

ABSORPTION AND REABSORPTION CURRENTS IN NaCl  
SINGLE CRYSTALS

H.G. Riveros\* and L. Rosas

Instituto de Física, Universidad Nacional de México

(Recibido: 23 enero 1968)

ABSTRACT

*The present paper attempts to determine the mechanism responsible for the decay of the electric current in alkali halides under constant electric field, taking into account the two mechanisms proposed previously: dipole-orientation and accumulation of space charge. The work was done with crystals of NaCl, some of them with  $Mn^{++}$  impurities. Rectangular voltage pulses were applied to crystals for different duration (30 s - 3600 s) and at different temperatures (100° C - 200° C), with the following results: a) the magnitude of discharge current and its decay rate depends on the pulse duration, b) the discharge current do not obey Ohm's law, c) the decay of the discharge current is slower at higher temperatures, d) the explanation of the time decay of the current requires both dipole-*

---

\* Facultad de Ciencias, Universidad Nacional de México.

*orientation and space-charge accumulation. Consequently, the conductivity must be measured after the dipole-orientation current transient and before the accumulation of space charge.*

## RESUMEN

*En el presente trabajo se trata de determinar el mecanismo responsable del decaimiento de la corriente eléctrica en el tiempo (en halogenuro alcalino a campo eléctrico constante), tomando como base los dos mecanismos propuestos para su explicación: orientación de dipolos y acumulación de carga espacial. Para efectuar este trabajo, a varios cristales de NaCl, algunos de ellos con impurezas de  $Mn^{++}$ , se les aplicaron pulsos rectangulares de voltaje durante tiempos diferentes (30-3600seg) y a distintas temperaturas (100-200° C) obteniéndose como resultados: a) la magnitud de la corriente de descarga y la rapidez de decaimiento dependen del tiempo de duración del pulso, b) las corrientes de descarga no obedecen la ley de Ohm, c) la rapidez de decaimiento de la corriente de descarga disminuye conforme aumenta la temperatura, d) el decaimiento de la corriente en el tiempo se debe a la orientación de dipolos y a la acumulación de carga espacial. En consecuencia, la conductividad se debe medir después del transitorio de orientación dipolar y antes de que se produzca la acumulación de carga espacial.*

## INTRODUCTION

It has long been known that the conductivity in insulators and particularly in alkali halides is time dependent<sup>1,2</sup>. The experiments to be described were performed in an attempt to determine the mechanism responsible for the decay with time of the current which flows upon application of a steady direct voltage. Two mechanisms have been proposed previously: (a) orientation of dipolar imperfections<sup>3,4</sup>, and (b) accumulation of space charge<sup>2</sup>.

When the current decay is due to the orientation of dipolar imperfections

such as divalent impurities linked with vacancies, etc., the internal electric field is not modified and the true ionic conductivity is obtained after sufficient time has elapsed for the transient to die away and the current to become constant. It is then expected that Ohm's law will be obeyed because the number of dipoles oriented at time  $t$ ,  $n_i(t)$ , is described by a monomolecular law<sup>5</sup>:

$$n_i(t) = N_i \frac{p_i E}{3kT} [1 - \exp\{-t/\tau_i\}]$$

with

$$p_i E/kT \ll 1$$

where

$\tau_i$  is the relaxation time,

$E$  the electric field,

$p_i$  the dipole moment of the dipole type  $i$ , and

$N_i$  the total number of  $i$ -type dipoles.

According to the second mechanism, a space charge accumulates at one or both electrodes, due to the finite discharging rate of the current carriers. Thus, the internal electric field is modified, and so the interpretation of conductivity measurements is rendered difficult, except at the instant applying the voltage ( $t = 0$ ) when the space charge has not had time to accumulate. In this case deviations from Ohm's law are to be expected<sup>4,6</sup> if observations are made at  $t \neq 0$ , as is normally the case. Also the duration of the re-absorption current transient, which occurs when the voltage is removed and the specimen is short circuited, should depend on the charge transported during the preceding period of voltage application.

P.H. Sutter and A.S. Nowick<sup>4</sup> showed that the polarization effects in NaCl were due to orientation of dipolar imperfections. They define the discharge conduc-

tivity as the ratio of current density at an instant after the voltage has been removed to the applied mean electric field. They showed that for corresponding instants in the absorption and re-absorption transients (see Fig. 1) the conductivity and the discharge conductivity obey Ohm's law. They also found that the current flow as a function of time during the re-absorption transient was the same as that during the absorption transient minus the stationary current. Moreover they found that the re-absorption current transient was independent of the applied voltage duration provided this was such that the absorption transient could achieve the steady value.

Sutter and Nowick used rectangular voltage pulses and, in general, currents were measured in the interval extending from  $20 \times 10^{-3}$  s to 10 s after applying the voltage. The temperature range extended from  $50^\circ$  C to  $200^\circ$  C and nominally pure Harshaw crystals were used.

