

and lower temperatures under [110] stress and of examining the dependence of peak height upon controlled and well characterized reduction. The present data, while not sufficient for unique identification of defects causing various peaks, do strongly suggest that the motion of interstitial cations is involved and that some combination of defects occurs upon reduction of Cr- or Ni-doped rutile.

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Ionic Thermocurrents in Dielectrics*†

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The ionic thermoconductivity (ITC) method, consisting of the study of the thermally activated release of dielectric polarization, is studied in great detail in alkali halide crystals. The (divalent metal ion, cation vacancy) dipoles give rise to an ITC band below 0°C, whose area is proportional to the polarizing field. The activation energy for dipole orientation can be obtained with an accuracy of 0.1%, when there are no overlapping bands. It is shown that the sensitivity of the ITC in detecting small contributions to the polarization (down to 2×10^{16} dipoles per cm^3) or in separating overlapping relaxation processes is greater than that of methods presently employed. The solubility of the impurities can be studied by measuring the ITC of samples subjected to annealing at a fixed temperature. Intense ITC bands appearing in KCl between 280 and 430°K are probably due to contact effects. Measurements on other substances such as quartz, calcite, and Teflon show that by means of a single ITC measurement one obtains a complete qualitative picture of the polarization in a dielectric.

1. INTRODUCTION

THE dielectric relaxations in solid materials are detected in general by means of dielectric-loss measurements: alternating electric fields with frequencies ranging from 10^{-1} to 10^{12} cps have been employed on different types of solids in a very broad range of temperatures.¹ In the case of the dipolar relaxation the maximum of the dielectric loss occurs at the resonance frequency ω_0 , inversely proportional to the relaxation time of the dipole at the temperature of the measurements [$\tau(T) = \tau_0 \exp\{E/kT\}$]. By measuring the τ at different temperatures one obtains the characteristic parameters of the dipoles, i.e., τ_0 and E .

In some cases, when the relaxation time of the dipoles is of the order of a few seconds, their relaxation can be studied by measuring the charging and discharging current of the dielectric in a constant electric field, at

constant temperature.² When a static field \mathcal{E}_p is suddenly applied to the dielectric, the kinetics of orientation of the dipoles are of the first order, provided one can neglect their mutual interactions. In this case too, the parameters τ_0 and E can be obtained from a series of isothermal measurements.

Recently a new method has been proposed (ionic thermo-currents: ITC) which gives a complete picture of the temperature-dependent relaxations and allows the parameters τ_0 and E to be obtained by means of a single measurement.³ The purpose of this paper is to explain in detail the method and to show how it works when applied to the case of alkali halides. The effect of thermal treatments and the ITC of other dielectrics will also be considered.

Let us consider for the moment an ideal dielectric, containing only one type of noninteracting dipoles of moment p and relaxation time τ (Fig. 1): (1) In the absence of an electric field the dipoles are oriented randomly. (2) If one applies an electric field \mathcal{E}_p at the temperature T_p for an interval of time $t_p \gg \tau(T_p)$, the dipoles will be polarized at saturation and in the meantime an exponential current decay will be observed.

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¹ R. F. Meakins, in *Progress in Dielectrics*, edited by J. B. Birks (John Wiley & Sons, Inc., New York, 1961), Vol. 3.

² R. W. Dreyfus, *Phys. Rev.* **121**, 1675 (1961).

³ C. Bucci and R. Fieschi, *Phys. Rev. Letters* **12**, 16 (1964).

(3) At this point the dielectric is cooled down to such a low temperature (T_0) that the relaxation time $\tau(T_0)$ is of the order of several hours or longer. (4) At $T=T_0$ the electric field \mathcal{E}_p is turned off and the condenser containing the dielectric is directly connected to the input of the current detector. While the electronic and atomic polarization relax, the dipoles remain oriented in the same configuration obtained at T_p .⁴ Then the dielectric is warmed up with a constant rate $b=dT/dt$: the relaxation time gets shorter and shorter and a depolarization current $i(T)$ will be detected as the dipoles lose their preferred orientation; during the time this process occurs, the current will first increase exponentially, reach a maximum and then drop to zero; we call this current ionic thermo-current (ITC). The function $i(T)$ is the same as the one describing the thermoluminescence with a monomolecular kinetic:

$$i(T) = N_{\text{dip}} \frac{p^2 \alpha \mathcal{E}_p}{kT_p} \left[\tau_0 \exp\left\{\frac{E}{kT}\right\} \right]^{-1} \times \exp\left(-\int_0^T \left[b\tau_0 \exp\left\{\frac{E}{kT'}\right\} \right]^{-1} dT'\right), \quad (1)$$

where α is a geometrical factor depending on the possible dipolar orientation (for free rotating dipoles $\alpha = \frac{1}{3}$).

