HIGH TEMPERATURE ELECTRICAL BREAKDOWN IN SODIUM CHLORIDE

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Summary

Doubt exists as to the mechanism responsible for electrical breakdown in alkali halide crystals at temperatures where the breakdown strength has generally been found to fall with rise in temperature. As thermal breakdown may be involved, experiments designed to examine this possibility in sodium chloride at 350 °C have been conducted. It is shown that when linearly rising voltage transients are applied the dependence of breakdown strength on electrical conductivity, time, and energy input is in agreement with the impulse thermal theory for times to breakdown of the order of milliseconds. Conduction of heat is found to be an important factor as the time to breakdown is increased. Effects, such as dendrite growth, which are seen after breakdown with 10-second transients, are also discussed.

I. INTRODUCTION

The d.c. electric strength of alkali halide monocrystals as a function of temperature exhibits a maximum in the neighbourhood of 50 °C. In the low temperature region, where measurements have been taken at temperatures down to that of liquid air, the electric strength rises slowly with increasing temperature and is, generally speaking, independent of the rate of application of voltage. Breakdown is believed to be primarily the result of an electronic instability and the various theories (e.g. Frohlich 1937 ; Frohlich and Paranjape 1956) based on this mechanism are in reasonable agreement with experiment.

In the high temperature region where the upper limit of most measurements is about 200 °C, the situation is much more obscure. In tests employing d.c. voltages rising to breakdown in times of the order of seconds, the electric strength generally falls rapidly with rise in temperature ; but there is disagreement when breakdown is initiated in much shorter times. Thus Alger and von Hippel (1949) and Konorova and Sorokina (1957) find an increase in breakdown strength resulting from the application of a single linearly rising transient to breakdown. On the other hand, Calderwood and Cooper (1953) find no time dependence when breakdown results from a succession of 1/50 μs impulses of increasing amplitude.

As a qualitative explanation of their results, Alger and von Hippel suggested that breakdown in the high temperature region is still basically the result of an electronic instability but modified by the presence of ionic space charge. The time dependence suggests also the possibility of thermal breakdown, but most authors tend to discount this. O'Dwyer (1960), however, recently considered

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such mechanism as a serious possibility and suggested that this temperature region may be a transitional one in which thermal and intrinsic breakdown compete. Experimentally, there is some evidence both for and against thermal breakdown at temperatures above 200 °C (cf. Inge and Walther 1925 ; Inge, Semenoff, and Walther 1925 ; von Hippel 1936 ; Andreev 1958).

It is to be noted also that differences in ionic conductivity of alkali halide crystals should influence the breakdown strength if breakdown is of thermal nature. An investigation at temperatures between $-195°$ and 220 °C with crystals of varying conductivity due to the addition of divalent impurities was recently conducted by Cooper, Higgin, and Smith (1960). A pronounced effect was found in the case of potassium chloride and this result was interpreted qualitatively in terms of ionic space charge. However, the conductivity appeared to have little effect on the breakdown strength of sodium chloride in the high temperature region.

In view of the above, it is considered that in the first instance a thorough study of breakdown at a sufficiently high temperature should be attempted. If features characteristic of thermal breakdown are found, then these features may well prove of assistance in sorting out the difficulties of the lower temperature region.

The following work reports an attempt to elucidate the breakdown mechanism in sodium chloride at 350 °C, by specifically seeking to test the predictions of the impulse thermal theory at this temperature.

II. The Thermal Theory of Breakdown

The theoretical treatment of thermal breakdown starts with the general equation

$$C_v dT/dt - \text{div} (\varkappa \text{ grad } T) = \sigma F^2, \qquad (1)$$

where C_v is the specific heat per unit volume, $\varkappa$ the thermal and σ the electrical conductivity of the material, F the field strength, T the temperature, and t the time.

Solutions of this equation can be found for two limiting cases. The first of these relates to what may be termed steady-state thermal breakdown, for which the first term is small. It can then be shown that a maximum thermal voltage V^* exists for an indefinitely thick specimen (Whitehead 1950).

The second approximation relates to impulse thermal breakdown when the rate of increase of field is such that the heat conduction term may be neglected. For alkali halides when subject to a linear dependence of field on time, O'Dwyer's result† is

$$F^* = \{3 C_v k T_0^2 / \sigma_1 \varphi t^*\}^{\frac{1}{2}}, \qquad (2)$$

where F^* is the breakdown field strength, t^* time to breakdown, σ_1 ionic conductivity at ambient temperature T_0, φ activation energy for processes involved in ionic conduction.