In the present investigation "pure" single crystals of NaCl and single crystals of NaCl containing the divalent impurity Mn were used. The crystals were grown from the melt in air by the method of Czochralski<sup>3</sup>. The NaCl was obtained from Mallinckrodt Chemical Works. The crystals were cleaved into  $10 \times 10 \times 1$  mm, plates, and colloidal graphite electrodes were painted on opposite  $10 \times 10$  mm faces. The sample was held in a metallic container without any insulator, except that of the electrometer input (teflon). Rectangular voltage pulses were applied for times from 30 s to 3600 s in the temperature interval from  $100^\circ$  C to  $200^\circ$  C. The experiments were performed using a 408 B Fluke power supply and a 417 Keithley picoammeter.

As a typical result, Fig. 2 shows how the re-absorption currents varied in the present experiments after the application of voltage pulses all having the same amplitude but with different duration. In every case the steady current while the voltage pulse lasted was  $10^{-10}$  A. Extrapolation of the curves seems to show that the initial current ( $t = 0$ ) is the same for all cases, in agreement with Sutter and Nowick's results<sup>4</sup>; nevertheless, it can be seen that the rate of current decay clearly decreases with increase in the duration of the voltage pulse. This observation may be explained if a space charge accumulates, since a larger space charge needs more time for re-absorption. In terms of dipolar orientation only one curve is expected, except if the relaxation times are greater than the pulse width.

In practice it was found impossible to wait until the re-absorption current became zero. Consequently it cannot be said that the crystal is in exactly the same conditions at the instant of application of each of a succession of voltage impulses, and it is necessary to adopt some method of normalizing the observations. The method adopted is illustrated by Fig. 3. This shows the discharge current in a crystal to which a pulse of 1000 V amplitude was applied for 30s (curve A). It can be seen that appreciable current was still flowing after 600s; after 630s the voltage pulse was again applied for 30s. The resulting discharge current is shown in curve B of Fig. 3a. It can be seen that a difference exists between the two curves. They are plotted on a log-log base in Fig. 3b and it is clear that the relationship between  $\log i$  and  $\log t$  is almost linear. Consequently extrapolation is relatively easy and corrections can be made to any discharge curve for the effects remaining from any previous application of voltage (see insert in Fig. 3a). The curve A'B' in Fig. 3a is a curve obtained by correcting curve A and curve B by the above method.

To enhance the effect, some of the measurements were made on crystals doped with divalent impurities. It is well known that the effect of these impurities, is to increase the conductivity, because they increase the positive vacancy density, and also the magnitude of the discharging current. Fig. 4 shows the influence of adding divalent Mn ( $1.5 \times 10^{-1}\%$  atomic) to NaCl. The effect of Mn impurities on the current  $I$  during the application of the electric field is greater than the effect on the discharge current, but the rate of current decay is slower for the NaCl(Mn) crystal. This result can be accounted for by the accumulation of space charges. In terms of dipolar orientation the same decay rate is expected.

Fig. 5 shows curves of re-absorption conductivity following the application of voltage impulses of the same duration (120s) but with different amplitudes as indicated on the curves. It can be seen that Ohm's law is not obeyed, and also that the rate of current decay decreases with increase in the amplitude of the voltage pulse. In this connection it must be borne in mind that the quantity of charge transported by the absorption current increases proportionally with the

applied field. If the charge is accumulating and the value of the discharge current does not increase linearly with the applied field, then the discharging time should be longer at higher fields. In terms of dipolar orientation only one curve is expected, because of the proportionality between field and number of oriented dipoles.

Fig. 6 illustrates the influence of temperature on the absorption and re-absorption current flowing through a crystal of NaCl, with a voltage of 1000 V applied for 30 s. At any instant in this period the absorption current at 182° C exceeded the corresponding current at 92° C by a factor of  $10^4$ . It can be seen that the rate of decay of the re-absorption current at 92° C greatly exceeded that at 182° C, but the re-absorption current at the latter temperature exceeded that at the lower temperature by a factor between 10 and  $10^2$ , depending on the absorption time. This result cannot be accounted for in terms of dipolar orientation, because this process should occur more rapidly at higher temperature.

The experiments show that the re-absorption current transient which flows after removing the voltage depends on the magnitude and duration of the applied voltage, on the impurity content, and the temperature.

One of the NaCl (Mn) crystal showed a decrease of 30% in conductivity after being under 1000 V at 155° C for 40 hours. This is in opposition to the time-independent current expected from the dipole orientation mechanism when the time is very large.

The experiments have brought to light a small but systematic deviation from Ohm's law for both pure crystals and crystals containing Mn impurities. It can be seen from Fig. 7 that the effect increases with temperature.

