

teresis observed.<sup>4,5</sup> Experiments are currently underway to see if improved surface preparation and avoidance of end effects will produce evidence of the large nucleation barrier to flux penetration calculated here.

The present elementary treatment has only considered  $E(x)$  for a single flux thread. To calculate the detailed hysteresis curves expected, one must consider an assembly of flux threads and the interactions between them. For a more exact calculation of  $H_S$  and removal of the limitation  $\lambda \gg \xi$ , detailed consideration of the core of the flux thread and use of the Ginzburg-Landau equations will be required.

We gratefully acknowledge discussion with P. G. deGennes, who had independently considered the image flux thread and the resulting energy barrier.

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<sup>7</sup>Our calculation of  $H_S$  in this approximation is inexact because of uncertainties in the image term in  $E(x)$  for  $x \lesssim \xi$ . Choosing to cut off  $K_0(2x/\lambda)$  at  $x = \xi$ , the maximum image force then occurs here, and we get  $H_S = \varphi_0/4\pi\lambda\xi \approx H_C/\sqrt{2}$ , where  $H_C$  is the thermodynamic critical field.

## IONIC THERMOCONDUCTIVITY. METHOD FOR THE INVESTIGATION OF POLARIZATION IN INSULATORS\*

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Polarization effects due to ionic motion in insulators have been studied over a great many years, essentially following two different methods: by considering the change in time of the electrical current in a sample subjected to a dc external field<sup>1,2</sup> or by measuring the dielectric losses<sup>3</sup>; these measurements are carried out at fixed temperature. Alkali halides were one of the subjects studied more extensively.

We propose here a different method of investigation; it is based on a phenomenon, analogous to thermoluminescence, which could be called ionic thermoconductivity (ITC). The method is as follows:

(1) The sample is first polarized in a static field  $E$ , for a time  $t$ , at a temperature  $T_p$ ; the temperature should be enough to allow the complete orientation of all the dipoles that one wishes to consider, and not too high, in order to avoid heavy space-charge contributions. In alkali halides, reasonable polarization temperature is around 0°C.

(2) The solid is cooled down to a temperature  $T_0 < T_p$ , where any ionic motion is completely

hindered, then the external field is taken off.

(3) The solid is subsequently warmed up at a constant rate  $b$ , and the discharge current is registered as a function of temperature. One expects "electrical glow" curves, similar to those characteristic of thermoluminescence<sup>4</sup> or of electronic glow.<sup>5</sup>

When the release of the electrostatic energy is due to relaxation of electric dipoles, the peaks of the function  $i(T)$  correspond to various dipolar imperfections present in the crystal, and can give information as to relaxation time and number of dipoles. The situation is in some respects simpler than in the case of thermoluminescence, because the relaxation mechanism is monomolecular; the only exception to be expected is the case of release of the accumulated space charge, where decay is complex and slower.<sup>6</sup>

Briefly, the following information can be obtained by analyzing a peak of ITC: (1) The area delimited by the function  $i(T)$  is proportional to the number of dipoles of a given kind present in the sample:

$$\text{area} \propto N_{\text{dip}} \tau(T_p) \{1 - \exp[-t/\tau(T_p)]\},$$

where  $\tau(T_p)$  is the relaxation time at temperature  $T_p$ , at which the crystal is polarized for a time interval  $t$ . (2) The following relation connects the temperature corresponding to the maximum current  $T_m$  with  $\tau$ :

$$kT_m^2 = bE\tau(T_m) = bE\tau_0 \exp(E/kT_m),$$

where  $E$  is the activation energy for the dipole orientation; it follows that the temperature corresponding to the maximum current is approximately proportional to the activation energy for the dipole orientation; the proportion is to be expected much better than for thermoluminescence because the pre-exponential factor should not depend much on the nature of dipole. (3) The activation energy is given by the initial slope of  $\ln[i(T)/i_0]$ :

$$\ln[i(T)/i_0] \cong \text{const} - E/kT.$$

(4) The current intensity is directly proportional to the polarizing field, because even at breakdown fields, at  $T \gg 0^\circ\text{K}$ , one is far from saturation conditions.

The experiments are carried out with the usual apparatus for measuring very weak currents; in our case it was a vibrating capacitor electrometer, and the weakest detectable current was  $10^{-16} \pm 10\%$  ampere. Much care must be used to avoid the presence of insulators in the region of the sample's container subjected to thermal cycles; even quartz or Teflon yield competitive ITC.