Let us summarize briefly the features of this function:

(1) It is represented by an asymmetric band with a maximum at a temperature

$$T_M = \{bE\tau(T_M)/k\}^{1/2}, \quad (2)$$

independent of T_p and \mathcal{E}_p ; (2) its low-temperature tail is such that

$$\ln i(T) = \text{const} - E/kT; \quad (3)$$

(3) the area delimited by the band is proportional to the initial dipolar moment per unit volume⁵; the polarization induced at saturation is

$$\mathcal{P} = N_{\text{dip}} \frac{\alpha p^2 \mathcal{E}_p}{kT_p} = \int_0^\infty \sigma(t) dt. \quad (4)$$

One obtains easily E from relation (3) and then τ_0 from relation (2). It is noteworthy that the evaluation of τ_0 from $\tan \delta$ and current decay measurements is always achieved with difficulty and lack of accuracy. Equation (4) allows the evaluation of the number of dipoles contained in the dielectric; consequently any change in it due to thermal, mechanical, and optical treatments can be easily measured.

⁴ More precisely, since the cooling rate is not instantaneous, the real temperature of polarization is lower than T_p (the slower the cooling rate, the lower it is): in the present conditions the effective T_p corresponds to a relaxation time of ~ 1 sec.

⁵ The study of the area delimited by the depolarization current, with the purpose of obtaining information about the dipolar moment of electrets, has been previously undertaken by B. Gross and S. F. Danard, Phys. Rev. 67, 253 (1945).

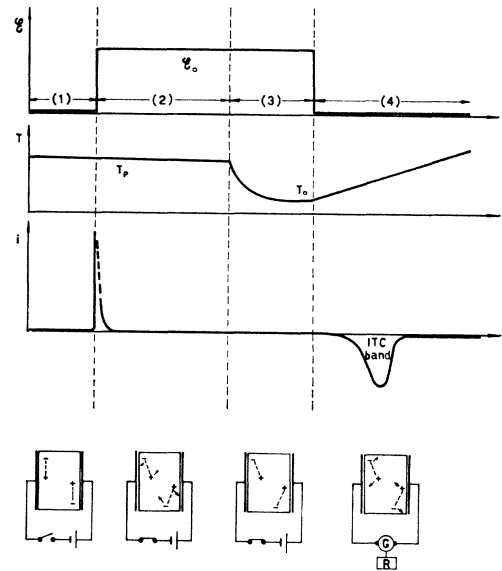


FIG. 1. The process of ionic thermoconductivity. (a) External electric field, temperature of the sample and electric current are plotted schematically as a function of time: (1) temperature T_p : the electric field is zero and the dipoles of the sample are at random; (2) the field is on and the dipoles are partially oriented; (3) the temperature is lowered to T_0 , where the rotation of dipoles is hindered; (4) field off; by slowly heating the sample, one obtains the ITC discharge bands and the dipoles again reach a random orientation. (b) Scheme of the dipole motion in the sample, corresponding to the physical situation described in (a).

A peculiar feature of curve (1) is that the activation energy E can be measured not only from the tail of the band but also by utilizing the whole curve $i(T)$. In fact the following relation holds:

$$\ln \tau(T) = \ln \tau_0 + \frac{E}{kT} = \ln \left[\int_{i(T)}^\infty i(t') dt' \right] - \ln i(T). \quad (5)$$

The integral in (5) can be estimated with fairly good accuracy by graphical integration of curve (1): by plotting in τ as a function of $1/kT$ one obtains a straight line. The slope and the intercept of this line gives the values of E and $\ln \tau_0$, respectively. Notice that (5) does not depend on the heating rate.

Let us now discuss briefly the properties of the ITC for crystals where complex relaxations are present:

(a) *Many overlapping bands.* In several cases, two or more kinds of dipoles originate partially overlapping ITC bands. Suppose we have, for example, two bands 1 and 2; let T_{M1} and T_{M2} ($T_{M1} < T_{M2}$) be the temperature of their maxima, close enough to each other to give a superposition. In order to obtain a separation of the two bands the following procedure can be pursued: by polarizing the dielectric at T_p such that $T_{M1} < T_p < T_{M2}$ for an interval of time $t_p \sim \tau_1(T_p) \ll \tau_2(T_p)$, the dipoles of the kind 1 will be polarized at saturation, while the dipoles of the kind 2 remain practically distributed at random. The ITC curve will then show only band 1

(eventually a very small band 2 is present). In order to obtain band 2 only, one should simply polarize both bands to saturation, and follow the usual cycle to obtain the ITC; but, instead of recording the whole discharge at one time, one should first discharge the lower temperature band, then cool again the sample and finally obtain the discharge of band 2, pure or nearly pure. Similar procedures have been followed in the attempt to study the components of even more complex bands (see Fig. 9).

(b) *Release of space charge.* The theory of space-charge polarization has been recently developed by MacDonald.⁶ The equation describing the build-up or the release of space-charge cannot be integrated exactly. When an ionic space charge builds up during the polarization of the dielectric, there will be a band in the ITC spectrum, representing its thermal release, which has the following properties: (1) The temperature of its maximum T_M is not well defined; the higher T_p is the higher T_M will be; (2) the area delimited by the band is not a linear function of the applied electric field, particularly at low fields; (3) the shape of the band does not allow the measurement of any activation energy.

