

## Effect of Plastic Deformation on the Low-Temperature Ionic Conductivity of Potassium Chloride\*

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Measurements were made on the ionic conductivity of KCl in the temperature range between 25° and 250°C. Both "as received" crystals and specimens having up to 24% plastic deformation were examined and the activation energies for ionic motion determined. It was found that up to 4% plastic deformation produced no change in the activation energy over the "as received" specimens, whereas deformations above 10% produce a decrease of about 0.2 ev. After such deformation, structure normally present in the  $\ln(IT)$  vs  $T^{-1}$  plot is absent and the decrease in activation energy can be attributed to the generation of ion vacancies not associated with divalent impurities. Measurements on a deformed and annealed specimen support this view.

### I. INTRODUCTION

THE behavior of the ionic conductivity of alkali halides as a function of temperature may be divided into two main sections, namely, the intrinsic ionic conductivity region, typically present in pure materials above 500°C, and the structure-sensitive conductivity region below this temperature. In general, the conductivity in each of these regions is characterized by an activation energy that involves both an energy of motion and some energy of dissociation or formation of carriers, the conductivity relationship being of the form  $\sigma = (A/T) \times \exp(-E/kT)$  in both temperature ranges. The temperature at which the conductivity becomes structure sensitive has been shown to depend upon the presence of divalent impurity atoms, and changes in activation energy in the structure-sensitive region have been associated with the dissociation of positive-ion vacancies from such impurities. It might be expected that pretreatment affecting the location or number of the ion vacancies in a lattice would alter the activation energy in this region.

The effect of plastic deformation on melt-grown crystals has been investigated by Fischbach and Nowick<sup>1</sup> who concluded that for amounts of plastic deformation up to 2% in NaCl no change in activation energy for ionic motion was apparent although a decrease in the ionic conductivity of deformed specimens was observed. It is the purpose of this paper to report on measurements made in single crystals of melt-grown KCl over a range of deformation extending up to 24%.

### II. EXPERIMENTAL METHOD

The crystals used in these experiments were obtained from the Harshaw Chemical Company. Specimens were cleaved from the "as received" crystal, all the faces on the final specimen being freshly cleaved, the final size being 15 mm×10 mm×1 mm. Aquadag guard ring electrodes were painted on the specimen (after suitable

pretreatment), this then being affixed to the crystal holder and transferred to the vacuum system within 40 min of cleaving. The vacuum system was flushed with dry helium to remove oxygen, reported by Ingham<sup>2</sup> and Halperin<sup>3</sup> to cause undesirable effects on the conductivity, and the system then evacuated to pressures less than  $5 \times 10^{-5}$  mm Hg. The Dewar was designed so that liquid nitrogen could be maintained in the proximity of the crystal, the temperature of which could be varied at will between room temperature and 250°C by means of a heating coil attached to the crystal holder. The temperature of the crystal was measured and controlled by a thermocouple embedded in the specimen, an alternative thermocouple in the crystal holder being used as a additional check on the sample temperature. Fields from 100 v cm<sup>-1</sup> to several thousand v cm<sup>-1</sup> could be applied to the specimen from a potential divider driven by a Fluke model 400 BDA power supply. The current in the crystal was measured with an EKCO N572 vibrating reed electrometer having a current sensitivity of  $5 \times 10^{-15}$  amp. The output of the electrometer was taken to an Esterline Angus 1 mA strip chart recorder and continuous current recording was employed.

Crystals that were to be plastically deformed by more than a few percent were cleaved under DC550 silicone oil. Crystals treated in this way deformed more for a low applied stress than crystals cleaved and then exposed to air for some minutes. Plastic deformation was accomplished by placing the oil-covered crystal between two polished tool steel anvils, these being in contact with the one inch square faces of the sample. A hydraulic press was used to apply up to 1000 lb/in.<sup>2</sup> across the millimeter dimension of the crystal. The pressure was not removed rapidly but allowed to decay away under the natural leak rate of the press, taking about 20 min to go to zero. This technique was found to minimize the formation of cracks in the more heavily deformed crystals. The specimen was then freed of the oil by

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<sup>1</sup> D. B. Fischbach and A. S. Nowick, *J. Phys. Chem. Solids* **2**, 226 (1957).

<sup>2</sup> H. S. Ingham, Jr. and R. Smoluchowski, *Phys. Rev.* **117**, 1207 (1960), and H. S. Ingham, Jr., Ph.D. thesis, Carnegie Institute of Technology, 1958 (unpublished).