The results on KCl either pure or doped with  $\text{SrCl}_2$  (0.06%) (purchased from K. Korth), polarized at  $237 \pm 1^\circ\text{K}$ , are shown in Fig. 1.

The dipoles  $\text{Sr}^{++}$  (positive ion vacancy) give the strong band at  $T_m^I = 235^\circ\text{K}$  (the temperature of the sample may be some degrees lower than the detected one); in contaminated samples it is 30 times stronger than in nominally pure crystals. We have shown that it is a single band:

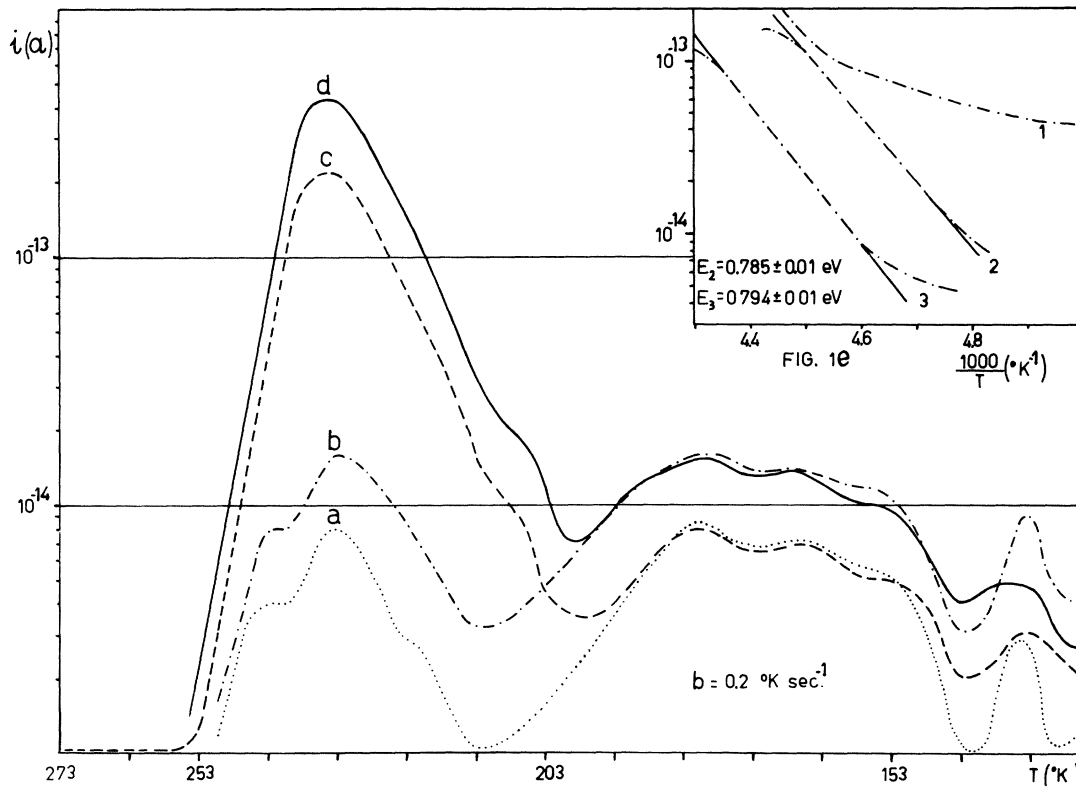


FIG. 1. (a) ITC of nominally pure KCl polarized at  $237^\circ\text{K}$  with 305 volts. (b) ITC of nominally pure KCl polarized at  $237^\circ\text{K}$  with 610 volts. (c) ITC  $\text{KCl}:\text{SrCl}_2$  (0.06%) polarized at  $237^\circ\text{K}$  with 305 volts. (d) ITC  $\text{KCl}:\text{SrCl}_2$  (0.06%) polarized at  $237^\circ\text{K}$  with 610 volts. (e) Activation energies of the dipole relaxation time, obtained from the slope of  $\log i(T)$  versus  $1/T$  in the low-temperature tail of the peak at  $235^\circ\text{K}$ .

