10^{-11}$	$\sum Q/S$ $\times 10^{-11}$	$\sum Q/S$ $\times 10^{-11}$	
	K^{-1}	K	Ccm^{-2}	eV	K	Ccm^{-2}	eV	K	Ccm^{-2}	Ccm^{-2}	Ccm^{-2}	
Undoped crystal, $E \parallel c$												
TSP	0.09	110.8 ¹⁾	2.95	0.18	228 ²⁾	2.60 ³⁾	0.35 ⁴⁾			5.55	4.28	
TSD	0.09	113.8	3.02	0.15	260	2.47	0.37			5.49		
TSP	0.09	114.4	3.56	0.16	269	2.01	0.35			5.57		
TSD	0.11	115.7	2.87	0.14	241	2.28	0.35			5.15		
average		114 $\pm 1\%$	3.10 $\pm 5\%$	0.15 $\pm 6\%$		2.34 $\pm 6\%$	0.35 $\pm 2\%$			5.45 $\pm 2\%$	+27%	
Undoped crystal, $E \perp c$												
TSP	0.11	95	0.57		187.5	7.64	0.28	320 ⁵⁾	0.73	8.94	8.49	
TSD	0.09	125	0.16		191.1	6.43	0.32	320	0.80	7.39		
TSP	0.07	95	0.83		183.5	7.48	0.30	320	0.94	9.25		
TSD	0.08	123	0.41		189.9	6.66	0.29	320	0.71	7.78		
average			0.50 $\pm 30\%$		188	7.0	0.30 $\pm 3\%$	320	0.80 $\pm 7\%$	8.34 $\pm 5\%$	-3.4%	
Fe doped crystal, $E \parallel c$												
TSP	0.07	90.5	0.39		181.5	3.50	0.20	280	0.11	4.10	4.28	
TSD	0.09	92.0	0.58		183.9	3.67	0.17	280	0.32	4.57		
TSP	0.09	90.3	0.88		182.1	3.91	0.20	280	0.31	5.10		
TSD	0.09	91.0	0.42		184.5	3.57	0.19	280	0.14	4.13		
average		91 $\pm 0.5\%$	0.57 $\pm 20\%$		183	3.70	0.19 $\pm 3\%$	280	0.22 $\pm 25\%$	4.47 $\pm 5\%$	+4.4%	
Fe doped crystal, $E \perp c$												
TSP	0.09	91.3	0.41		220.5	7.08	0.22			7.49	8.49	
TSD	0.08	92.5	0.58		216.9	7.00	0.22			7.58		
TSP	0.08	90.5	1.16		220.5	7.50	0.22			8.66		
TSD	0.08	93.0	0.32		219.8	7.18	0.22			7.50		
average		92 $\pm 0.6\%$	0.61 $\pm 30\%$		219	7.19	0.22			7.80 $\pm 3\%$	-8.1%	

Table 2. Comparison of the activation enthalpies of σ and the charge densities of the steady state SP caused by the individual kind of carriers with the depth's and densities found by TSC and TL measurements [16]. 1) The accumulated charge is estimated as if this was a SP peak. 2) Range of values published; 3) Deep reaching space-charge is formed ([3], Fig. 1) and the charge cannot be established.

crystal	TSRC, crystal insulated				TSC and TL		
	T_{mx} K	U eV	$w(\text{co})/e$ cm^{-2}	T_{mx} K	U_T eV	n_T cm^{-3}	
undoped	$E c$	$0.15 \pm 6\%$	3.0×10^9	103	0.13 ($0.13-0.18$) ²⁾	2×10^{13}	
	$E \perp c$	$0.35 \pm 2\%$	1.2×10^9	176	0.37 ($0.21-0.56$)	1×10^{14}	
	$E c$	-	1.2×10^9				
Fe, doped	$E \perp c$	$0.30 \pm 3\%$	5.3×10^9	120	0.24 ($0.14-0.2$)	4×10^{13}	
	$E c$	$0.19 \pm 4\%$	5.3×10^9				
TSRC, undoped crystal, contacted	$E \perp c$	$0.22 \pm 0\%$	5.3×10^9	243	0.51	2×10^{16}	
	$E c$	0.53	- ³⁾	294	0.61	2×10^{16}	
TSRC, undoped crystal, contacted	$E c$	-	-	326	0.69	3×10^{16}	