<sup>3</sup> A. Halperin, *Proceedings of International Color Center Symposium*, Oregon State College, Corvallis, Oregon, September, 8-11, 1959 (unpublished).

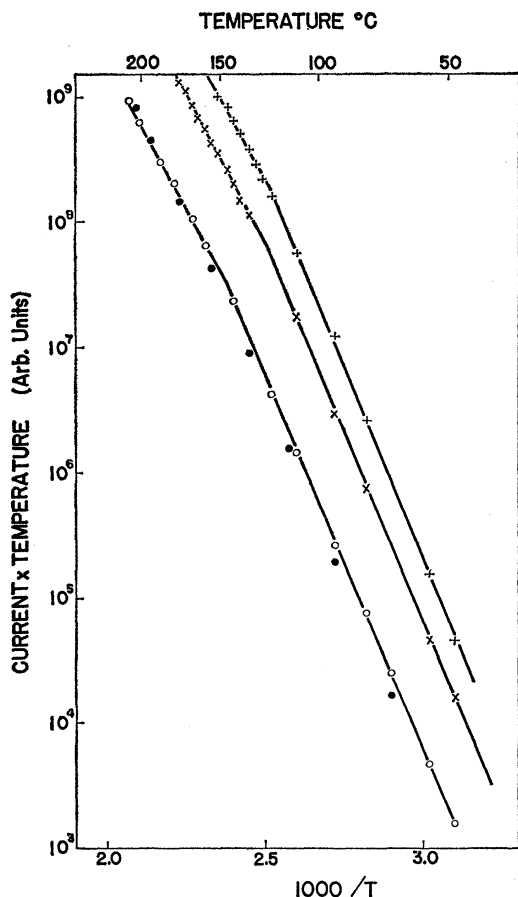


FIG. 1. Typical activation energy plot for (a) undeformed specimen (X for 25 v, + for 100 v), and (b) 2.4% deformed specimen (O for cooling, ● for isothermal).

washing in suitable solvents, the surface air-dried, and the Aquadag guard ring electrodes applied, the crystal then being "cleaved" to its final size and placed in the vacuum system.

The conductivities of the specimens were measured over the temperature range between 25° and 250°C both isothermally and at constant rates of heating and cooling. In general, the electric field to be used in any given run was established across the specimen some 30 min before any measurements were made and maintained continuously during data taking at this field value, including the period during which temperature equilibrium was being established in the isothermal measurements. This technique made it more probable that the value of the current measured during the isothermal runs corresponded to  $\sigma_{\infty}$ , the decayed value of the conductivity which takes account of the possible establishment of a polarization field in the specimen. As discussed more fully below, the majority of runs on a given specimen were made at a constant rate of cooling, isothermal measurements being made as a further check of the observed phenomena.

### III. RESULTS

The experimental results are best considered in three main groups: (a) those crystals having no deformation or samples with 2.4% and 4% plastic deformation, (b) crystals that have been plastically deformed between 10 and 24%, and (c) a sample that was deformed 10% and annealed in a dry helium atmosphere for 4 hr at 650°C with subsequent cooling to room temperature over 73 hr.

For the first group of specimens, a plot of  $\ln(IT)$  vs  $T^{-1}$  exhibits two linear regions, Fig. 1, the break in the curve occurring at about 130°C. The high-temperature region has a characteristic activation energy of  $1.0 \pm 0.05$  ev and the low-temperature region an activation energy of  $1.23 \pm 0.05$  ev. These regions are well defined and, over the temperature range 25° to 200°C, a current change of six orders of magnitude was followed. For these specimens, the activation energies are only slightly dependent on the method of the temperature variation, best agreement being obtained between the isothermal data and data taken at a constant rate of cooling. The effect of applied field and heating rate on the measured activation energy was examined, and a change in these