2. EXPERIMENTAL

The apparatus for the ITC measurements presented here includes a vibrating grid electrometer (Electronic Instruments Ltd.) model 33C with input resistance larger than $10^{17} \Omega$, a two-pen recorder with a time constant of 0.5 sec, and a sample container with which measurements can be performed in vacuum or in controlled atmosphere in the range of temperatures between liquid-nitrogen temperature and 500°C . In the container the insulation between the electrodes is accomplished by means of Teflon located far from the region where the changes in temperature occur, in order to avoid spurious currents due to the insulating material. The insulation resistance must be very high in order to detect currents as low as 10^{-16} A. The sample is short-circuited with a precision resistance (R_n) [a common value of it is $10^{12} \Omega$], and the current originating during the ITC measurement gives rise to a difference of potential across R_n [usually between 10^{-4} and 1 V] which is detected by means of the electrometer. The total capacity of the circuit is about 30 pF and consequently the response time, RC , is always smaller than 10 sec. The precision in the measurements is of the order of 1% for currents of $\sim 10^{-15}$ A (it will be as low as 0.3% for currents of $\sim 10^{-12}$ A). The variation with time of the current during an ITC measurement is always so slow that the precision of the reading is not affected even by a time constant of 10 sec. The reproducibility of the measurements on different samples of the same single crystal depends not only upon the homogeneity of the crystal (from the viewpoint of the

impurities), but also upon the type of contact between the sample and the electrodes. Several measurements carried out on adjacent samples showed a reproducibility of $\sim 4\%$, provided the surfaces of the sample in contact with the electrodes are painted with colloidal graphite: in the absence of this conductive layer the reproducibility is slightly worse. However, if the measurements are performed on the same sample, the reproducibility is of $\sim 2\%$. It is important to notice that these errors arise mainly from a translation of the scale of the current and therefore they do not affect the values of E and τ_0 .

The temperature is measured by means of a thermocouple located on one of the electrodes. In order to maintain a good electrical insulation between the electrodes, it is not convenient to have a thermocouple on each electrode. The heating of the sample, during the ITC measurement, is performed in inert atmosphere [dry nitrogen at ~ 10 mm Hg]; the atmosphere is kept dry by means of a liquid-air trap. The warming rate can be chosen in a very broad range, according to the type of measurement; it has been established, however, that warming rates larger than $0.3^\circ\text{K sec}^{-1}$ do not ascertain a uniform temperature inside the sample: temperature gradients in it, of course, give rise to misleading results. A very convenient warming rate is about $0.1^\circ\text{K sec}^{-1}$.

3. ITC IN THE ALKALI HALIDES

A. Reliability of the ITC Method

In order to know whether the ITC method is reliable and what are its limits, it is necessary to apply it to a dielectric containing permanent dielectric dipoles whose relaxation is already known. The alkali halide crystals containing metallic divalent impurities are very suitable for this purpose; for a systematic analysis we have chosen KCl crystals containing Sr Cl₂. It is known that a fraction of the divalent Sr ions diluted in the KCl crystal are associated with positive ion vacancies: the complex impurity vacancy has an electric dipole moment and we will refer to them as to the IV dipoles⁷; the evidence for the existence of these complexes comes from dielectric-loss measurements⁸ from current decay at constant temperatures,² from electron paramagnetic resonance (EPR) measurements,⁹ and finally from internal friction measurements.¹⁰ At $T < 0^\circ\text{C}$ the number of I.V. dipoles is very close to the number of impurities introduced in the crystal. By extrapolating the data of Dryden and Meakins,¹¹ one notices that the relaxation time of the I.V. dipoles at 0°C is still less than 10^{-2} sec; this fact allows us to predict the temperature range in

⁷ A. B. Lidiard, in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1957), Vol. XX, p. 288.

⁸ Y. Haven, *J. Chem. Phys.* **21**, 171 (1953).

⁹ G. P. Watkins, *Phys. Rev.* **113**, 91 (1958).

¹⁰ R. W. Dreyfus and R. B. Leibowitz, *Phys. Rev.* **135**, A1413 (1964).

¹¹ J. S. Dryden and R. I. Meakins, *Discussions Faraday Soc.* **23**, 39 (1957).

⁶ J. R. MacDonald, *J. Chem. Phys.* **29**, 1346 (1958); **30**, 806 (1959).

which the I.V. dipoles give rise to an ITC band, because during the ITC measurements one expects that the frozen-in polarization is released when the relaxation time of the dipoles is of the order of a few seconds. In the case of the $\text{KCl}:\text{SrCl}_2$ crystals, we expect an I.V. band at temperatures lower than 270°K .