Table 3. Comparison of a) σ_0 established from T_{mx} and U obtained by fitting the peak and from the initial rise, i.e. $T < T_{mx}$, b) of σ and σ_{av} at T_{mx} 1) σ_0 (Ωcm^{-1}); 2) Because of the distortion of the peak $\sigma(T_{mx})$ is extrapolated from the initial rise.

crystal	E	T_{mx}	U	$\sigma_0, T < T_{mx}$		$\sigma(T_{mx})$		T_k	$\sigma_{av}(T_{mx})$
				σ_0	$\sigma(T_{mx})$	$\sigma(T_{mx})$	$\sigma(T_{mx})$		
undoped	$E c$	114 (2)	0.15	3.5×10^{-8}	4.6×10^{-8}	1.0×10^{-14}	182	6.0×10^{-16}	
	$E \perp c$	240	0.35	2.6×10^{-6}	2.7×10^{-7}	1.1×10^{-13}	182	7.8×10^{-13}	
Fe	$E c$	188	0.30	9.4×10^{-6}	2.3×10^{-5}	7.5×10^{-14}	134	8.3×10^{-13}	
	$E \perp c$	219	0.22	1.8×10^{-8}	2.4×10^{-8}	9.9×10^{-14}	170	7.7×10^{-15}	
doped	$E c$	219	0.22	4.7×10^{-9}	1.0×10^{-7}	4.0×10^{-14}	175	1.1×10^{-13}	

The present measurements were carried out as a sequence of consecutive thermally stimulated polarization and depolarizations. That is, first the polarization current was caused by the applied voltage ($V = 100\text{V}$) during a temperature increasing linearly with time t , $T = T_0 + bt$ ($b > 0$, $T_0 \approx 80\text{K}$), was obtained. As soon as T reached about 500 K the sample was quickly cooled down to T_0 again and shorted. Next, during a heating procedure as before was obtained and the sample cooled down again. Finally the complete cycle was repeated a second time. The heating rate b (cf. Tab. 1) was held low enough to guarantee a quasi equilibrium concentration of carriers in the bulk. On the other side however b had to be as high as possible because with increasing b the height of the peaks is decreased and the width enlarged, making the analysis increasingly more difficult.

To realize the basic condition presupposed by the SP-model (see [5]) the crystal samples were insulated by 470 μm thick sapphire disks. These, for themselves, show up 500 K with 100 V on a "leakage current" of about 10^{-14} A, without any sign of relaxation, i.e. polarization. Electrodes and insulation were also ground plane parallel and polished to form with the crystal a close fitting sandwich. The complete sandwich

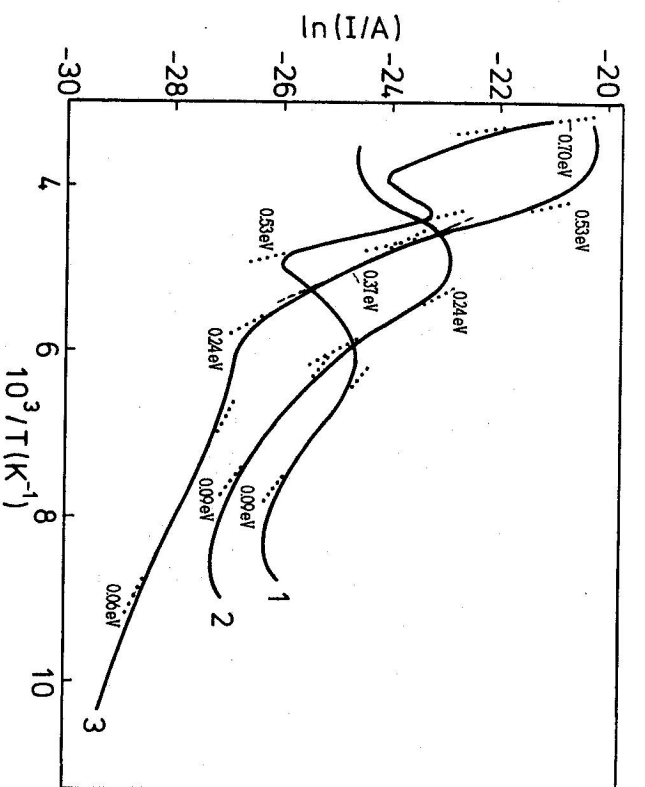


Fig. 1. Subsequent TSPC (1) and TSDC (2) compared with the quasi-stationary FI-current (3) following a polarization represented as $\ln \sigma$ vs. $10^3/T$.

placed in the measuring cell showed under 100 V at T_0 a background current of the order of a few 10^{-15} A only; hence the samples may be, no doubt, considered as nearly ideally insulated. They were held before measurement overnight shorted at 500 K in a vacuum of about 10^{-4} torr to remove moisture, adsorbed gases and any accidentally formed polarization. When commencing then the TSR measurement proper by cooling down the samples to T_0 , the electrodes were connected directly to the measuring device to check that no spontaneous current exceeding the offset current of the instrument flows, a corroboration that the initial polarization is really zero.