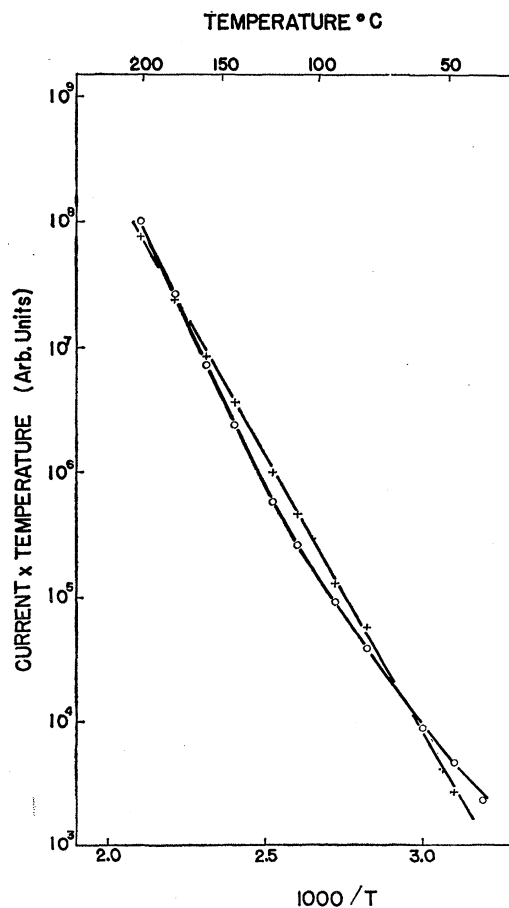


FIG. 2. Typical activation energy plot for 24% deformed specimen (+ for cooling, O for heating).

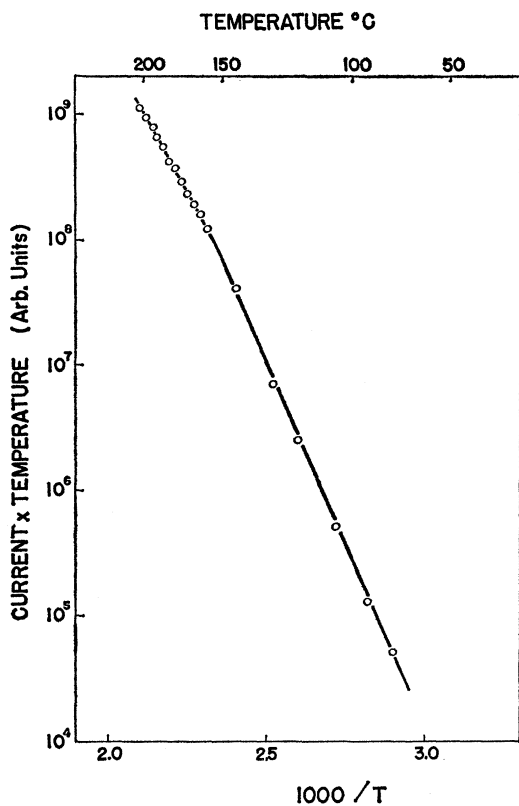


FIG. 3. Typical activation energy plot for deformed and annealed specimen.

parameters by a factor of two did not measurably alter the activation energy.

Those specimens that had received amounts of deformation between 10 and 24% no longer exhibited two regions of different activation energy, Fig. 2. The isothermal and cooling data were characterized by a single activation energy of  $1.0 \pm 0.05$  eV, a value associated with the high-temperature region in the undeformed crystals. In this case, the data taken at a constant rate of heating exhibited no unique activation energy, although at temperatures near 200°C the curve tended to become parallel to the isothermal curve. It should be emphasized that the data presented are not the result of a single warmup and cooling run. All specimens were taken through four or five cycles and, in the case of the isothermal measurements, maintained at temperatures up to 200°C for periods of an hour. No change in the form of the curves was observed as a result of this treatment.

The deformed and annealed crystal again exhibited two regions of different activation energy as determined from the  $\ln(IT)$  vs  $T^{-1}$  plot, Fig. 3. The break in the curve was within 10°C of the position expected for a nondeformed crystal and, to within the errors of this experiment, the observed activation energies agreed with those for the first group of crystals. This agreement is also present in the form of the data taken at a constant

rate of heating which also shows two regions of well defined activation energy, although energy values obtained are higher than for the cooling data.

Although no great reliance is placed upon the absolute values of the conductivities, it should be noted that, in general, at 50°C, the conductivities of specimens that had been plastically deformed were about an order of magnitude smaller than those that had received no deformation.

#### IV. DISCUSSION

The data obtained for crystals having up to 4% plastic deformation are in general agreement with the observations of Fischbach and Nowick<sup>1</sup> on the low-temperature conductivity of NaCl. In this range of deformation, no change in the activation energy was observed and, in general, the conductivity of the deformed samples was about an order of magnitude lower than that of the undeformed specimens.

