

are satisfied. Then  $N = (\eta/A_1)^{1/2}$  and  $\rho \cong \gamma/(\eta A_1)^{1/2} \gg 1$ . The conditions [Eq. (6)] state that the photoelectroluminescence process should prevail; that the radiation intensity  $\eta$  should not be too large; that a certain but not too large number of traps is necessary, depending on the efficiency  $\gamma$  of the photoelectroluminescence process. This is in agreement with the qualitative aspects of the observations and their interpretation.

Under other conditions, Eq. (5) leads to other functions  $\rho = \rho(\eta)$ , which can easily be derived. In many cases,  $\rho$  does not deviate much from unity. If the electrophotoluminescence effect is prevalent ( $\gamma$  small), it readily follows from Eq. (4) that  $\rho \cong 1$ .

<sup>1</sup> D. A. Cusano, Phys. Rev. **98**, 546 (1955).

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<sup>3</sup> F. E. Williams, Electrochemical Society Meeting in Cincinnati, May, 1955 (unpublished).

<sup>4</sup> F. Matossi, Phys. Rev. **94**, 1151 (1954).

## Deformation-Induced Charge Flow in NaCl Crystals\*

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WHEN a single crystal of NaCl is plastically deformed in an inhomogeneous fashion, a transient electric current flows through the crystal, even when no external electric field is applied. This effect was observed when cleaved single crystal plates of NaCl approximately 1 mm × 10 mm × 10 mm, obtained from the Harshaw Chemical Company, were deformed in compression at room temperature. The deforming load was applied to a smaller area on one face of the specimen than on the other. A vacuum tube electrometer amplifier was used to measure the voltage developed across a 10<sup>11</sup> ohm resistor connecting the two electrodes (which also served as press platens). The resistance of the crystal specimens at room temperature was of the order of 10<sup>16</sup> ohms, as determined from the ionic conductivity.

The greatest charge flow occurs whenever a given stress is applied to the crystal for the first time; reapplication of the same stress gives much smaller effects, especially if flow had been allowed to go to completion on the first loading (as discussed below). The direction of flow is determined by the sense of the deforming stress *gradient*; negative charge flows in the external circuit away from the side of the crystal to which the higher stress is applied. This phenomenon was apparently first observed by Stepanow,<sup>1</sup> who did not, however, appreciate that the deformation must be inhomogeneous to cause a charge flow, and thus was not able to control the direction of the effect.

An example of the deformation-induced charge flow is shown in Fig. 1, where the total charge flow is about 3 × 10<sup>-11</sup> coulomb. If the deforming load increment is removed before the current has decayed to zero, the residual current drops immediately to a value near zero, as shown in Fig. 2. It should be noted that only the increment is removed; the major part of the total load remains on the crystal. On reapplying the load increment, the charge flow is resumed. Successive cycles of removal and reapplication produce successively smaller effects, as shown in Fig. 2. Removal and reapplication of the load after the current has decayed to zero produces little effect.

This deformation-induced charge flow may be observed with or without colloidal graphite electrodes painted on the crystal, with the stress axis parallel as well as perpendicular to the plane of the electrodes, and with various geometries of inhomogeneous stress. Applied electric fields have little influence on the effect. Even under fields as large as 10<sup>8</sup> v/cm, the direction of the initial charge flow produced by deformation is determined by the sense of the stress gradient rather than by the direction of the applied electric field.

The observed current cannot be attributed to a polarization process, since all charge flow produced by a given deformation is in one direction, with no appreciable current in the reverse direction even on removing the total load from the crystal. The effect of the applied stress gradient must then be similar to that of an electric field, i.e., it produces actual electrolysis of the crystal. It seems reasonable to expect that charges are liberated in the initial deformation and are continuously separated by maintaining the load (to account for the decay with time shown in Fig. 1). The results of Fig. 2 show that it is the load *increment* and not the total load which operates to separate the charge carriers in time. This suggests that the charge carriers moved by the stress must be charged dislocations. Such a concept is not unreasonable. Seitz<sup>2</sup> has shown that a jog on an edge dislocation in NaCl possesses a charge of ±e/2 depending on the sign of the last ion before the jog. Since a moving dislocation should generate vacancies

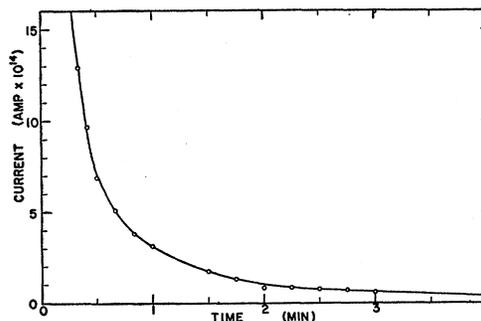


Fig. 1. Transient current produced by the inhomogeneous deformation of a NaCl crystal. At time equal zero, the load applied to the crystal was increased from 3 to 4 kg.