Figure 2 shows the discharge current as a function of the temperature for three KCl samples of different purity which have been polarized at $T_p = 220^\circ\text{K}$ for 3 min and warmed up from liquid-nitrogen temperature with a rate $b = 0.1^\circ\text{K sec}^{-1}$. The samples grown from "proanalysis" Merck's salts (divalent impurities content: $\sim 2 \times 10^{-5}\%$) show a very weak ITC band with $T_M = 200^\circ\text{K}$, corresponding to Ca^{++} I.V. dipoles, and a second even weaker band at T_M slightly higher; from Eq. (4), by putting $p = 1.5 \times 10^{-17}$ esu, $\alpha = \frac{2}{3}$, $T_p = 220^\circ\text{K}$, we obtain $N_{\text{Ca}} = 6.5 \times 10^{15} \text{ cm}^{-3}$. The number of calcium-vacancy dipoles is therefore much less than the number of calcium ions contained in the crystal: this fact seems

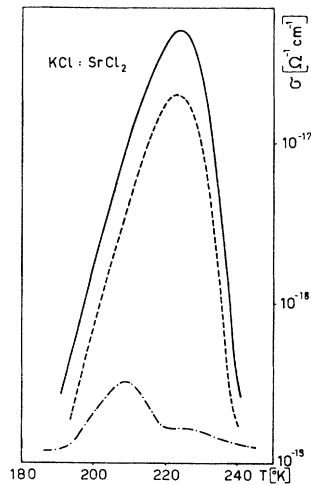


FIG. 2. ITC of KCl crystals of different purity; $b = 0.1^\circ\text{K sec}^{-1}$, $T_p = 220^\circ\text{K}$. Dot dashline—sample grown from pure Merck powders; broken line—from melt containing $\sim 2.8 \times 10^{17}$ Sr atoms per cm^3 ; solid line—from melt containing $\sim 1.6 \times 10^{18}$ Sr atoms per cm^3 .

to be due to the neutralization of Ca ions by other impurities such as OH^- , giving dipoles of negligible mobility.¹² The following measurements have been carried out on crystals purposely doped with strontium added to the melt in the amount of 3.8×10^{17} and 3.8×10^{18} atoms of Sr per cm^3 . The ITC band which occurs at $T_M = 223^\circ\text{K}$ is clearly due to the disorientation of the Sr-vacancy dipoles. From Eq. (4) we obtain for the concentrations of Sr, respectively, $2.8 \times 10^{17} \text{ cm}^{-3}$ and $1.6 \times 10^{18} \text{ cm}^{-3}$: when the concentration of impurities in the melt is larger, a relatively smaller fraction of them enters into the crystal.

In addition it has been observed that, provided larger electric fields are employed for the polarization, a concentration of divalent impurities, N_d , as low as $2 \times 10^{15} \text{ cm}^{-3}$ can be detected: the ITC method therefore shows a sensitivity 50 times higher than the dielectric-loss method. However, the precision on N_d , as discussed

¹² H. W. Etzel and D. A. Patterson, Phys. Rev. **112**, 1113 (1958).

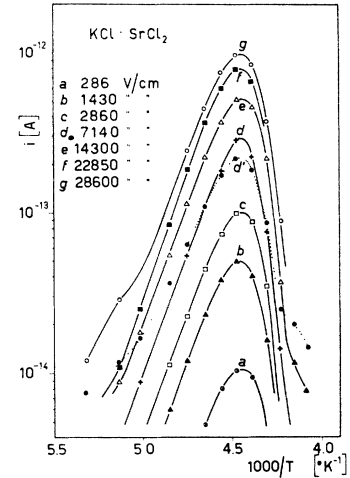


FIG. 3. ITC of $\text{KCl}:\text{SrCl}_2$ (previously heated at 200°C for 3 min) polarized with different fields—curve d' is the ITC of the sample before heat treatment, polarized with the same field as sample d .

in Sec. 2, is not as good as on the other parameters E and τ_0 because of the contact's electrode crystal.

In Fig. 3 the same I.V. band is shown as a function of the polarizing field \mathcal{E}_p . In agreement with Eq. (2) the T_M does not depend upon \mathcal{E}_p . Figure 4 shows $\sigma(T_M)$ as a function of \mathcal{E}_p : the observed linearity agrees with Eq. (1). These results confirm that the polarization of the Sr-vacancy dipoles is described by means of first-order laws, as expected for noninteracting dipoles, and show, at the same time, the reliability of the method proposed here.

B. Analysis of the Parameters of Motion

In Fig. 5 an example is shown of how the activation energy E is determined by means of a single measurement. The $\ln \sigma$ is plotted as a function of T^{-1} for several partial discharges of the same sample previously polarized at $T_p = 220^\circ\text{K}$ in an electric field $\mathcal{E}_p = 1.4 \times 10^4 \text{ V cm}^{-1}$. The first partial discharge (curve 1), having a different slope from the following ones, is surely affected

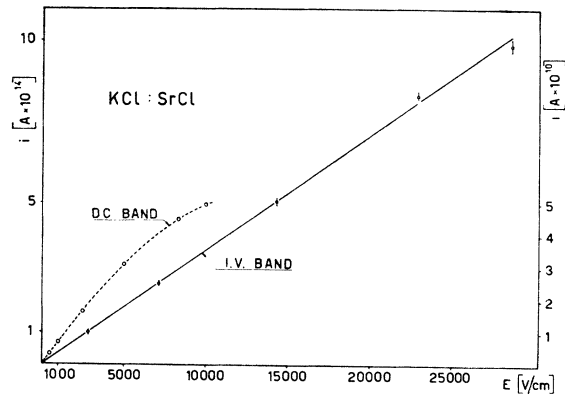


FIG. 4. Maximum current of ITC bands as a function of applied field. The scale at left refers to the IV band, the scale at right refers to the DC band.

