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Scattering, Trapping, and Release of Electrons in NaCl and in Mixed Crystals of NaCl and AgCl

A. von Hippel and G. M. Lee
Massachusetts Institute of Technology, Cambridge, Massachusetts

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The dielectric strength of the alkali-halide crystals decreases steeply with temperature in the higher temperature range. This fact cannot be explained by thermal breakdown, but it points towards a new mechanism which has been investigated in rocksalt and mixed crystals of NaCl and AgCl. The facts observed can be explained by the assumption that the intensity of the electron avalanches is decisively influenced by trapping of secondary electrons in the lattice, and their release by heat vibrations. New spectroscopic evidence for the trapping mechanism is presented.

In the preceding paper[1] an intimate connection was found between the periodic structure of an ionic crystal and the increase of its dielectric strength with temperature. Still unexplained remains the fact that the breakdown characteristic, as our measurements on KBr show,[2] traverses a maximum and falls steeply again at higher temperatures. Thermal breakdown cannot be held responsible: our current-voltage characteristics indicate a discontinuous break without creeping; the breakdown path follows preferential directions; and moreover, the heat conductivity of the alkali halides is comparable to that of iron. To learn more about the situation, we investigated the breakdown characteristic of rocksalt and the influence of increasing amounts of AgCl upon it.

Mixed Crystals of NaCl and AgCl

Sodium ions in rocksalt can be replaced to some extent by silver ions, effecting a remarkable increase in the breakdown strength of the crystal at room temperature. This had been previously established[3] but because the research had to be interrupted, a characteristic of dielectric strength *versus* composition had been given, based upon the concentration of the melt.* In our new investigation we have checked the silver concentration of the crystal samples used: pieces of the same section were dissolved in a 0.01 normal solution of KCN containing an addition of KI and ammonia. The solution was back-titrated with a 0.01 normal $AgNO_3$ solution, and the turbidity point observed.[4] This method gave very consistent and reproducible results in the crystals weighing as little as $\frac{1}{10}$ g and showed that 10 percent, 5 percent, and 1 percent molar concentration of AgCl in the melt corresponded to about 3 to 5 percent, 1.5 to 3 percent, and 0.3 to 0.5 percent concentration in the crystal. The silver content of a mixed crystal showed local variations from section to section, according to the concentration of the remaining molten material.

Figure 1 gives our new characteristic of breakdown strength *versus* composition at 22°C. The values measured agree well with the old ones if the changed horizontal scale is taken into account. Preliminary measurements indicate that the breakdown strength of the clean silver chloride is of the order of 1.7×10^5 v/cm.

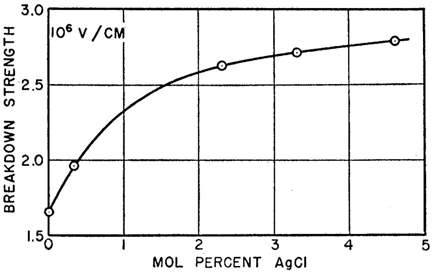

Fig. 1. Breakdown strength of mixed AgCl–NaCl crystals at 22°C.

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[1] A. von Hippel and R. J. Maurer, Phys. Rev. **59**, 820 (1941).

[2] R. C. Buehl and A. von Hippel, Phys. Rev. **56**, 941 (1939).

[3] A. von Hippel, Zeits. f. Physik **88**, 358 (1934).

* The crystals used by us were grown by the Kyropoulos method (S. Kyropoulos, Zeits. f. anorg. Chemie **154**, 308 (1926)). The samples used in breakdown measurements were split from them to between 1 to 2×10^{-2} cm thickness.

[4] J. M. Kolthoff and J. B. Sandell, *Textbook of Quantitative Inorganic Analysis* (Macmillan, New York, 1936), p. 545.