## CONCLUSIONS

The present observations show that the tail of the re-absorption current does not obey Ohm's law, that it depends on the duration of the applied field and that the decay is slower at higher temperatures. These effects can be accounted for by the mechanism of space-charge accumulation. It seems evident that both

mechanisms must be involved to explain the current decay with time, and their relative importance depends on the temperature. At low temperatures the dominant term is the dipolar orientation<sup>3</sup> and at high temperatures, the dominant term is the accumulation of space charge<sup>6</sup>. This last conclusion is in agreement with the results of Bucci and Riva<sup>5</sup> in KCl crystals.

Therefore the conductivity must be measured at some intermediate time, after the dipole orientation current transient and before the accumulation of space charge, this corresponds to the knee of the curve clearly seen between 100° C and 200° C. Experiments are under way to determine the best procedure for higher temperatures. The applied field must be high enough in order to have a negligible circulating current before the application of the field.

#### ACKNOWLEDGEMENTS

The authors wish to thank Prof. R. Cooper of Manchester University for his discussion of the work and help in the preparation of the manuscript, and to the members of the Solid State Group at Mexico University for their suggestions.

#### REFERENCES

1. J. Curie, and P. Curie, *Ann.Chim.Phys.* **17**, 385 (1889); **18**, 203 (1889).
2. A.F. Joffé, *The Physics of Crystals* McGraw-Hill Book Company, Inc., New York (1928).
3. R.W. Dreyfus, *Physical Review* **121**, 1675 (1961).
4. P.H. Sutter and A.S. Nowick, *J.Appl.Phys.* **34**, 734 (1963).
5. C.A. Bucci and S.C. Riva, *J.Phys.Chem. Solids* **26**, 363 (1965).
6. A.R. Allnatt, P.W. M. Jacobs and J.N. Maycock, *J. of Chem. Phys.* **43**, 2526 (1965).
7. J.Z. Czochralski, *Phys.Chem.* **92**, 219 (1917) **144**, 131 (1925).

