Kanzaki, H.: There are several differences between anisotropy observed here in KC1 and the one in AgBr which was observed by Dr. Johnston for the first time in ionic crystals. The anisotropy ratio in KC1 is greater than in AgBr and the frequency dependence is large in AgBr but not in the present case of KC1. We feel that the origin of these differences is that in AgBr you treated distributed dislocation walls with interruptions and in KC1 we treated distribution of more or less dispersed dislocation lines. The reason for this may be partly due to the difference of slip modes between two crystals.

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Pipe Diffusion in LiF*

R. TUCKER**, A. LASKAR*** AND R. THOMSON
University of Illinois, Urbana, Illinois, U.S.A.

Impurity diffusion of Na ions along dislocations in LiF has been studied by both DC and transient techniques. The Na impurity is injected into the LiF by plating NaCl on one surface of the LiF and placing a potential across the crystal at an elevated temperature. Large scale diffusion with Na dendrite formation is observable in a DC arrangement and the diffusion can be measured by either radioactive tracer methods or measurement of charge transport. Transient experiments yield an activation energy for diffusion of approximately 0.3 eV for both edge and screw dislocations, and $D_0=0.01\ \mathrm{cm^2/sec}$. Analysis of the charge effects in the core of the dislocations leads one to propose a very large vacancy density in the core, and the experiments are even best understood in terms of a hollow of atomic dimensions along the dislocation core.

Introduction

Most measurements of dislocation pipe diffusion have been made by means of conventional tracer techniques in metals. Gibbs and Tucker[1] were the first to recognize the possibility in Al_2O_3 of making pipe diffusion measurements in ionic crystals by means of the ionic conductivity associated with the ion transport. In the present work, the methods of tracer diffusion and ionic conductivity are combined in an experiment on a relatively simple alkali halide in order to make measurements which are as quantitative as possible.

When sodium chloride is evaporated on one surface of the lithium fluoride crystal and a negative potential is placed across the crystal, at elevated temperatures sodium is drawn through the crystal along the dislocation lines. The large easily measurable currents, the easily detected deposits of sodium, and the availability of a suitable radioactive isotope, Na^{24}, make the lithium fluoride-sodium chloride system an attractive one for study.

In addition to the combined dc conductivity and tracer measurements, we have also measured a transient ac conductivity associated with sodium impurity diffusion along the dislocations. Once the diffusion of sodium ions along the dislocations is demonstrated by the dc measurements, it is difficult to distinguish quantitatively between processes taking place along the dislocation after the sodium ions are injected into the dislocation pipes from processes having to do with the injection process itself. For example, an

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* Supported by USAF Office of Scientific Research.

** Now at Arthur D. Little, Inc., San Francisco, California.

*** Now at Department of Physics, Indian Institute of Technology, Karaghpur, India.

activation energy can be measured for the dc conductivity along the dislocations, but undoubtedly part of this activation energy is associated with the breakdown of the sodium chloride in the plated film and the injection of the sodium ions into the lithium fluoride crystal. For this reason, we injected sodium impurity ions into the dislocation of a highly deformed crystal and then, after washing off the plated film, we observed the transient response of the injected ions under the influence of a pulsed square wave potential. In this way it is felt that the mobility of sodium ions along the dislocations can be measured, uncomplicated by other effects.

Experimental

The samples used in the experiments were cleaved on (100) planes from single crystal Harshaw lithium fluoride blanks. After plating with sodium chloride, the crystals were placed in the heated stage of a microscope with the associated dc measuring apparatus shown schematically in Fig. 1.

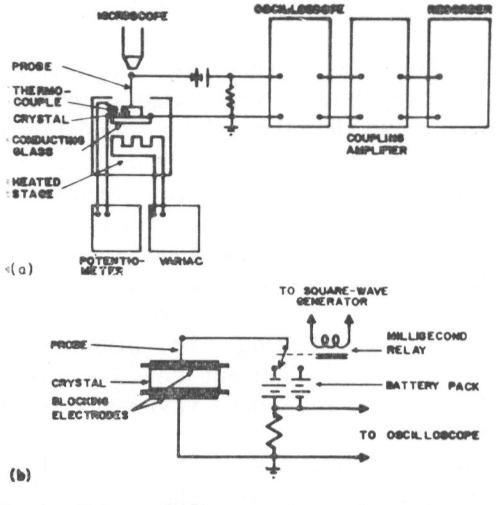

Fig. 1. Schematic diagram of experimental set-up. (a) dc experiments. (b) Modification for ac experiment.

Dc Results

When the negative electrode (a relatively sharp probe electrode) is placed on the crystal, the current flowing in the probe as a function of time has the characteristic shape shown in Figs. 2 and 3.