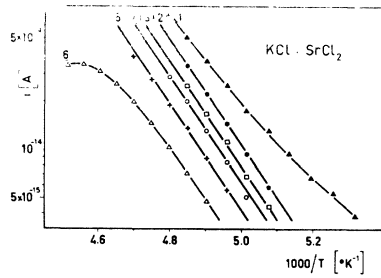


FIG. 5. Six successive discharges of a KCl:SrCl₂ crystal polarized at 220°K with 10⁴ V/cm.

by the superposition of the tail of the I.V. band with some unknown small band. The four next partial discharges have the same slope and suggest that the I.V. band, except for the fraction first discharged (curve 1), is due to a single process. From their slope, using Eq. (3), we obtain the activation energy $E = 0.657 \pm 0.01$ eV.¹³ The slope of the last and final discharge (curve 6) is not constant any more, as expected, because Eq. (3) is valid only for $T < T_M$. The value of E thus determined has been confirmed by the *independent* analysis of the whole ITC band, by verifying Eq. (5): in Fig. 6, the values of $\ln \tau$ as a function of T^{-1} are plotted, for different samples and for different warming rates. The value obtained for E , as an average over several measurements, is 0.657 ± 0.002 eV, in excellent agreement with the one obtained from the Fig. 5. The different slope of curve *a* in the low-temperature region is due to the same superposition responsible for the deviation of curve 1 in Fig. 5, and shows that a careful quantita-

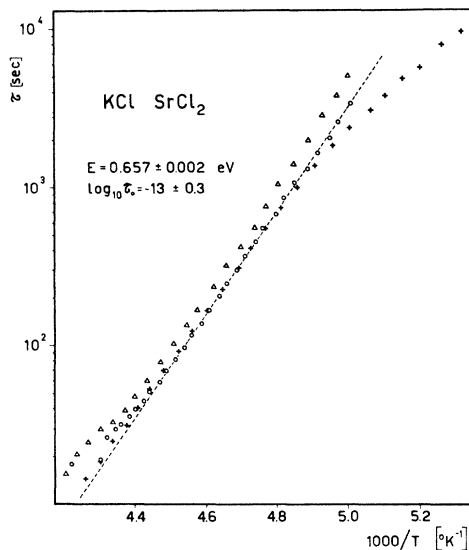


FIG. 6. The $\log_{10} \tau$ as a function of $1000/T$, from ITC bands of KCl:SrCl₂. +—without any discharge; $b = 0.1^\circ\text{K sec}^{-1}$; Δ —from band previously partially discharged; $b = 0.1^\circ\text{K sec}^{-1}$; \circ —same as Δ ; $b = 0.05^\circ\text{K sec}^{-1}$.

¹³ The value reported in Ref. (3) should be corrected, because it was obtained by means of too fast a warming rate, which affected the result.

tive analysis can be carried out only when the ITC band is pure, i.e., previously made free, by means of partial discharges, of the presence of overlapping relaxations. Not yet clear is, however, the nature of the deviations in the high-temperature region. Because of the small error in the value of E , the value of τ_0 can be determined from Fig. 6 with good accuracy: one obtains thus $\log_{10} \tau_0 = -12.96 \pm 0.10$. As was done for E , τ_0 can also be estimated independently by using, this time, Eq. (2), in which the proper values of b and T_M have been introduced; the result is $\log_{10} \tau_0 = -12.94 \pm 0.15$.

Similarly the activation energies for other crystals as well as for other impurities have been determined:

Crystal	E (eV)
KCl: CaCl ₂	0.63
NaCl: CdCl ₂	0.68
NaCl: CaCl ₂	0.67
KBr: BaBr ₂	0.69

In all of these cases the I.V. band overlaps many small satellite bands which prevent us from measuring E with a better accuracy than 3%, and therefore the determination of τ_0 becomes less reliable.

C. ITC in Higher Temperature Region

Region D. C.

The properties of the bands occurring in KCl between 280 and 430°K can be briefly summarized¹⁴ as follows: Three partially superimposed bands are always

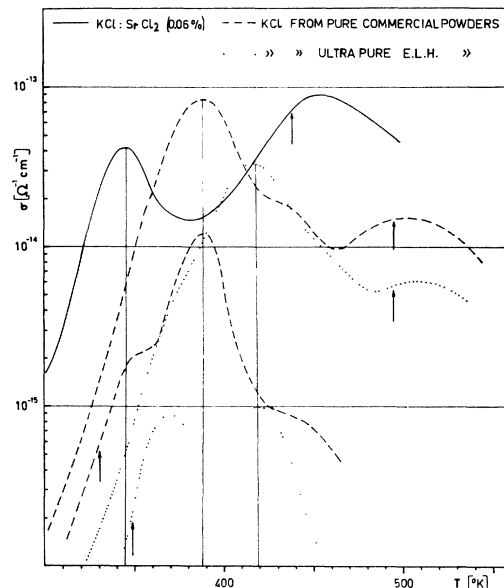


FIG. 7. ITC above room temperature for KCl of different purity. E. L. H. is a purity grade of the manufacturer (E. Merck, A. G., Frankfurterstrasse 250, 61 Darmstadt, Germany). The arrows indicate the polarization temperature T_p .