† Equation (2) differs from O'Dwyer's equation (10) in the power of T_0. This is corrected by O'Dwyer (personal communication).

Implicit in (2) is the fact that, in the absence of heat conduction, the total prebreakdown energy input per unit volume to the crystal should be a constant at a given ambient temperature; independent of the time of application of voltage or conductivity of specimen.

III. METHOD

Many workers (see e.g. Kelting and Witt 1949) have shown that in the "structure sensitive" region the ionic conductivity of the alkali halides is markedly influenced by the addition of small amounts of divalent impurities. Thus, in order to investigate the dependence of F^* on σ_1, both "pure" specimens and specimens containing the divalent impurity manganese were grown from the melt.

The conductivities of the specimens, which were of the plane-recessed type, were not measured directly. Instead, care was taken to produce specimens of nearly the same minimum thickness and cavity shape. With such specimens it was possible to compare individual behaviour. In particular, the variation of conductivity with samples of differing purity could be obtained in terms of their variation in resistance and prebreakdown energy inputs could be compared at different rise times.

In order to obtain as many measurements as possible on a single boule, the slab size was made approximately 1 by 1 by $0 \cdot 25$ cm. The crystal recess was produced on a spherical lap of radius $0 \cdot 4$ cm, and the minimum thickness was held within the limits $0 \cdot 20 - 0 \cdot 22$ mm as read by a dial-gauge micrometer.

The specimens were usually highly polished prior to coating under vacuum. A thin film of silver was evaporated onto the cavity and its projection on the plane side. This relatively clean and uniform film was then thickened by painting with a suspension of silver in toluene, as experience showed that the evaporated film was unable to withstand the high prebreakdown currents observed. The specimens were not annealed or heat treated apart from the steady raising of their temperature to 350 °C prior to the application of voltage.

To prevent damage to the film and stress on the crystal in the region of minimum thickness, the upper electrode contacted the walls of the recess near the rim. For low field strength measurements, this electrode was a stainless steel sphere. For higher fields a stainless steel disk suitably contoured at the edges was used. The latter was surrounded by a quartz tube which rested on the top of the crystal. Silicone grease was smeared on the surface of the crystal and this combination proved very effective in preventing flash-over. The lower electrode in both cases was a polished flat aluminium block on which the crystal was placed. Of the various electrodes, only the lower one could have any appreciable influence on the thermal conditions of test. Dry, oxygen-free nitrogen gas was continuously passed through the breakdown apparatus.

Measurements were made with linearly rising voltages, the time to breakdown being variable between 10 s and $3 \cdot 5$ ms. For the 10-second measurements, the crystal was placed across the output of a rectified supply and the voltage increased linearly by means of a motor-driven auto-transformer connected to the input in the manner adopted by Andreev (1958). For impulse measurements between

PLATE 1

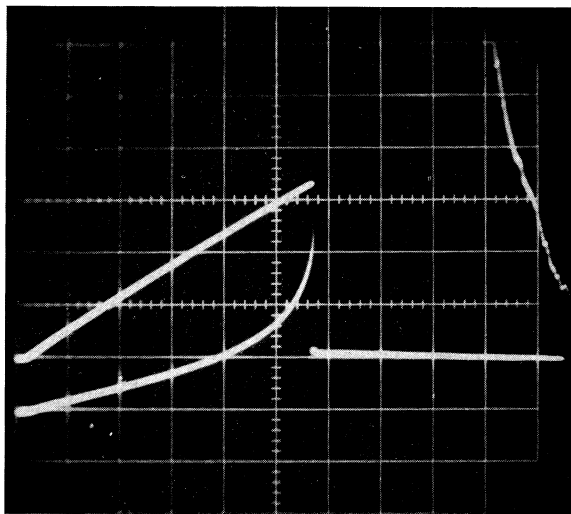ELECTRICAL BREAKDOWN IN SODIUM CHLORIDE

Fig. 1.—Oscillogram of voltage across crystal (upper trace) and current through crystal (lower trace) as function of time up to breakdown. Time/cm = 20 ms; current/cm = 5 mA; voltage/cm = 1000 V.
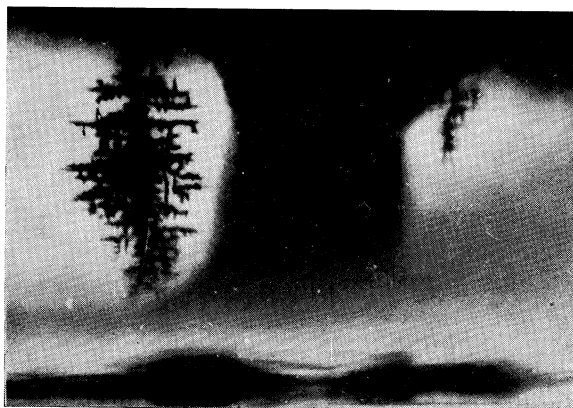

Fig. 2.—Alkali metal dendrites to either side of the breakdown track in sodium chloride doped with Mn^{++}. Specimen viewed through a plane at right angles to the plane of the cathode. Cathode uppermost.