The observed knee in the activation energy curve at about 130°C is probably due to the completion of the dissociation process between the positive-ion vacancies responsible for the conductivity and divalent impurities in the lattice. In this case, the 1.23-eV activation energy in the temperature region below 130°C represents an energy of motion plus an energy of association, while the 1.0-eV activation energy above this temperature represents an energy of motion only. The value of the association energy obtained from this change of slope is in good agreement with that obtained by Gruendig<sup>4</sup> from measurements on zone-refined alkali halides having divalent calcium impurities, although the high-temperature slope does not give an energy of motion in agreement with his value. The major effect of deformation above 10% would, therefore, seem to be the production of a large number of vacancies that are *not* associated with divalent impurities.

Seitz<sup>5</sup> has explained the transient conductivity increase observed in the Gyulai-Hartley effect in terms of the decay of positive- and negative-ion vacancies produced by the intersection of moving dislocations during deformation. Fischbach and Nowick<sup>6</sup> favor the concept of the breaking up of positive-ion vacancy-impurity complexes to explain this effect, and associate the current decay with the recombination time of such a complex. It seems probable that at high amounts of plastic deformation both mechanisms are operative. Transient effects of the Gyulai-Hartley type are completed before the experimental observations begin, and it is considered that the formation of positive-ion vacancy-impurity complexes during this period is the probable mechanism of these effects. On the other hand, the decay of the positive- and negative-ion vacancies formed during the deformation process will probably occur at dislocation

<sup>4</sup> H. Gruendig, Z. Physik **158**, 577 (1960).

<sup>5</sup> F. Seitz, Revs. Modern Phys. **26**, 25 (1954).

<sup>6</sup> D. B. Fischbach and A. S. Nowick, J. Phys. Chem. Solids **4**, 302 (1958).

jogs and by direct recombination in pairs. Since at the temperature of the experiments only the positive-ion vacancies have appreciable mobilities, it is to be expected that decay sites for positive-ion vacancies on the dislocation will soon be saturated, the formation of new sites requiring the diffusion of negative-ion vacancies to the dislocation, a process that is slow at these temperatures. The negative-ion vacancies formed during deformation will not be uniformly distributed throughout the crystal<sup>7</sup> and, because of their low mobility, will retain spacial positions close to the sites of origin. The distribution of positive-ion vacancies is expected to be more uniform. It is postulated that this spacial restriction, placed on the negative-ion vacancies, limits the recombination rate with positive-ion vacancies, a concept that is supported by the observed increase in the initial rate of *F*-center formation in deformed specimens<sup>7</sup> of KCl. These positive-ion vacancies are unassociated and would be expected to participate in the conduction process with an activation energy characteristic of a free vacancy, the activation energy observed at temperatures above 125°C in the undeformed samples. The apparent reversibility of the current-temperature data is also accounted for by these restricted recombination mechanisms.

The results of the high-temperature anneal are also explicable on this model. In KCl at 600°, the transport

number<sup>8</sup> for negative-ion vacancies is 0.12 and, hence, at the temperature of the anneal, the negative-ion vacancies are probably sufficiently mobile to enhance the recombination rate on dislocations or the rate of pair formation. After such a high-temperature anneal, therefore, it would be the impurity associated vacancies that determine the conduction behavior as a consequence of which two regions of activation energy are again expected. The cause of the curvature in the warmup data for deformed crystals is not clear, but it is suggested that this may be due to an electronic peak superposed on the linear ionic conductivity curve. Such an explanation is made more plausible by the observation of a thermally excited "current glow peak" in this temperature range in samples having short periods of x-ray irradiation.

It does not seem probable that the main effect of the deformation was to increase the conductivity along dislocation bundles or grain boundaries for, although this would be expected to have a lower activation energy, it would seem fortuitous that this value of activation energy should agree so precisely with the value obtained in undeformed samples above 130°C. The effects of annealing on this type of mechanism would, however, be qualitatively similar to the experimental observations, and this possibility should not be completely disregarded until experiments to ascertain the importance of dislocation short circuits have been performed.

<sup>7</sup> P. V. Mitchell, D. A. Wiegand, and R. Smoluchowski, *Phys. Rev.* **121**, 484 (1961), and P. V. Mitchell, Ph.D. thesis, Carnegie Institute of Technology, 1959 (unpublished).

<sup>8</sup> C. Turbant, H. Reinhold, and G. Liebold, *Z. anorg. u. allgem. Chem.* **197**, 225 (1931).