2.3 FI - current measurements of contacted crystals: Samples were provided on the contact surfaces with colloidal graphite and to establish the conductivity of the samples, I in dependence on the temperature T at a given field strength $E = V/L$ was obtained. The measurements were established because of practical reasons under quasi steady conditions during a decreasing T . As this decrease was realized by means of a combination of thermal conduction and convection the cooling rate $b = dT/dt$ was increasingly slowing down at lower temperatures. Generally any change of T requires a certain time before a steady current is obtained and $I(T)$ is consequently a function of b , too. With b lower than a certain critical value in the beginning of the cooling, however, a reproducible fixed $I(T)$ could be obtained, so to say a $\lim I(T; b)$, $b \rightarrow 0$.

2.4 FI - TSR measurements of contacted crystals: Measurements of a contacted undoped sample with the field $E||c$ were carried out under the same temperature and voltage regime as described in par. 2.2 and for the purpose of comparison in addition

at any temperature. If they are not any more retained by the field at the electrode after shorting the sandwich before the TSD, they should, necessarily, recombine. They are however some situations which allow yet the surface charge to remain in place. Once, if the conduction is of the hopping type, like in the case of polaron forming, which is known to occur in rutil. As the activation energy of polarons is comparatively low, this could however come true at best in the case of the 0.13 eV peak. Then, carriers could be trapped near the surfaces to form a kind of electret. If this is the case a concentration of traps considerably higher than $1/eL$ times the density of the steady state SP, $w(\infty)/eL$, would be required in the first place. Further the activation enthalpy of the traps U_{tr} must not be noticeably lower than U of the concerned peak. Otherwise the polarization would decay before the inherent conduction sets in and the mirror image thermogram could form. If U_{tr} happened to be higher than U , during the TSD the surface charge would be in due time compensated by inherent carriers first, to vanish then at some higher temperature unnoticed by recombination. Further the concentration in the bulk of carriers with an activation enthalpy U must not be noticeably lessened by the polarization if a mirror image TSDC is to emerge etc.

Some authors, e.g. [9] and [14] suggest there exist in rutil also surface states which make themselves felt as traps. These however cannot provide a $\sigma(T) = \sigma_0 \exp(-U/kT)$ prerequisite of the formation of the observed peaks. First σ_0 cannot remain constant, it is to decay more or less quickly. Second the released electrons with their life time of 10^{-8} s and mobility of about $1 \text{ cm}^2/\text{Vs}$ [3] would be necessarily trapped near the surface by the traps existing in the bulk.

5. Comparison of the data with the SP model, obtaining peak parameters and σ

5.1 The SP equation [6]. The formation and decay respectively of a SP caused by the inherent, i.e. the bulk conductivity σ of the crystal and constant voltages V and $V = 0$ resp. become manifest by a displacement current density $j(t) = I/S$ caused by accumulation and drain respectively of a charge density w_{el} on the electrodes. And this again is caused by an accumulation and drain resp. of a charge carrier density n in the crystal surfaces. $j(t) = dw_{el}/dt$ is equal to $K dw/dt$, where K is determined by the parameters of the dielectric sandwich and

$$dw(t)/dt = \tau^{-1} [w_{\infty} - w(t)], \quad T = f(t)$$

τ is the limit of w for $t \rightarrow \infty$ and τ is the relaxation time of the process. To obtain closed solution of eq. (1) T is made as mentioned in par. 2.2 proportional to t . To obtain a numerical solution this is however not stringent.