¹⁴ C. Bucci, R. Fieschi and G. Guidi, Report No. 4, Grant No. AF EOAR 63-27, 1964 (unpublished).

present, with maxima at 350, 385, and 420°K. One of these bands is generally much more intense than the others; as can be recognized from Fig. 7, the predominant band occurs at lower temperatures if the impurity content is larger. Furthermore, (a) the intensity of such bands is exceptionally high (about 10^3 times the intensity of the I.V. bands) and does not depend upon the impurity content of the crystal: (b) the temperature of the maxima T_M is well defined (it does not depend on T_p) and, as mentioned before, it depends only on the purity of the crystals. (c) The intensity of each band is a linear function of the applied electric field only up to 1000 V/cm: (Fig. 4, dashed curve) for higher field saturation effects are present. If they were due to volume dipolar polarization, arising from about 10^{18} imperfections/cm³, the dipoles would have a dipole moment of 10^8 charges times lattice distance. (d) The position as well as the intensity of the "dielectric-chaos" (D.C.) bands depends upon the type of contact between the crystal and the electrodes. Point (c) shows that the polarization giving rise to the D.C. bands is not due to ionic dipoles, distributed uniformly in the volume of the crystal. It might be due to surface polarization or to contact effects, the origin of which, however, is not yet clear.

Space-Charge Region

The very intense band measured usually at temperatures above 420°K represents the release of ionic space-charge accumulated during the polarization at T_p . This conclusion has been drawn¹⁵ by verifying that the behavior of the space-charge band corresponds to the one expected for a space-charge system (Sec. 1B), and by comparing ITC measurements with the current decays at constant temperatures.

4. COMPLEX RELAXATION DUE TO METALLIC IMPURITIES

In the alkali halides the divalent metallic impurities give rise, by associating with a cation vacancy, to dipoles with various lattice configurations^{9,16} or can associate into more complex units, such as trimers.¹⁷ There is some evidence that these imperfections give rise to different relaxation modes.^{10,18}

The method of the ITC has been successfully applied to the analysis of such a system of overlapping relaxations. We report here, as an example, the case of NaCl containing small amounts of CaCl_2 (10^{-5} $\text{Ca}^{++}/\text{Na}^+$). Figure 8 shows the ITC of such a crystal polarized at $T_p = 233^\circ\text{K}$ for 1 min. Following the procedure indicated in Sec. 1A, it is possible to distinguish six different

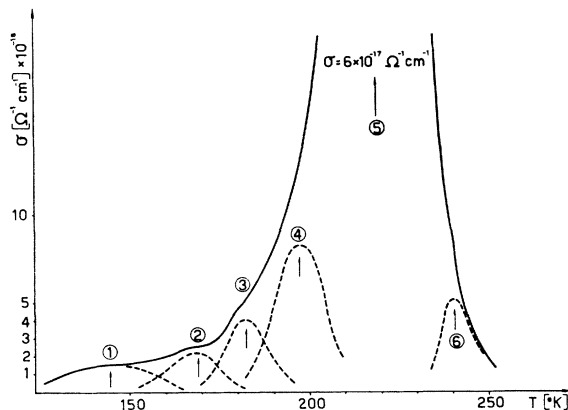


Fig. 8. ITC of $\text{NaCl}:\text{CaCl}_2$. Decomposition of the complex discharge band (continuous line); the components (weak dashed bands) are obtained from independent measurements, on samples polarized at a suitable low temperature (see Fig. 9).

contributions (see dashed curves). Figure 9 shows three recorded ITC obtained from the same sample, polarized at suitable temperatures in order to distinguish the secondary processes (the straight line indicates the temperature). Curve *a*, resulting from the polarization at $T_p = 163^\circ\text{K}$, shows only the existence of two fast relaxations giving rise to two weak bands; curves *b* and *c*, for which T_p is, respectively, 177°K and 194°K , allow us to individuate eventually the different processes, as schematically shown in Fig. 8. The dominant one occurs at $T_{M5} = 222^\circ\text{K}$ while the other occurs, respectively, at $T_{M1} = 144^\circ\text{K}$, $T_{M2} = 159^\circ\text{K}$, $T_{M3} = 192^\circ\text{K}$, $T_{M4} = 198^\circ\text{K}$, $T_{M6} = 243^\circ\text{K}$. The activation energy of the dominant process, as we said, is $E = 0.67 \pm 0.02$ eV. Some of these bands might be due to I.V. complexes originated by metallic impurities different from Ca^{++} , which are present in concentration smaller than 10^{-6} .