0·1 s and 3·5 ms a generator having a maximum output of 10 kV was developed. The linearly rising output of this generator could be preset as desired and was not influenced by load currents of magnitudes less than 250 mA. The voltage across the specimen and the current through it were displayed on a precision double-beam oscilloscope. The breakdown voltage was also recorded on a peak voltmeter. The error in voltage measurement should not exceed $\pm 3\%$.

IV. Results and Discussion
(a) Crystal Properties

The crystals used have been classified according to their properties as shown in Table 1.

The values quoted for the resistances have been obtained from the oscillograms of current through the specimen and voltage applied as function of time. A typical oscillogram is shown in Plate 1, Figure 1. Only values on the linear portion of the I,t curve where Ohm's law is valid have been chosen to compute R_1. No systematic change in this initial value of resistance was found with

TABLE 1
SODIUM CHLORIDE CRYSTALS

Crystals	Concentration of Mn++ in the Crystal (approx. mole fraction)	Mean Resistance R_1 of Samples at 350 °C (MΩ)
Pure 1	—	1·26
Pure 2	—	0·56
Pure 3	—	0·36
Doped 1 ..	$1·2 \times 10^{-5}$	0·16
Doped 2 ..	8×10^{-4}	0·0175

impulses of differing duration. The scatter in resistance from sample to sample of the same crystal was of the order of $\pm 10\%$ about the mean and was dependent to some extent on variation in thickness and coated area. It is to be noted that, while individual members of each " pure " crystal do not differ greatly, the variation between types 1, 2, and 3 is marked, even though each was grown using the same technique from reagent grade salt.

To determine whether the activation energy φ differed significantly between crystals, a low voltage measurement was made of R over the temperature range 150–350 °C for selected specimens. In every case, a linear plot of log R versus $1/T$ was obtained and φ determined from the slope. For all specimens the values of φ were found to lie in the range $0·94$–$1·1$ eV; the first four crystals of Table 1 being close to the lower value.

It can be concluded that the effect on F^* of variation in φ need not be considered in testing the predictions of (2).

(b) Breakdown Measurements

Each breakdown resulted from the application of a single linearly rising transient to the specimen. A summary of the breakdown measurements taken

on 110 samples at 350 °C is given in Table 2.   The field in all cases was applied in the (100) direction.   The scatter in F^* for the 10-second breakdowns was as high as $\pm 30\%$ about the mean.   For all other measurements, however, the scatter did not exceed $\pm 10\%$.

(i) *Input Energy to Specimens.*—The prebreakdown energy input to the samples, namely $\int_0^{t^*} VI\,dt$, was evaluated graphically using the oscillogram data.   Errors involved should not exceed $\pm 15\%$.   The results as shown in columns (3) of Table 2 are of interest in two respects.   Firstly, the energy requirements for the faster rise times are considerably less than those for the 10-second breakdowns ; and secondly, the values tend to a constant $0\cdot4$ joule, irrespective of the type of crystal, as the time to breakdown is reduced.

A natural interpretation is provided by the thermal mechanism.   At 10 s, and to a lesser extent at $0\cdot1$ s, it would appear that conduction of heat from the hottest region of the specimen is of importance.   To interpret fully these results would require the solution of the complete equation (1) subject to the thermal and electrical conditions of test.   On the other hand, the constancy of energy input at times of the order of milliseconds is strongly indicative of impulse thermal breakdown and it is expected that equation (2) would then be applicable.

O'Dwyer (1960) estimated the order of the rise time which separates steady state from impulse thermal breakdown.   His estimate of $0\cdot1$ s is seen to be in reasonable agreement with these results.

Another feature of the results, most noticeable at $0\cdot1$ s, is a diminishing energy requirement for samples of decreasing purity.   This may possibly be interpreted in terms of a reduced thermal conductivity for impure specimens.

