

NOTES ON DIELECTRIC DISPERSION IN IONIC SOLIDS

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NOTES ON DIELECTRIC DISPERSION IN IONIC SOLIDS

By

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Abstract

Effect of electric potential due to static double layer on a.c. capacitance is here discussed for ionic solids. It is emphasized that resultant field, arising from mobile space charge, ordinary dielectric polarization and static double layer, may explain high capacitance values measured by Friauf. Finally precise measurements of dielectric loss vs. temperatures for silver halides with various purities are proposed in order to provide useful informations on static double layer.

Outline of the problems

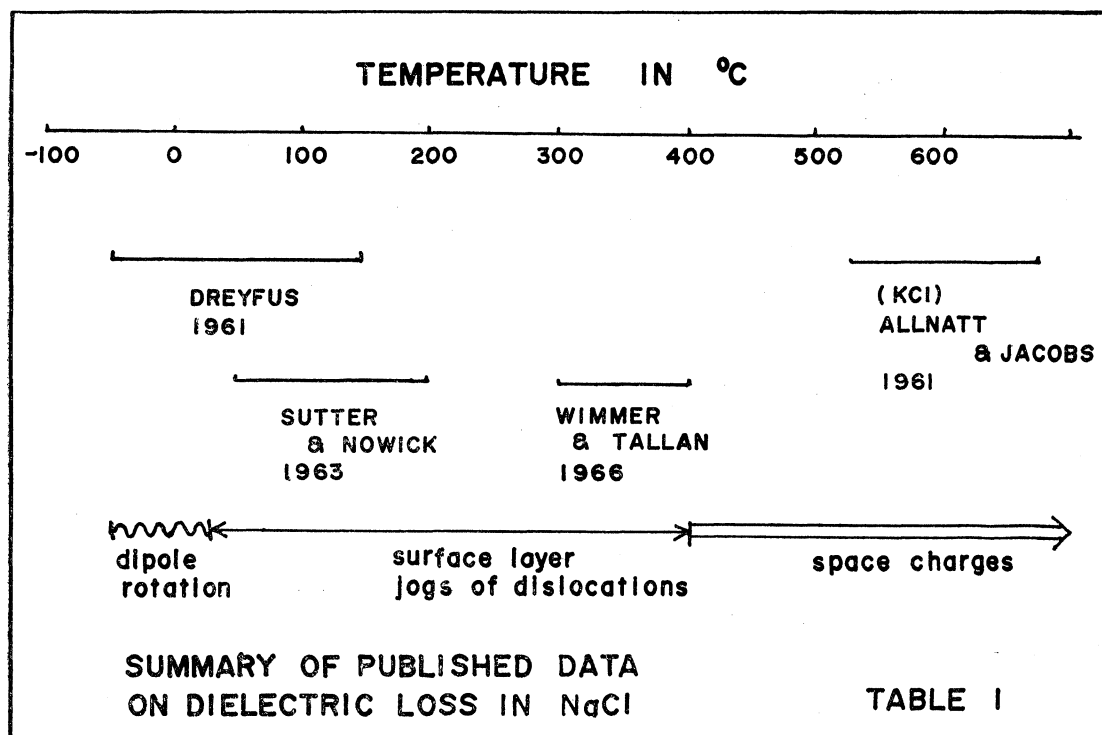
Since the pioneering works on dipole relaxations in ionic solids by Breckenridge¹⁾, many stimulating experiments²⁾ have been carried out for the past two decades in order to explore dielectric loss mechanism in ionic solids and more recently in ionic thin films³⁾. In reviewing existing data, it seems that dipole relaxation (so-called center relaxation) and space charge polarization are two predominant causes. Wimmer and Tallan⁴⁾, however, insist that what they call surface insulating layer plays a central role in the temperature range of 300° to 400°C in sodium chlorides. Also Solomon *et al.*⁵⁾ have done the measurements on low frequency capacitance and current decay in a unique ionic solid, Lanthanum trifluoride LaF₃. Their data are well understood in terms of ionic surface states very near the surface.

In case of alkali halides one could summarize the data already published as shown in Table I. One mechanism is predominant over the other depending on temperatures, although clear separation among these may be difficult. Mobile space charge contributes to polarization at higher temperatures in the range of 400°C and up.

There are only scattering works on dielectric dispersions for silver halides. Friauf⁶⁾ measured a.c. capacitance of AgBr sandwiched by silver and gold electrodes at the temperatures of 200°C through 280°C. Qualitative agreement was obtained between experiment and theory. Raleigh⁷⁾ developed the sophisticated solid polarization cell to measure differential capacitance under no bulk ionic current. His results are in accord with the surface double layer model.

The main objects of this paper are to put an emphasis on importance of the presence of static double layers inherent in ionic solids and to propose some interesting experiments.

Table 1



Discussion

Let us consider a block of silver halide single crystal in a complete thermal equilibrium. If the sample is cleaved into two halves by some means, then one could find a potential difference between the old surface and freshly cleaved surface. This is due to the fact that energies of formation of silver vacancies and interstitial silvers are different. Since crystal surface acts as a source of lattice defects, excess concentration of silver vacancies is formed just under the crystal surface, which in turn gives an interior of crystal a negative potential. Sign of the potential is dependent on temperature at which crystal maintains a thermal equilibrium; it alternates across isoelectric temperature which is roughly the same as a knee point of the plot of logarithm of conductivity vs. inverse of absolute temperature.