5. INFLUENCE OF THERMAL TREATMENTS

It is well known that the ionic conductivity and the polarization of the alkali halides are extremely sensitive to thermal treatments, either annealing or quenching, because of the precipitation of impurities or of the inverse process. As far as polarization effects are concerned, small agglomerates of I.V. dipoles can be dissolved by means of an annealing at $T > 200^\circ\text{C}$ followed by a quenching, obtaining thereby an increase in the intensity of the dielectric relaxation. The analysis of such a process is very easy if carried out by means of ITC measurements because the I.V. bands occur at T much lower than room temperature, where the precipitation processes are very slow.

A comparison of curves *d'* and *d''* of Fig. 3 shows how a thermal treatment affects the ITC in a sample containing a rather small concentration of divalent metal impurities (10^{-4} SrCl_2 , in the melt): the weaker ITC at low temperature (curve *d'*) disappears after the sample has been heated to $T = 200^\circ\text{K}$ and cooled quickly, while

¹⁵ C. Bucci and S. Riva, *J. Chem. Phys. Solids* **26**, 363 (1965).

¹⁶ M. Tosi and F. Fumi, *Nuovo Cimento* **7**, 35, (1958).

¹⁷ J. S. Cook and J. S. Dryden, *Proc. Phys. Soc. (London)* **80**, 479 (1962).

¹⁸ V. N. Lozovskij, *Izv. Akad. Nauk SSSR* **24**, 161 (1960).

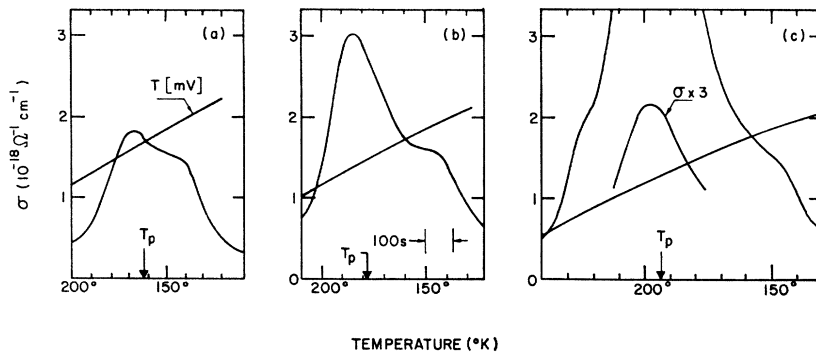


FIG. 9. ITC of NaCl:CaCl₂. Registration of bands from samples polarized at low temperature (the total ITC is given in Fig. 8). (a) $T_p=163^\circ\text{K}$; only the two low-temperature bands appear; (b) $T_p=167^\circ\text{K}$; band (3) appears; (c) $T_p=194^\circ\text{K}$; band (4) overlaps the lower temperature processes; a weak band (5) is also visible.

the main I.V. band increases by a factor ~ 1.3 . If the sample is more heavily doped, the effect of heat treatment is more pronounced.

The effect of successive heating in NaCl:SrCl₂ is shown in Fig. 10. Beyond the main I.V. band, $T_M = 223^\circ\text{K}$, a second relaxation takes place at higher temperatures. The initial band is weak, indicating that the solubility of SrCl₂ in NaCl is rather low; after heating at 300°C the dissolved Sr increases by nearly an order of magnitude.

By means of successive ITC cycles on a sample containing a number of I.V. dipoles in excess of the solubility value, the precipitation of the impurities can also be followed. The ITC method is of advantage over the $\tan\delta$ method in those cases where the precipitation is appreciable at temperatures where the dielectric losses are very slow, such as for Cd in NaCl¹⁹; moreover, owing to its higher sensitivity, by means of ITC the

precipitation process can be followed down to very low concentrations of dipoles $\sim 2 \cdot 10^{15} \text{ cm}^{-3}$.

6. OTHER DIELECTRICS

The method here described can be employed in studying every dielectric, for which the same information as for the alkali halides will be obtained.

The release of the polarization of Teflon (Fig. 11), of quartz (Fig. 12), and of calcite (Fig. 13) shows clearly,

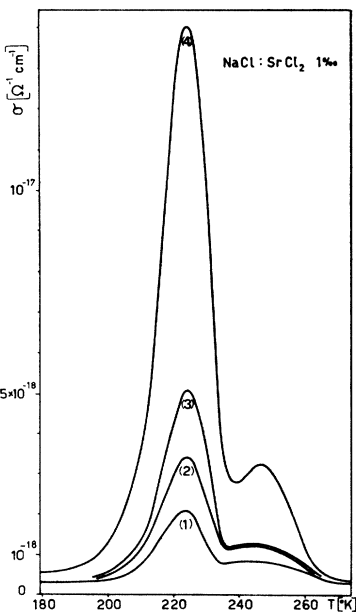


FIG. 10. Effect of thermal treatment on ITC of NaCl:SrCl₂. (1) Untreated sample; (2) after heating at 100°C for 5 min; (3) after heating at 160°C for 5 min; (4) after heating at 300°C for 5 min.