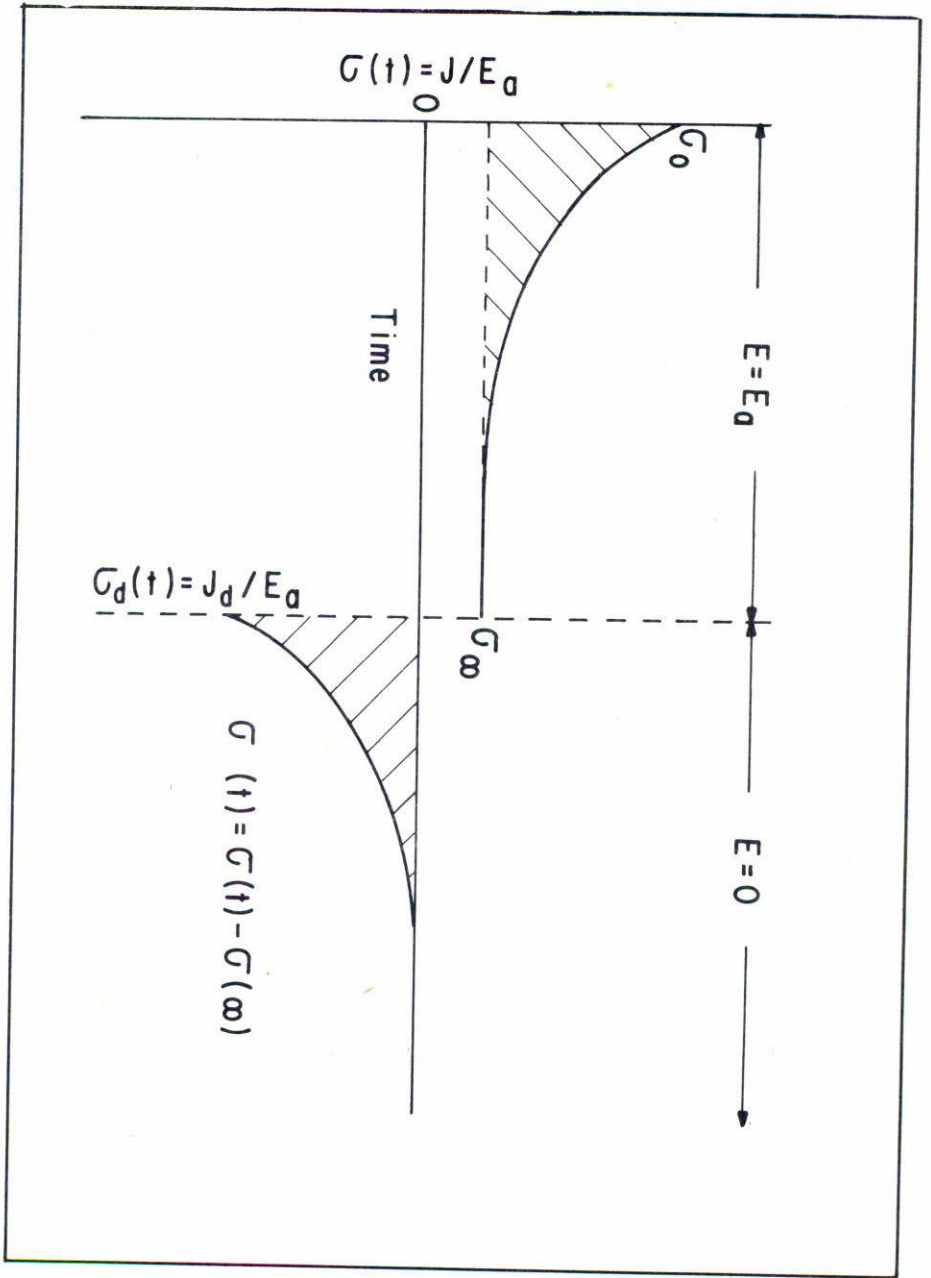


Fig. 1 Schematic diagram showing the variation of conductivity with time under an applied electric field  $E_a$  (the "The charging curve"), and the after effect when the field is abruptly dropped to zero (the discharging curve). After P.H. Sutter and A.S. Nowick



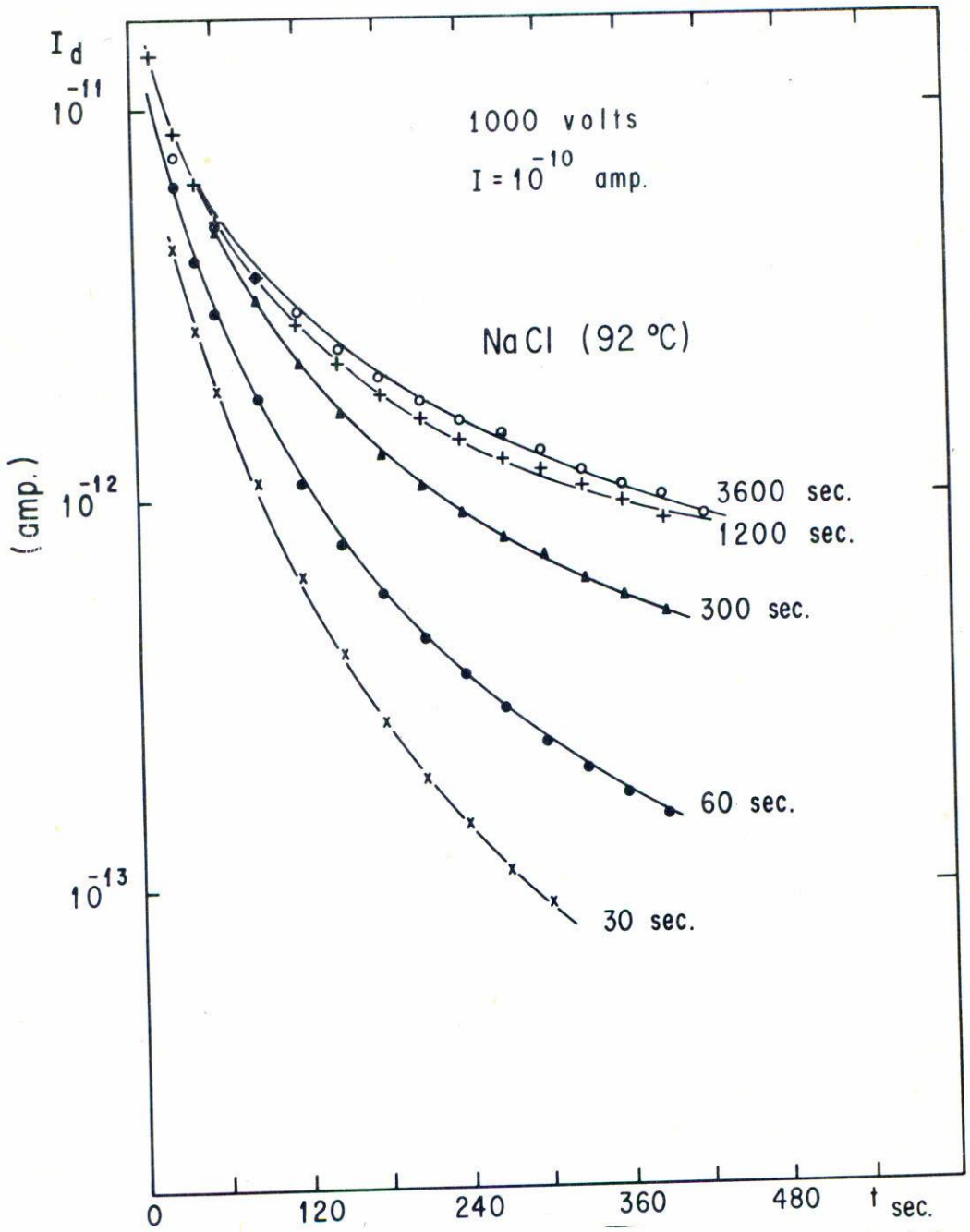


Fig. 2 Discharge current vs. time for a single crystal.  $I$  is the current circulating during the application of electric field.