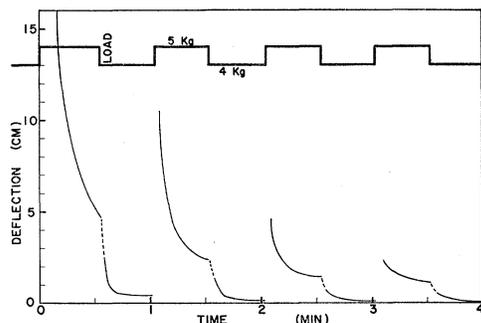


FIG. 2. The effect on the deformation-induced charge flow of removing and reapplying a load increment. The loading schedule is indicated by the heavy line at the top of the diagram. The current in amperes may be obtained by multiplying the deflection by  $5 \times 10^{-15}$ .

at jogs,<sup>3</sup> and since the energy of formation of a positive ion vacancy is probably less than that of a negative ion vacancy,<sup>4</sup> it follows that plastic flow should produce positively charged dislocations and leave behind in the lattice a net excess of (negatively charged) positive ion vacancies. When the deformation is inhomogeneous, it is then reasonable that the side on which the stress is concentrated develop a negative charge, as observed, since the positive dislocations move into the crystal, leaving behind negatively charged vacancies.

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## Self-Diffusion and Ionic Conduction in Crystals

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THE coefficient of self-diffusion  $D$  and the ionic conductivity  $\sigma$  of ionic crystals, both referring to one type of transport mechanism, are customarily related by the Einstein relation

$$\sigma/D = Ne^2/kT, \quad (1)$$

where  $N$  is the number of ions of a given kind,  $e$  the electron charge,  $T$  the absolute temperature and  $k$  Boltzmann's constant.

If the carrier of the ionic current is capable of forming electrically neutral aggregates with another imperfection (for example, with vacancies of opposite sign or divalent ions) then these neutral aggregates cannot con-

tribute to the conductivity but they may contribute appreciably to the self-diffusion. In such cases deviations from (1) may be expected (and have been found) such that  $\sigma/D < Ne^2/kT$ .<sup>1</sup>

Recently a careful study on AgCl yielded an example where  $\sigma/D > Ne^2/kT$ .<sup>2</sup> The purpose of the present note is to point to a probable explanation of this type of deviation from (1). It is based on a correction which must be applied to the customary derivations of (1)<sup>3</sup> in the case of dielectrics.

The force which an external electric potential difference  $V$ , applied across a crystal of length  $l$ , exerts on a charge  $e$  inside a polarizable medium is not  $eV/l = eE$ , but greater. The effective field  $E^*$  and the field  $E = V/l$  are related by

$$E^* = E(1 \pm \Delta). \quad (2)$$

If the charge carrier is assumed to be a sphere with dielectric constant  $\epsilon_1$  in a homogeneous medium of dielectric constant  $\epsilon_0$ , then

$$\Delta = \epsilon_1(\epsilon_0 - 1)/(2\epsilon_0 + \epsilon_1). \quad (3)$$

Equation (2) leads straightforward to a generalized Einstein equation for dielectrics:

$$\sigma/D = Ne^2(1 + \Delta)/kT > Ne^2/kT. \quad (4)$$

Equation (4) qualitatively explains the discrepancy observed by Compton and Maurer for AgCl. The conditions under which Eq. (3) is valid are not well satisfied for a conducting ionic vacancy or interstitial ion, so that (3) is only a rough approximation of the true value of  $\Delta$ . Because the polarization on an atomic scale is not homogeneous and the path of the vacancy or interstitial ion avoids places where the polarization is high, it is reasonable to multiply the right side of (3) by a correction factor of the order  $\frac{1}{2}$ . We shall now discuss two typical cases: AgCl and NaBr. For interstitial ions the dielectric constant will be taken equal to the dielectric constant of the material since their contribution to the over-all dielectric constant is greatest by far. Thus one expects for interstitial ions for AgCl ( $\epsilon = 12$ )  $\Delta = 1.85$  and for NaBr ( $\epsilon = 6$ )  $\Delta = 0.84$ .

For vacancies one may either take  $\epsilon_1 = 1$ , yielding for AgCl  $\Delta = 0.22$  and for NaBr  $\Delta = 0.19$ , or one may make an estimate of  $\Delta$  with  $\epsilon_1 = \epsilon_0$  by considering the motion of the ion jumping into the hole. This ion moves through the central part of a region with an extremely low polarization field exerted by other  $\text{Ag}^+$  ions. Depending on which of several crude approximations one uses, he finds that this field is from 10 to 25 times as weak as that through which an interstitial ion moves, leading to  $0.19 > \Delta > 0.08$  for AgCl and  $0.1 > \Delta > 0.04$  for NaBr.

The essential conclusion of this crude analysis is that for vacancy transport  $\Delta$  is so small that it may well have escaped detection but for interstitial transport, especially for ionic crystals with high dielectric