Activation energy obtained from the slope at  $T < T_m$  [Fig. 1(e)] is  $E^I = (0.794 \pm 0.01)$  eV; relaxation time at  $T_m = 235^\circ\text{K}$  is 27 sec. These results are in good agreement with the results of Matsonaskrili<sup>7</sup> ( $E = 0.81$  eV) but agree less well with Dryden's and Meakins'<sup>8</sup> ( $E = 0.67$  eV).

In pure as well as doped crystals there are other ITC peaks at lower temperatures:  $T_m^{\text{II}} = 178^\circ\text{K}$ ;  $T_m^{\text{III}} = 168^\circ\text{K}$ ;  $T_m^{\text{IV}} = 153^\circ\text{K}$ ;  $T_m^{\text{V}} = 135^\circ\text{K}$ ; if we suppose the pre-exponential factor unchanged, the corresponding activation energies are the following:  $E^{\text{II}} = 0.60$  eV;  $E^{\text{III}} = 0.56$  eV;  $E^{\text{IV}} = 0.51$  eV;  $E^{\text{V}} = 0.46$  eV.

The band at  $235^\circ\text{K}$  in pure crystals is associated with other little peaks, probably due to

different divalent impurities, always present in the nominally pure crystals. Notice that associated divalent impurities in nominally pure crystals are detectable neither in dielectric losses nor in dc measurements.

It can be noticed that in both pure and doped samples the ITC doubles when the polarizing field grows from 305 to 610 volts.

Figure 2 shows the results of KCl: SrCl<sub>2</sub> and pure KCl polarized at higher temperatures. The peak due to dipoles becomes wide and a new band grows at higher temperatures (Fig. 2, curves b and c). This does not seem characteristic of a dipolar relaxation process, and we believe it due to space-charge relaxation, ac-