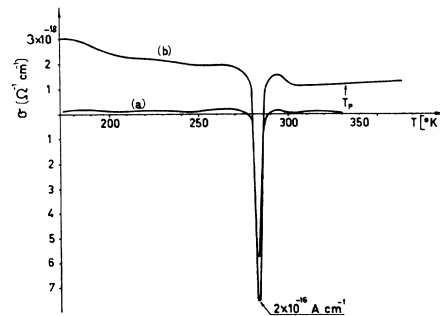


FIG. 11. ITC of Teflon: curve (a) is obtained from an unpolarized sample; the peak at $T \approx 330^\circ\text{K}$ reverses its sign when the sample is cooled instead of heated.

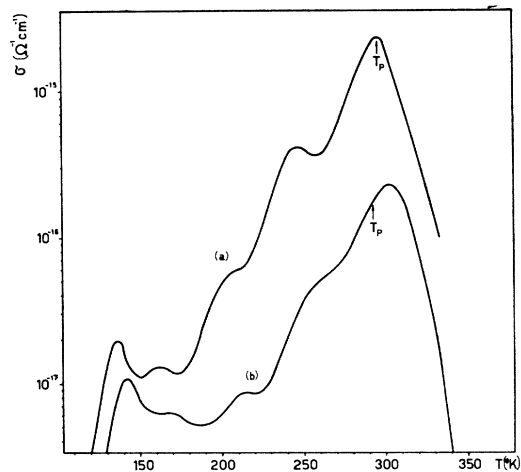


FIG. 12. ITC of (a) amorphous and (b) crystalline quartz polarized at $T_p \approx 290^\circ\text{K}$.

¹⁹ R. Cappelletti and E. De Benedetti, Bull. Italian Phys. Soc. 46, 24 (1965).

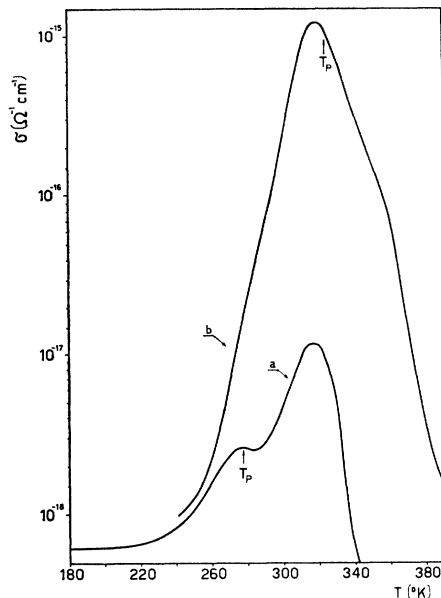


FIG. 13. ITC of calcite, polarized at two different temperatures.

as one would expect, that Teflon has the weakest dielectric relaxations. It shows, however, in Teflon a surprising behavior at temperatures close to room temperature, where temperature-dependent currents arise also when the sample was not previously polarized. The sign of such a current, in the nonpolarized sample, changes if the sample is inverted with respect to the electrodes, or if the temperature is decreased instead of increased. This might be due to the rotation of molecular complexes belonging to the polymeric chain, in the sample of laminated Teflon. Figure 12 shows that the dielectric relaxations of amorphous quartz are more intense than the crystalline quartz.

7. CONCLUSIONS

The ionic thermoconductivity method (ITC), consisting in the study of the thermal activated release of dielectric polarization, is studied in great detail in

SrCl₂-doped KCl crystals and in other alkali halides. The following results are obtained:

1. The ITC band due to I.V. dipoles (Sr ion-cation vacancy) is centered at $T_M = 223^\circ\text{K}$ (for $dT/dt = 0.1^\circ\text{K sec}^{-1}$); the area of the band is proportional to the polarizing field up to at least $28\,000\text{ V cm}^{-1}$.

2. Thanks to the sensitivity of the method, it is possible to detect a number of dipoles $\geq 2 \cdot 10^{15}\text{ cm}^{-3}$.

3. The activation energy can be obtained with an accuracy of 0.1% when there are no overlapping bands, the pre-exponential factor can also be evaluated with fair accuracy. The agreement with the results obtained by Dryden and Meakins by means of dielectric-loss measurements is good.

4. The presence of polarization processes of low intensity overlapping the main ITC band can easily be detected by polarizing the sample at a suitable temperature.

5. The solubility of the impurities can be studied by measuring the ITC of samples subjected to annealing at a fixed temperature.

6. In other works, it is shown that the precipitation process¹⁹ and the influence of ionizing radiation²⁰ can also be investigated by measuring the changes of the ITC band intensity.

7. Intense ITC bands, appearing in KCl between 280 and 430°K are not due to bulk polarization, but probably to effects of the contact dielectric-electrodes; bands at still higher temperatures, as previously known¹⁵ are due to space-charge.

Measurements on other substances show that by means of a single ITC measurement one obtains a complete qualitative picture of the polarization in the dielectric.

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²⁰ M. Beltrami, R. Cappelletti, and R. Fieschi, Phys. Letters 10, 3 (1964).