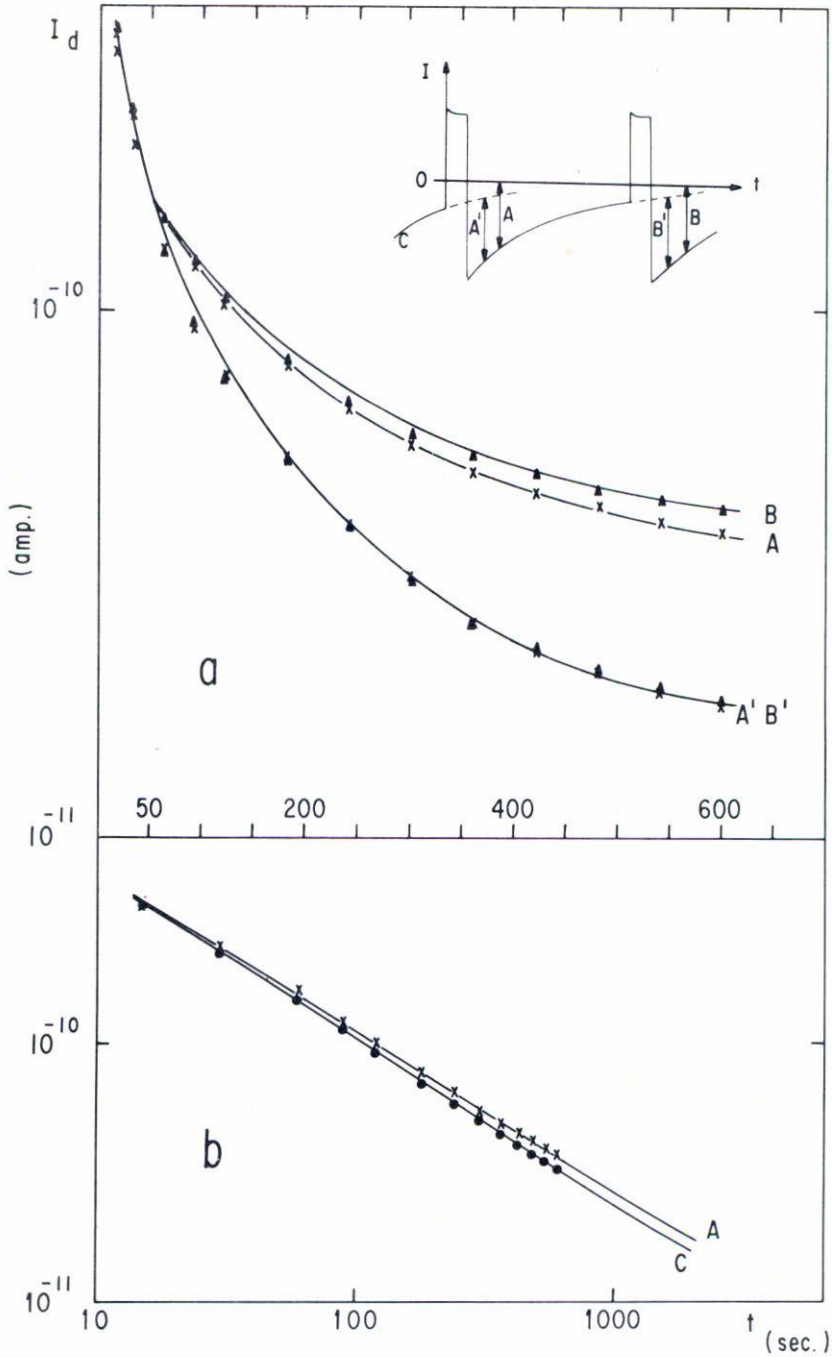


Fig. 3a and 3b Discharge currents, after having applied 1000 V during 30 sec. Curve B was obtained after the application of another pulse at the end of curve A. The insert shows the relationship between C, A', A, B' and B.