(ii) *Conductivity and Time Dependence.*—In Figure 1 mean breakdown field strength is plotted against the square root of resistance (as obtained from Table 1) for various values of time to breakdown.   The linear relationship obtained strongly supports the dependence of F^* on σ_1 as given in (2) for the range of times investigated.   It is to be noted that a linear dependence is obtained not only at times appropriate to impulse thermal breakdown but also at times to breakdown of $0\cdot1$ and 10 s.   This is to be expected on the basis of thermal theory (Whitehead 1950).   Hence the results support the deduction made in Section IV (b) (i) relating to appreciable heat conduction at these longer times to breakdown.

In Figure 2 the dependence of F^* on t^* is shown for the different conductivity crystals.   The prediction of (2) in this respect is reasonably well obeyed for times of the order of milliseconds (as indicated by the solid lines).   In view of the discussion in (i), the time dependence would need to be modified at the longer rise times when heat conduction is a factor.   It is not to be anticipated that in this case a simple relationship of the type found in (2) would apply.

(iii) *The Current Curve.*—For all measurements the current curve displayed the same characteristic form as shown in Plate 1, Figure 1, namely, a linear portion giving way to gradually increasing curvature as breakdown is approached. This implies that the same basic breakdown mechanism was operative in all cases.   It is interesting also to compare the current curve obtained for samples

TABLE 2

ANALYSIS OF BREAKDOWN MEASUREMENTS ON SODIUM CHLORIDE AT 350 °C

Time to Break-down (s)	Pure 1			Pure 2			Pure 3			Doped 1			Doped 2		
	(1)	(2)	(3)	(1)	(2)	(3)	(1)	(2)	(3)	(1)	(2)	(3)	(1)	(2)	(3)
10	0·096	11	15–20	0·053	6	15–20	0·048	8	15–20	0·032	15	15–20	0·011	10	15–20
0·1	—	—	—	0·142	3	1·2	0·108	5	0·88	0·076	7	0·80	0·024	6	0·67
0·012	—	—	—	0·298	3	0·49	0·24	5	0·49	0·15	5	0·39	0·053	4	0·40
0·0035	—	—	—	—	—	—	0·43	8	0·43	0·30	7	0·42	0·088	7	0·40

(1) Mean breakdown field strength (MV/cm).
(2) Number of observations.
(3) Prebreakdown energy input to crystal (J).

of a given crystal at a fast rise time with the current curve obtained for samples of the same crystal at a slow rise time. It is then found that the curve in the first case is linear at fields where in the second case curvature is apparent. Thus it may be concluded that the conductivity is an implicit function of the field and not an explicit one. An interpretation of this implicit behaviour in terms of the thermal mechanism is provided by the strong dependence of ionic conductivity on temperature ; both increasing as thermal instability sets in.

The magnitudes of the currents near breakdown are of interest. These were relatively high and ranged from a few milliamperes for pure specimens in the case of the 10-second measurements to nearly 200 mA at 3·5 ms for the most impure samples.
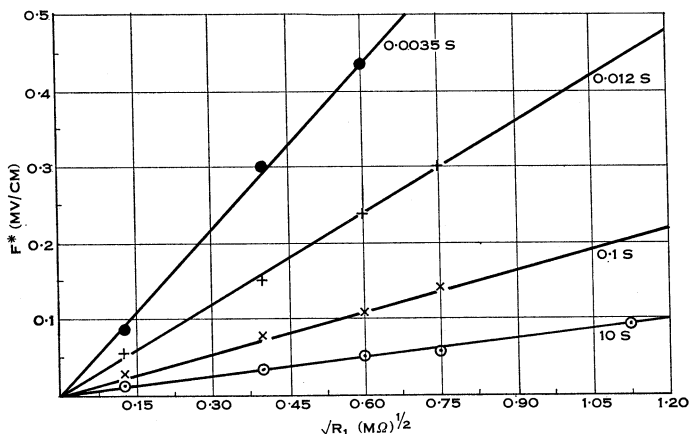

Fig. 1.—Mean breakdown strengths of sodium chloride crystals as a function of the square root of their mean resistances at 350 °C (given in Table 1) for various times to breakdown.

The current through the specimen is an aspect which has received relatively little attention in the past. Buehl and von Hippel (1939) carried out measurements at room temperature with slowly increasing fields and other workers (cf. Cooper, Higgin, and Smith 1960) have commented on the current attained just prior to breakdown. The difficulties involved in measuring small currents, particularly under pulse conditions at low temperatures, are considerable. However, it is considered that the possibility which this feature presents of obtaining additional information regarding the breakdown mechanisms deserves further attention.