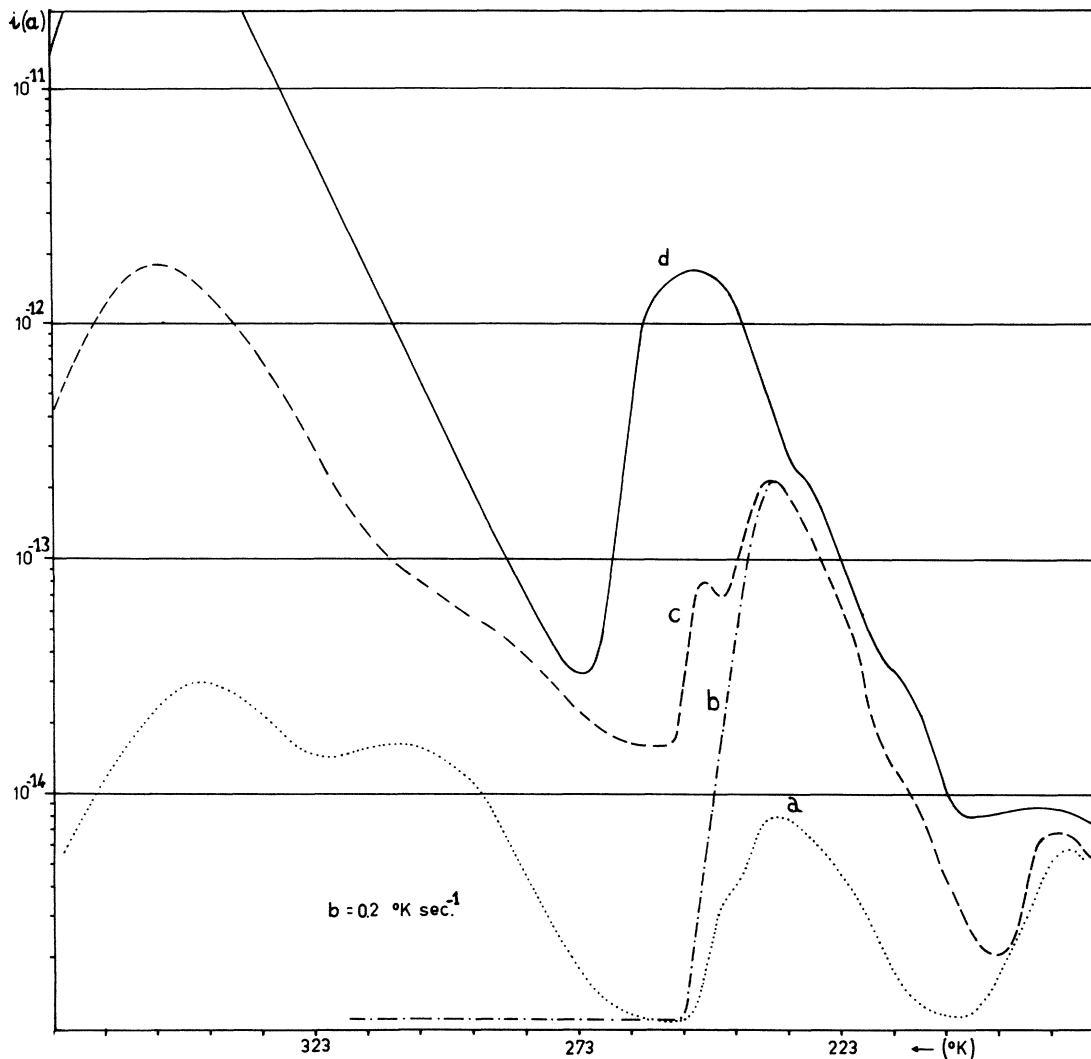


FIG. 2. (a) ITC of nominally pure KCl polarized at  $295^\circ\text{K}$  for three minutes with 305 volts. (b) ITC of KCl: SrCl<sub>2</sub> (0.06%) polarized at  $237^\circ\text{K}$  for three minutes with 305 volts. (c) ITC of KCl: SrCl<sub>2</sub> (0.06%) polarized at  $295^\circ\text{K}$  for three minutes with 305 volts. (d) ITC of KCl: SrCl<sub>2</sub> (0.06%) polarized at  $295^\circ\text{K}$  for 60 minutes with 305 volts.

ording to previous evidence for space-charge formation in dc polarization.<sup>9,10</sup>

Summarizing, the method is more sensitive than, and at least as accurate as, the analysis of the current decay at fixed  $T$ , for measuring the activation energy of the relaxation process, and reveals finer detail of the phenomenon.

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### EFFECT OF PRESSURE ON THE RESISTANCE OF CESIUM\*

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The electrical resistance of cesium has been measured to pressures of several hundred kilobars. Bridgman<sup>1</sup> measured the resistance to 65 kilobars. He found a small discontinuous rise at 22 kilobars, and a rise of several fold accompanied by a very sharp cusp at 41 kilobars. (All pressures have been corrected to the values most generally accepted today.) His  $p$ - $v$  measurements<sup>2</sup> also indicated volume discontinuities at these pressures.

It is generally assumed that the first discontinuity in resistance and volume corresponds to a transition from a bcc to fcc structure. Sternheimer<sup>3</sup> has postulated that the second volume change (and cusp) correspond to the promotion of the 6s electron to a vacant band arising from the atomic 5d shell. His calculations indicated that this is indeed feasible. His work has been criticized<sup>4</sup> based on more recent calculations of band structure for the alkali metals. His calculations must at best be approximate, since he assumed a fivefold degenerate spherically symmetric 5d band. The degeneracy must be at least partially removed by the crystal field of the lattice, and the bands arising from the atomic 5d state must have structures strongly dependent on direction in  $k$  space. Nevertheless, the notion of the promotion of conduction

electrons from a filled to an empty band is a fruitful one, and has been used to explain transitions in cerium<sup>5</sup> and in other metals.

In our studies 99.95% pure cesium from A. D. Mackay was used. The high-pressure techniques have been previously described.<sup>6-8</sup> The cell was loaded in a dry argon atmosphere. The cell was cooled to inhibit melting of the cesium. It was very difficult to obtain reproducible pressures due to initial flowing of the sample as pressure was first applied.

All of the electrical resistance features occurred on every run, but the 41-kilobar cusp appeared at apparent pressures from 20 to 70 kilobars. Figure 1 shows a composite average of twelve successful runs. The 22-kilobar transition is smeared out by problems of making contact, etc. The cusp at 41 kilobars is of the same magnitude as found by Bridgman. The important new feature is the very sharp rise in resistance initiating at an apparent pressure of 175 kilobars. The rise is accompanied by a strong upward drift with time. There is a definite maximum at a higher resistance than the first cusp. It should be emphasized that, while the pressures shown are nominal because of problems in handling cesium, the sharp rise and drifting occurred on every run. (There was no