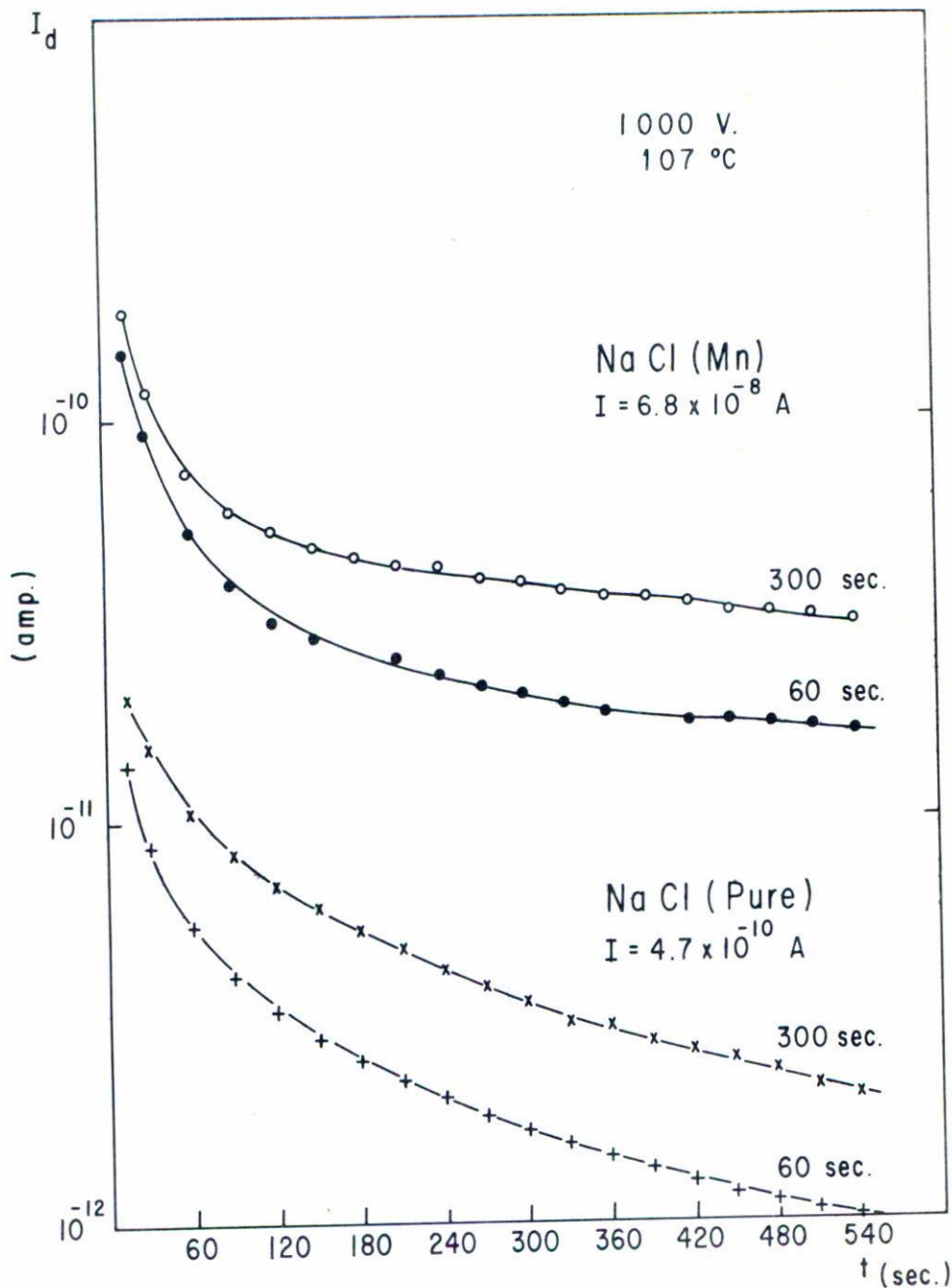


Fig. 4 The discharge current as a function of time showing the influence of impurity addition (Mn) and pulse width.