In agreement with the conditions of the experiments further $w(0) = 0$ for TSP and $w(\infty) = w(\infty)$ for a TSD have to be taken. If at $t = 0$ the voltage V is switched (TSP), due to the instantaneous polarization of the sandwich a charge $w_{el}(0) = \epsilon_1 V / (2\delta\epsilon + L\epsilon_1)$ appears at the measuring electrodes, whereas $w(0)$ remains zero. ϵ_1 and $\epsilon = \epsilon_1 / \epsilon_2$ are the dielectric constants of the vacuum, the insulation and the crystal, δ the thickness of the insulation. As, finally, at $t \rightarrow \infty$ E in the crystal becomes

so that dw/dt becomes zero too, $w_{el}(\infty) = w(\infty) = \epsilon_1 \epsilon_0 V / 2\delta$, because always $E_{2\delta} + EL = V$. E_i is the field strength in the insulation. From this follows that the theoretical SP peak area is

$$(Q/S)_{th} = \int_0^{\infty} j(t) dt = w_{el}(\infty) - w_{el}(0) = \left[\frac{\epsilon_0 \epsilon_1}{2\delta} - \frac{\epsilon_0 \epsilon_1 \epsilon}{(2\delta\epsilon + L\epsilon)} \right] V \quad (2a)$$

The theoretical peak area is at the same time the total peak area $\Sigma(O/S)$ because even if there existed several kinds of carriers or peaks due to other (homogeneous) polarization processes so that more than one peak would be obtained the sum of their areas must conform to eq. (2a). Hence, if there takes place besides the SP a dipole polarization with a polarizability P_i/E , built up before charge carrier get mobile, the actually obtained SP peak area will then be only

$$(Q/S)_{SP} = (Q/S)_{th} - (P_i) \quad (2b)$$

As all the parameters of eq. (2a) are known, in principle the total peak area presents a decisive proof for the occurrence of SP.

The individual characteristics of the SP peaks like activation enthalpy of the initial rise U , T_{mx} , a first order kinetics shape characterized by U too are determined by the relaxation time

$$\tau^{-1}(T) = [2\delta / (2\delta\epsilon + L\epsilon_1)] [\sigma(T) / \epsilon_0] \quad (1a)$$

Hence the obtained U is the activation enthalpy of σ [15] and as $\sigma(T)$ is the only really unknown in eq. (1) - all the other parameters are either given beforehand or are easily established - it can be obtained in the range of the SP peak from its data [7,8].

5.2 Examination of the total peak areas: In Tab. 1 the experimentally obtained $\Sigma(Q/S)$ are compared with the theoretically expected values. With exception of the peaks of Fig. 2a there is a reasonably good agreement between both kinds of values, well within the limits in general experienced in TSRC measurements obtained before with the same equipment and technique of measurement. It is to be noticed that the theoretical total peak areas too comprise experimental data, because of the limited accuracy of the dielectric constants and the dimensions of the materials of the sandwich, which define $(Q/S)_{th}$. Hence the deviation of the average of the experimental data from theory by +27, -3.4, +4.4 and -8.1% include also this kind of error. In the case of the undoped crystal, $E_{||c}$, where the difference is too high for random errors most probably the background current is in reality higher than assumed and that adds up for three smaller peaks. Also the individual total peak areas obtained in the TSP measurements, are somewhat higher on the average than that obtained in TSD's. This too suggests that the correction for the background current is too small here. Only no hold is seen at the moment to amend this.

It is to be noticed that the pointed out agreement between data and theory reflects also the anisotropy of rutil ($\epsilon_{||} = 180$ and $\epsilon_{\perp} = 86$) and, that in the case of the undoped crystal, $E_{||c}$, where a complete part of the TSP-band is missing in the TSD thermogram (see Fig. 2a, $T = 140$ to 210 K), $\Sigma(Q/S)$ is the same for TSP and TSD. Finally it follows that the crystals are below the (first) SP-peaks complete insulators. This, again, speaks

in favour of the dipolar origin of the small LT peaks and, more important, the notion that the initial current pulses are caused by the instantaneous polarization of the dielectrics.

Even if it is thus corroborated that the thermograms are caused by a SP necessary to explain still the other features of the thermograms from the SP. This shall be done in the next paragraphs.