Mixed crystals with more than about 7 percent of silver content are unstable, and the samples in the limiting range are inclined to form multicrystals and to crack easily. Consequently the characteristic can be measured only over a small range of concentrations, but its general shape and the known curves for mixed crystals between alkali halides[3] seem to imply that the increase in dielectric strength is an effect analogous to the increase in resistivity observed in metallic solutions.

BREAKDOWN CHARACTERISTICS AS A FUNCTION OF TEMPERATURE

Using the apparatus and procedure described in the preceding paper, we have measured the temperature characteristics of our mixed crystals (Fig. 2). The result is surprising and reveals a more complicated picture than was anticipated. At low temperatures the breakdown characteristics of pure NaCl and of the mixed crystals have about the same slope; increasing silver content displaces the curves to higher values. The higher the silver concentration the sooner the dielectric strength reaches a maximum and the steeper is the negative slope thereafter. Consequently the curves cross, and while at room temperature and below, the breakdown strength of rocksalt is increased by the addition of silver, the opposite is true above 100°C.

It has been demonstrated in the preceding paper[1] that the *motion* of electrons in ionic crystals is impeded by temperature vibrations disordering the lattice structure. Nevertheless, the formation of electron avalanches producing breakdown is favored by heating of the material, as the falling part of our characteristics indicates. It can only be concluded, if the avalanche picture is accepted, that the *number* of free electrons produced by impact per unit length of path increases rapidly with temperature.

At a first glance this conclusion seems strange but it can be supported by other evidence: We are accustomed by Townsend's theory of gas breakdown to assume that electrons multiply in avalanches in exponential fashion:

$$n = n_0 \exp\left[\int_0^x \alpha dx\right]. \tag{1}$$

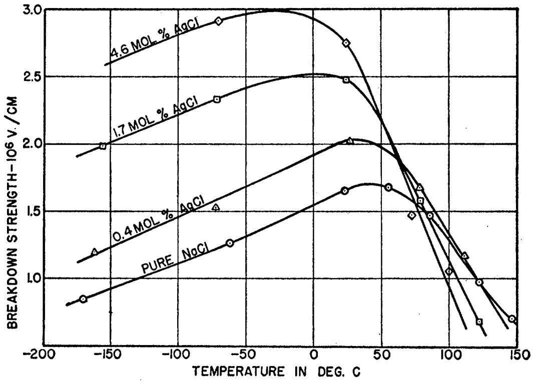

FIG. 2. Temperature dependence of the breakdown strength of mixed AgCl–NaCl crystals.

This formula assumes that the secondary electrons stay free and participate in the ionization process; the factor α describes the probability of ionization. For breakdown in electro-negative gases this is not true any more, because electrons may be *trapped* while they are slow. The intensity of ionization decreases with increasing probability of capture, c:

$$n = n_0 \exp\left[\int_0^x (\alpha - c) dx\right]. \tag{2}$$

A discharge is quenched by the addition of electro-negative gases. The negative ions formed may, on the other hand, release the trapped electrons again under the influence of violent collisions, as Loeb has first shown[5] for the O_2^- ion. Consequently a probability of reliberation, r, has to be introduced, and the increase of an avalanche, started by n_0 primary electrons and growing by impact ionization, has to be described by the general expression:

$$n = n_0 \exp\left[\int_0^x (\alpha - c + r)\right] dx. \tag{3}$$

This situation apparently exists in our ionic crystals. Electrons are trapped in the alkali halides, as the appearance of the "*F*" band indicates;[6] the spectral position of this band corresponds to the energy needed for their photoelectric liberation. Electrons can be reliberated

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[5] L. B. Loeb, Phys. Rev. **48**, 684 (1935).

[6] See, for instance, R. W. Pohl, Proc. Phys. Soc. **49**, 3 (1937).