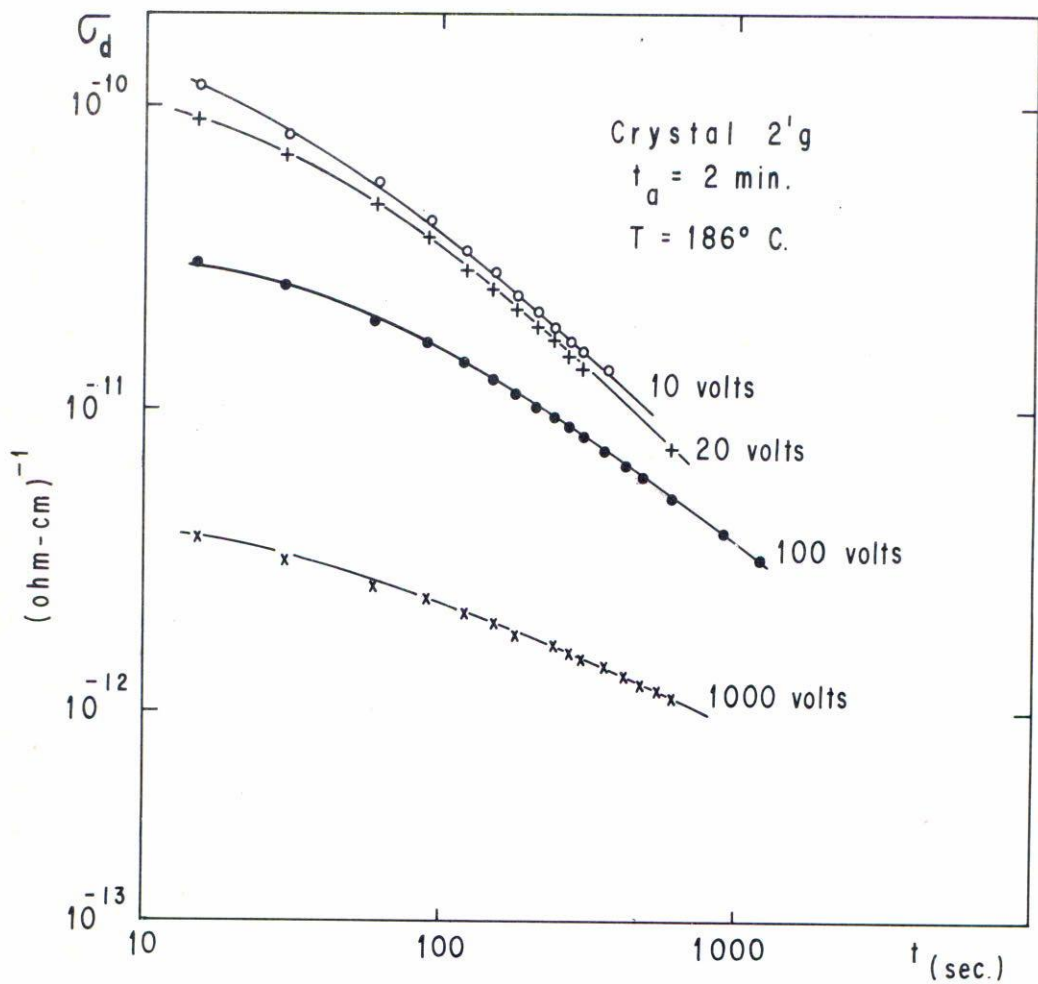


Fig. 5 Typical variation of discharge conductivity with time at different voltages in NaCl (Mn).