5.3 Shape and activation enthalpy of singular peaks: "Normally" like in the ionic conductors [6, 7, 8] in TSR measurements one single SP peak is obtained obeys eq. (2a,b) and shows a first order kinetics shape according eq. (1) which is given by σ_{o1} , U_1 , σ_{o2} and U_2 . Assumed that the conductivity σ is given by σ_{o1} , σ_{o2} and U_2 . If the ratio $\sigma_{o1} : \sigma_{o2}$ is large enough for a given U_1 and U_2 one singular normal, i.e. regular first order kinetics peak according eq. (1) can be obtained (see Fig. 2b), because a full polarization is reached before the second component can make itself felt. With a decreasing ratio or an increased b a shoulder however due to appear at the HT-side of the otherwise regular U_1 peak because the carriers become mobile before a full polarization is reached. With a further decrease the said ratio finally a more or less regular U_2 peak will be obtained with a shoulder [5] or only a knee at the LT-side, below which the obtained $j(T)$ shows an activation enthalpy equal to U_1 . And in fact if the peak of the doped crystal, E_{1c} , is plotted in $1/T$ vs. $1/T$ a distinct knee at the LT-side, at about 180 K is found, with a slope about 0.1 eV at lower temperatures. U of the peak above the knee is found again Tab.1.

5.4 Appearance of several under-size SP peaks, their areas, activation enthalpy and shapes: In the generally accepted notion of the SP it is tacitly assumed that the concentration of mobile carriers in the bulk of the crystal is not affected by accumulation of carriers at the surface. This is, as far as electrolytic conductors are concerned no doubt correct, as in consequence of the low mobility of the point defects necessarily their concentration must be high if a TSRC is to be observed at all. In the case a SP is caused by electronic carriers with a high enough mobility this assumption need not to come true and a too low concentration of available carriers can give rise to a thermogram consisting of several under-size SP peaks; under-size with respect to a thermogram consisting of several under-size SP peaks; under-size with respect to eqs. (2a,b). Under these circumstances of course the charge transport constitutive and provided with Ohmic electrodes it would become at some temperature constant. It is however not primarily the low concentration of carriers available to accumulate on the surfaces which causes the effect. As emphasized before, the notion of a surface charge is but an approximation, which under suitable conditions complies with the experimental findings. This requires besides a nearly ideal insulation that the potential ΔV across the in reality occurring space-charge is negligible in comparison with the applied voltage. Otherwise is

$$(Q/S)_{in} = (\epsilon_0 \epsilon / 2d) [(V - \Delta V) - w_{el}(0)] \quad (2c)$$

whereas eq. (2a) precludes that ΔV is practically zero. Now with a decreasing concentration of available carriers n_0 the depletion zone of the space-charge $w_{el}(x) = x - \pi_0 < 0$ is necessarily widening and ΔV will accordingly increase so that in

more or less wide part of the crystal an $E = 0$ will exist. If there exists a second set of carriers which become mobile at some higher temperature a second under-size peak will then appear, overlapping the first or after some gap, so that in the end (Q/S) according eq. (2a) will be compiled with. At the same time then E becomes throughout the whole crystal and at the beginning of the TSD except the reversed direction the initial conditions of the preceding TSP are realized.

These deliberations show that the chaotic looking thermogram of the undoped crystal, E_{1c} , (Fig. 2a) may be explained by a too low concentration of carriers. It shows a $\sigma \sim 0.11$ eV first order peak of about half the theoretical area, which is too small being E down to zero. It is followed in a TSD by a gap from about 130 to 210 K where $j = 0$. This can be explained but by a complete lack of free carriers. In the TSP there is a weak band obtained instead of $j = 0$, what is however of no importance in this connection. It is caused probably by an occupation over a barrier of some surface states at the anode, the depletion of which in the TSD is concealed below an other band. All the same $\sum(Q/S)$ complies also in the TSP with the theoretical value.

This is however not the only "case" of an undersized SP peak. As may be seen in Tab.1 the 0.30 eV peak of the undoped crystal, E_{1c} , and the 0.19 eV peak of the doped crystal, E_{1c} too, are followed at different temperatures by small peaks. An addition of the areas of the LT and the 0.30 and 0.19 eV respectively shows that these cannot put E completely to zero. This suggests that the small third peaks are caused by some carriers with a higher U and that only these make finally the SP charge density equal to $w(\infty)$. It is conjectured that in these instances because of a low n_0 of the 0.30 and 0.19 eV carriers the width of the depletion zone just begins to cause a noticeable ΔV .