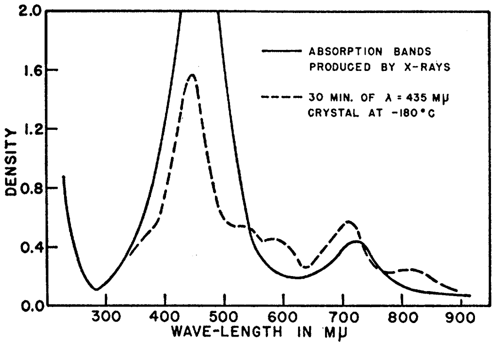

FIG. 3. Absorption bands in NaCl.

by heat vibrations, as Stasiw first found,[7] because the band of trapped electrons at high temperatures moves in an electric field like an electronic cloud. The probability of trapping is increased by the addition of AgCl to NaCl;[8] the migration of the color centers slows down and can be entirely suppressed if sufficient silver is added. If we could show that at moderate temperatures the probability of reliberation is sufficient for the electrons to be reinstated quickly into the avalanches, our results of Fig. 2 would be understood. The increase in breakdown strength with temperature would be due to the scattering and trapping of electrons; the decrease would result from their release, which apparently is favored by mounting silver concentration.

Avalanches producing breakdown will have a critical magnitude. On the basis of the mechanism proposed above, one would expect that the length of these avalanches is dependent on temperature. For sufficiently thin samples ($<10^{-4}$ cm) the breakdown strength should therefore be a function of thickness varying with temperature.

THE TRAPPING OF ELECTRONS

If the "*F*" band, as one of us believed until recently,[9] corresponds to the trapping in the free lattice, the chance of liberating electrons from the band indicated by this spectral position through thermal motion at the temperatures of our experiments would be small indeed. On the other hand, de Boer[10] and Mott and his coworkers[11] have proposed another model for the "*F*" band: an electron captured at a lattice defect where a negative ion is missing. If that is true, a band corresponding to the electron in the lattice should be found at a longer wave-length, because this state would be an excited state of the first one. To decide this question, J. P. Molnar has at our suggestion reinvestigated the absorption spectra of the alkali-halide crystals between 10,000 and 2000A. If the band in question exists, it should be found by exposing the crystals to x-rays at low temperatures. Electrons ejected into the lattice under this condition could be trapped with reasonable probability in the flatter but much more frequent potential hole of the free lattice[9] and stay there, while at higher temperatures they would be shaken out frequently enough so that they would all be found in the deeper hole corresponding to the "*F*" absorption.

This expectation has been fulfilled. Molnar has found in all the alkali halides a band accompanying the "*F*" band at longer wave-lengths. It is of the small width to be expected for atomic centers, can be bleached, and disappears by heating.* Figure 3 shows the situation for NaCl, indicating the position of the band at 1.75 ev. A theoretical calculation for the position of the band, made by a cycle process before this result was known,[9] gives 1.63 ev; the agreement, while encouraging, is better than the theoretical data justify.

That electrons are trapped high above the "*F*" band in our mixed crystals, and then released by heat vibrations, can be demonstrated in a different way. Under x-ray illumination the crystals are strongly phosphorescent at room temperature. The light emitted is bluish, and preliminary measurements indicate that the end state of the electrons lies in the near ultraviolet shortly below the "*F*" band. Measurements of the initial state and its sensitivity to temperature and field strength and of the light emitted will give us, we hope, the final link between the temperature dependence of the breakdown strength and the spectroscopic properties of our crystals. We are engaged in this study.

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[7] O. Stasiw, Goettingen Nach. No. 50 (1933).

[8] A. von Hippel, J. App. Phys. **8**, 829 (1937).

[9] A. von Hippel, J. Chem. Phys. **8**, 605 (1940).

[10] J. H. de Boer, Rec. Trav. Chim. Pays-Bas **56**, 301 (1937).

[11] N. F. Mott, Trans. Faraday Soc. **34**, 822 (1938).

* Doctorate thesis of J. P. Molnar, Massachusetts Institute of Technology (1940), to be published shortly.