(iv) *Other Effects.*—While the observations recorded in Table 2 all relate to breakdown through the region of minimum thickness of the crystal, a number of observations were recorded in which this was not the case. Examples were to be found in all crystals tested at 10 s but were particularly prevalent with the doped 2 specimens. In contrast to this not a single case of off-centre breakdown was observed at the faster rise times.

A natural explanation of this is in terms of the energy input to the samples. The latter amounted to some 15–20 joules, so that considerable heat must have

been conducted away from the hot region of the specimen. It may be expected that, if the flow of heat were impeded in any way, thermal instability could arise in regions other than the thinnest section. Such interference could conceivably arise from crystal imperfections or irregularities in thermal contact with the aluminium block.

Microscopic examination with transmitted light of most pure specimens and a few doped 1 specimens revealed patchy areas of blue colouration surrounding the breakdown track and nearest the cavity (10 and 0·1 s investigations only). A considerable body of evidence exists to show that such colouration in alkali halides is due to alkali metal colloidally precipitated (cf. Amelinckx 1956 ; Symons and Doyle 1960). Moreover, electrolysis of alkali halides in non-uniform
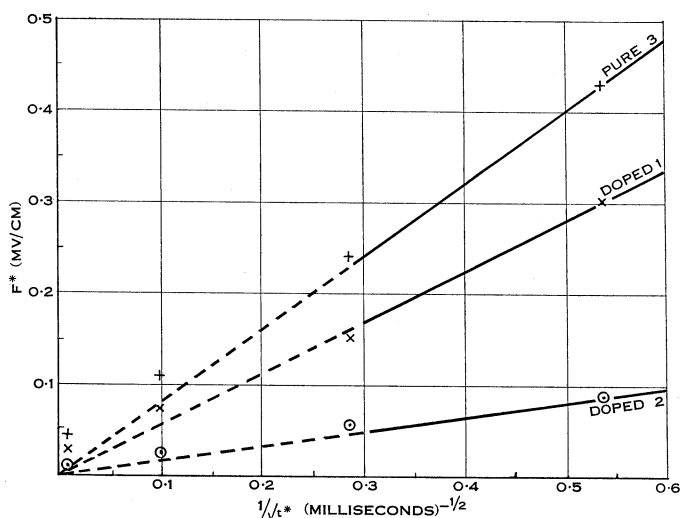

Fig. 2.—Mean breakdown strengths of sodium chloride crystals at 350 °C as a function of the inverse square root of time to breakdown.

fields at high temperatures is a well-known technique for production of F centres. Such centres in sodium chloride are not stable and readily transform to the colloid on slow cooling. In this regard, the absence of patchy colouration in the doped 2 specimens and in most doped 1 specimens is to be expected, as it is also known that small amounts of divalent cations can greatly inhibit colloid formation (Heiland and Kelting 1949).

On the other hand the doped specimens revealed in a few cases at 10 s colloids in the form of alkali metal dendrites of which Plate 1, Figure 2, is a particularly striking example. The presence of such dendrites in very non-uniform fields at high temperatures led von Hippel (1936) to propose dendrite breakdown as a possible mechanism.

The role played by impurities and dislocations in colloid formation is only partially understood. The absence of blue colouration and dendrites with decreased time to breakdown would seem to indicate that time or energy is an

important factor in their production. It may be that, while breakdown is primarily the result of an initial thermal instability, other processes such as dendrite formation take over if inhomogenities in the field develop with time. Such inhomogenities may result from non-uniform heating due to the current or from imperfections in the crystal or in the metal coatings. However, the agreement with the predictions of thermal breakdown found previously is such that whatever role these other effects play it would appear to be a secondary one only, at least when uniform fields are employed.

V. Conclusions

The evidence presented above supports the thermal mechanism as the one involved in the breakdown of sodium chloride at 350 °C for the range of rise times employed. The predictions of equation (2) relating to conductivity, time, and energy input are shown to be well obeyed when breakdown is initiated in times of the order of milliseconds. The results obtained with increased times to breakdown show the expected electrical conductivity dependence when heat conduction is a factor. Crystal purity is seen to have a most important influence on the breakdown strength at 350 °C. The current through the crystal provides additional evidence as to the operative mechanism. Extension of this work to successively lower temperatures may lead to some clarification of breakdown results found in that region.

VI. Acknowledgments

VII. References

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