If the concentration of carriers is too low, not only the peak area is affected, but also the shape of the peak. Eq. (1) includes the assumption that E is constant throughout the whole crystal. In the discussed situation however it is not. Besides the complications caused by an $E = f(x)$ the concentration of carriers in the transport bands will fall increasingly behind $\exp(-U/kT)$ of a normal $\sigma(T)$. The peak should rise, it is true, in the beginning with the genuine U of the carriers, but fall then gradually back behind the proportions of a hypothetical regular peak. Finally it might end with a lengthy tail like it is seen in Fig. 2a. In this case moreover the initial rise of the first undersized peak is overlapped by the, if small, real first LT peak. It can therefore be hardly exactly established. One can be sure yet that the sought for U is smaller than the 0.18 eV of the initial rise of the measured I and higher than the $U = 0.11$ eV of the first order fit of the separated undersized peak, say 0.13 eV.

As far as the second and third under-size peaks, Fig. 2a, are concerned they too could be separated into two first order peaks the first with U near to 0.35 eV. This value of course is somewhat uncertain. Assuming U does not depend on the crystallographic orientation one would expect to obtain in both directions the same value. Because further, as elaborated above, the 0.30 and 0.19 eV peaks are somewhat undersized their U will be, like in the case of the 0.11 eV peak a bit too small and so 0.35 and 0.22 eV are considered more correct. These deliberations show that the peak areas are obviously more indicative than the first order kinetics fit, which can because of the background

current not be made accurate enough.

5.5 Obtaining the bulk conductivity from the TSR data. As pointed out already in par. 5.1 the only unknown in the SP equation, eq. (1), is the bulk conductivity $\sigma(T)$. Consequently, in principle, inserting into the suitably rearranged equation $w(t)$ and $w(\infty)$ the respective integrals of $j(t)$ and for dw/dt too, it is possible to calculate straightforward $\sigma = f(T)$ from the data

$$\sigma(T) = K \epsilon_0 j(t) [(Q/S)SP - SP] \int j(t') dt' T^{-1}, \quad T = f(t)$$

Eq. (3) applies even when $\sigma(T)$ is caused by more than one single kind of carrier. In that case then the $\ln \sigma$ vs. $1/T$ does not form a straight line any more and individual components have to be established by regression. That way the $\sigma(T)$ component overlapping the 0.22 eV peak of the doped crystal, $E||c$, was separated.

When calculating $\sigma(T)$ from eq. (3) the LT peak should be taken into account. The data of this peak however are not good enough for this purpose eq. (3) was used only to calculate σ_0 from the initial rise of the peak (Tab. 3), where E was diminished only by the dipole polarization. That way of course only rough estimates are obtained because of the limited accuracy of the subtraction of the non-relaxational component from the data. As far as T_{mx} is concerned it is falsified only little by the background current, use was made of the SP maximum condition from [6]. Provided the SP peak obeys satisfactorily first order kinetics, U and T_{mx} may be obtained by fitting the data and $\sigma(T_{mx})$ from

$$T_{mx}^2 = (bU/k)\sigma(T_{mx}) = (bU/k)[(2\delta)/(2\delta + L\epsilon_1)][\epsilon_0/\sigma(T_{mx})],$$

independently of the appearance of a dipolar polarization. From $\sigma(T_{mx}; U)$ then a more accurate σ_0 were obtained (Tab. 3). A comparison of both kinds of σ_0 shows that the values are varying in some cases more or less in random, in general however the initial rise values are the higher ones, a sign that that $j(T)$ could not be cleansed completely from non-relaxational components. On the whole however the comparison confirms the rightness of the applied procedures.

6. Discussion of the results and conclusions

6.1 Comparison with data from TSD and TL measurements [16]: Starting with the question of the suggested existence of traps which make the freezing in of the SP possible, in Tab. 2 the obtained activation enthalpies, U , are compared with critical data on trap depth's U_r obtained by TSC measurements of crystals excited by critical light and by TL measurements. The investigated crystals were grown in an argon-oxygen atmosphere and showed a contamination of 0.1 to 0.9 at. ppm. of Cr^{3+} and 6 to 27 at. ppm. of iron. They come thus to lie somewhere between the undoped and the iron doped crystals of the present investigation. It is obvious that the activation enthalpies of the TSR peaks answer within error limits that of the lowest four observed traps. This suggests that the obtained crystal inherent σ is borne by carriers thermally released from these traps. It is important to stress that the agreement of the activation

enthalpies is past a mere coincidence and suggests hence, that traps play here the role of a kind of donors.