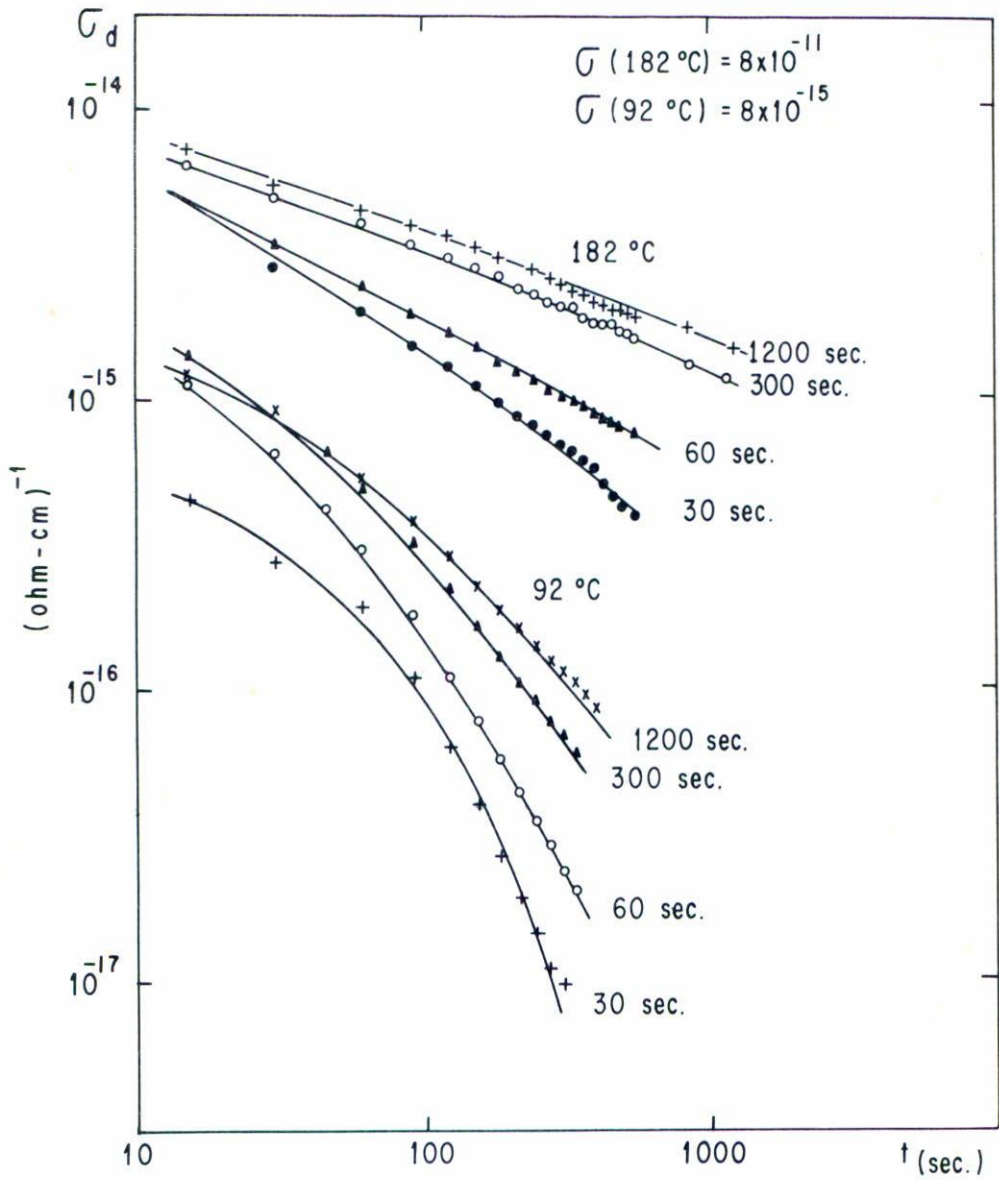


Fig. 6 The discharge conductivity as a function of time showing the influence of temperature and pulse width.

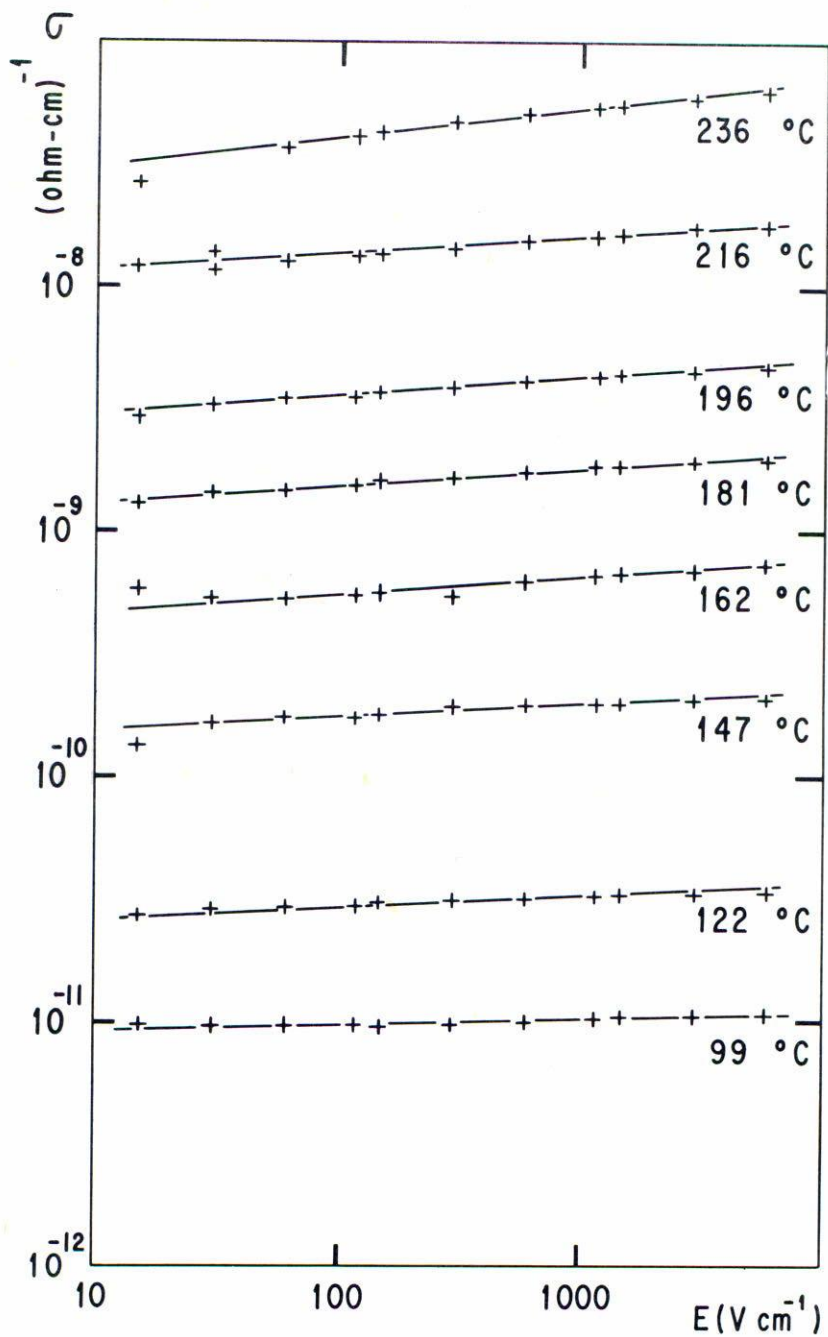


Fig. 7 Typical results obtained for  $\sigma$  v.s. Electric field.  $\sigma$  was measured after the application of the field.