To simplify our consideration, the following assumptions will be made: (1) an ionic crystal contains divalent impurities so that an isoelectric temperature exists, (2) crystals have very few dislocations and grain boundaries and (3) flow of ionic current is completely blocked at the electrodes. Temperature range must be the one in which mobile charge carrier contributes to ionic polarization considerably, that is, space charge polarization is dominant. (refer to Table I) In silver halides with normal purity, it will correspond to 100°C and up. Low temperature side of the temperature would not be suitable for application of our present discussion because polarization due to impurity-vacancy dipole rotation will overshadow the other. In order to assure the assumption (2), crystal may have to be care-

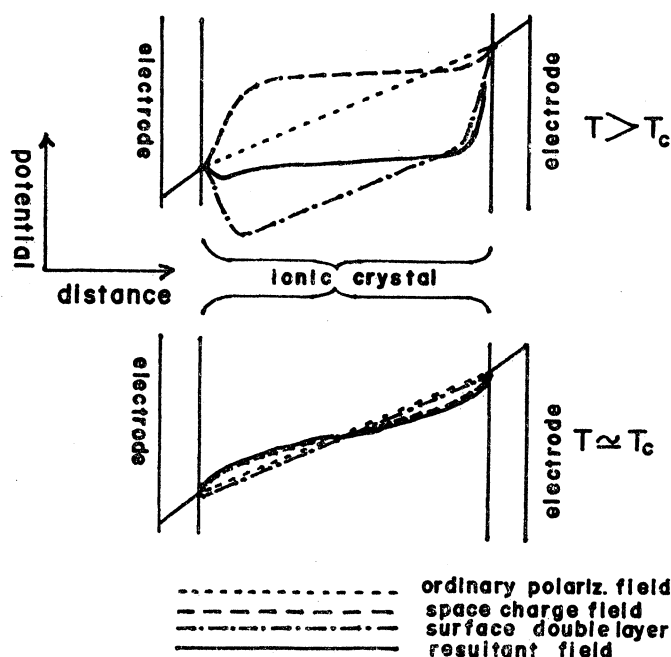


Fig. 1

fully prepared. Geometrical separation of electrodes from the crystal surface will satisfy the condition of assumption (3).

Taking into account an electrical potential due to static double layer, mobile charge carriers inside crystal under an external a.c. field are considered to be subject to three kinds of potentials due to (1) static double layer, (2) distribution of space charge blocked at electrodes and (3) ordinary polarization charges at crystal surfaces. Profile of static double layer potential depends on temperatures. Particularly, it completely vanishes at isoelectric temperature T_c . If one takes conveniently the sum of these three to find the internal field the mobile space charge would feel, then potential profile as shown in Fig. 1 may result. Here it is assumed that thickness of Debye-Hückel layer be comparable to that of static double layer.⁶⁾⁸⁾ It is seen that for temperatures above T_c rapid potential gradient occurs near crystal surface at the positive electrode. This field will accumulate negative charges. In the neighborhood of crystal surface facing negative electrode, net electrical charge would decrease because of comparable numbers of both negative and positive charge carriers. It is suggested that excess concentration just under crystal surface facing positive electrode does contribute to extra polarization. At T_c , an effect of static double layer would vanish only to leave potential due to space charges.

Friauf developed the theory on space charge polarization by solving differential equations governing time-dependent distribution of mobile charge carriers, subject to certain boundary conditions.⁶⁾ He intentionally omits the presence of static double layer because of mathematical convenience. His calculation predicts experimental results fairly well except right magnitude of a.c. capacitance. As remarked by Lidiard⁹⁾, extreme accumulation of charge carriers of one sign may lead to unexpectedly high capacitance value.

Considering the very thin layer of charge piling-up, its influence on polarization could be appreciable.

Proposed Experiments

There have been few experiments concerning dielectric loss particularly designed for sorting out the effects of static surface double layer. Prospective experiments are here proposed by using silver halide single crystals with normal purity under well-annealed conditions. Such silver halides have their isoelectric points near 100°C to 150°C, above which space charge polarization is expected to prevail. Single crystals must have the least density of grain boundaries that blocking of mobile charge carriers might be avoided at internal grain boundaries.

The first series of experiments are concerned with measurements of a.c. capacitance as a function of temperature, taking purity of specimens as a parameter. The relation between capacitance C and temperature T , expressed as logarithm of C versus $1/T$ would be essentially the same as obtained by Friauf.⁶⁾ Precise measurements will indicate, however, a 'dip' near T_c at which the effect of static surface double layer is expected to diminish. In addition, temperatures at which dips occur must be purity-dependent: the purer specimen has a depressed region at lower temperatures. It seems that the experiments must be done as precisely and continuously as possible, covering temperatures across isoelectric temperatures.

The second group of experiments involve measurements of dielectric loss at low frequencies by using silver halide thin films. Samples probably will have to be deposited at room temperature, and then annealed at desired temperatures the range of which contains an isoelectric temperature. Primary advantage in using thin films is that an effect of static double layer could be extensive compared to the case of bulk crystals.

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