It is to be noticed that the concentration of traps established by the quoted measurements appears high enough to accommodate the space-charge, the approximation of which the SP charge is: Thus, for instance, the singular 0.22 eV SP peak is formed by about $5.3 \times 10^{19} \text{cm}^{-2}$ charge carriers compared with a trap density of 4×10^{13} to $1 \times 10^{15} \text{cm}^{-3}$ established for this kind of trap. In contrast with this the 0.13 eV under-lying peak consists of about $3 \times 10^{19} \text{cm}^{-2}$ compared with the respective trap density of $2 \times 10^{13} \text{cm}^{-3}$ only. On the other hand the comparison of trap densities and SP charge densities shows that it is at all likelihood the low occupancy of the traps by carriers which makes under-size SP peaks appear, prominently in the case of the most shallow trap.

The fact requires still explanation, why in the TSR of undoped crystals appear only the 0.13 and 0.35 eV traps, whereas in the doped crystals only the 0.22 eV trap is found. In the TSC and TL appear all three together. An explanation gives, it is conjectured, eq. (1), which shows that the peak positions are shifted to higher temperatures if σ is decreased and vice versa. In the undoped crystal the about 10^3 times higher density and greater depth of the 0.37 eV traps are likely to bring forth a considerably higher conductivity than the 0.22 eV traps. Hence no 0.22 eV peak is observed. The decrease of the 0.35 eV conduction in the doped crystals reported in par. 3.1 is to shift the respective peak towards higher temperatures. But simultaneously the 0.22 eV component, for which no clear evidence was found in undoped crystals, has to appear and to polarize the crystal before the 0.37 eV carriers become mobile. Assumed a certain fraction of the anion vacancies created by doping form a complex with the Fe^{3+} ions, a phenomenon familiar in ionic crystals, with a trapping level of 0.22 eV. Then by doping the concentration of these complexes and that of 0.22 eV carriers would indeed be increased.

As far as the 0.13 eV peak of the undoped crystal, $E||c$, is concerned: At LT σ_{av} becomes with $E||c$ smaller and accordingly a tiny second LT peak shifted to 125 K appears (Fig. 2b). By doping σ_{av} becomes still smaller and only a respective knee in the initial rise or no sign of a 0.13 eV peak is obtained.

6.2 Comparison with the overall conductivity and the TSR par. 3.2: From the theoretical point of view it is expected that generally $\sigma_{av} < \sigma$ and in the case of the electrolytic conductor NaCl [8] for instance indeed a good agreement was found between the conduction through a graphite coated crystal, the bulk conductivity σ obtained from TSR data and the potential drop caused by space-charge formation. (On the other side it is just the high field strength caused by the latter at the surfaces, which procures the transfer of charge carriers to and from the inert electrodes.) The comparison of $\sigma(T_{mx})$ with $\sigma_{av}(T_{mx})$ (Tab. 3) reveals however that in the present case the effect of the electrodes is not as simple as that.

As reported in par. 3.1 $\ln \sigma_{av}$ vs. $1/T$ shows two straight sections. Above the knee they form at $T_k U$ was always around 0.35 eV, below around 0.07 eV. In the insulated undoped crystal, irrespective of the direction of E , the TSR reveals above T_k a σ with about the same U (0.30 and 0.35 eV), but σ itself is substantially lower than σ_{av} .

This suggests an increase of the carrier concentration by the electrodes on the top of the current. Also in the insulated doped crystal with E_{1c} the TSR shows that $T_0 \sigma_{av} > \sigma$, but U is 0.22 eV. Possibly the concentration of 0.35 eV carriers is probably is the cause of the small peak at 320 K (Tab. 1), was exceeding σ_{av} so that only a smooth knee in σ_{av} reminds of the 0.22 eV component. But σ_{av} 0.22 eV component was simultaneously diminished. The fact that with E_{1c} 0.35 eV component in favour of such a decrease of the 0.19 eV component besides an increase of 0.35 eV component which could not have been that extensive. Otherwise σ_{av} would be lower than σ .

All these findings seem to point to a reshuffle of the trap occupancy and the explanation is lastly supported also by the occurrence of the conductivity hysteresis (3.2). This too requires a redistribution of the occupancy of the traps etc. It cannot be caused by an overall increase of the carrier concentration due to electron injection this would violate the neutrality of the crystal.

At the moment one can but speculate that probably some of the injected electrons which due to their short life time should permanently drop out of the conduction band are caught by the traps in question instead of recombining for instance.

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