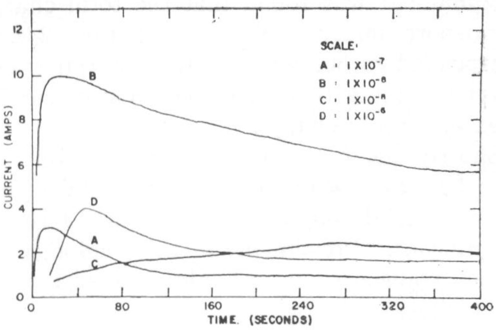

Fig. 2. Typical current *versus* time curves at 270 volts dc. (a) 440°C. (b) 375°C. (c) 275°C. (d) 370°C using 2 mm^2 plated gold electrode.

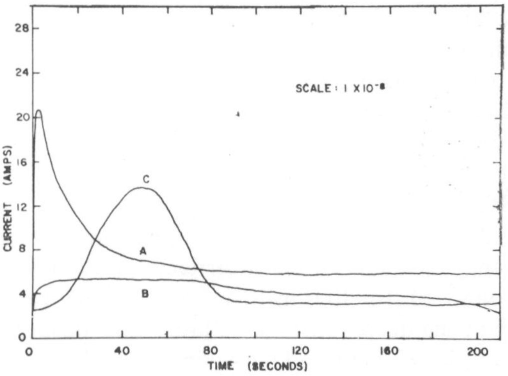

Fig. 3. Typical current *versus* time curves at 90 volts dc. (a) 590°C. (b) 405°C. (c) 494°C.

The crystals were etched to show the presence of dislocations on the top surface, and when the probe was placed in the vicinity of dislocation etchpits, the characteristic currents shown in Figs. 2 and 3 were observed. When the probe was placed in the region of the crystal where no dislocation etchpits are present, no current flow or dendrite formation occurred. Further, if only part of the lower surface of the crystal was plated with sodium chloride and the probe placed at dislocation etchpits in regions relatively far the plated region in the lower surface, then again no current was observed.

Metallic-like dendrites near the probe were observed growing during the initial flow of current.

Most of the dc experiments were performed using radioactive sodium chloride with the isotope sodium Na^{24} to determine the ratio between the mass transport and the conduction current. Successive scrapings were made from the top surface down through approximately half the thickness of the crystal to determine the total amount of deposited sodium. It was found that the total charge transport under the curve of Fig. 2 corresponded rather well to the material transport assuming that each sodium atom carries one electronic charge.

Shortly after the peak in the current is reached, the sodium deposit slows and comes to a stop, although the current still remains significant. Presumably in this region, electron transport occurs along the sodium dendrites.

Attempts to correlate the amount of current flow with the density of dislocations in the vicinity of the probe showed that the current was approximately proportional to the dislocation etchpit density. In addition, experiments on deformed crystals showed enhanced current along the dislocations when the dominant dislocations present were either edge or screw.

Ac Results

A second series of experiments were made using a square wave alternating potential (90 volts, 10 to 100 millisecond pulses) rather than the dc potentials. Plated and deformed samples were placed between direct electrodes, heated to about 350°C and a 90 volt negative potential applied to the unplated surface for about 200 to 400 msec. Samples were then removed from the furnace and the sodium chloride washed from the plated surface. These crystals with injected sodium ions were then replaced in the furnace at various temperatures below 400°C and were subjected to square wave pulses. The voltage and the current pulses are shown schematically in Fig. 4. The sharp initial current pulse which decays rapidly is characteristic of crystals prepared after deformation. In nondeformed crystals prepared as control crystals, the current pulses were not observed. The peak of the current pulse was measured as a function of temperature and an activation energy of approximately 0.3 eV was found. Crystals prepared in screw orientation seemed to have a slightly smaller activation energy than those prepared in edge orientation.

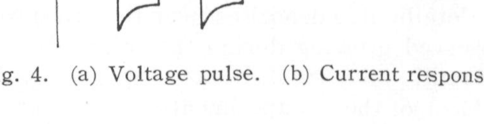

Fig. 4. (a) Voltage pulse. (b) Current response.

Discussion

One can attempt to analyze results in terms of vacancies where the sodium replaces lithium ions along the core of the dislocation and is transported along the dislocation core by the usual vacancy mechanism. Analysis shows, however, that in order for the diffusion to occur by means of vacancies that vacancies must be present in very large numbers in the core and that the sodium completely replaces the lithium of the dislocation cores. Neither of these possibilities seems very likely, and one, therefore, is led to consider the possibility that the dislocation core is hollow so that sodium ions can be directly injected into the lithium fluoride dislocations without transplanting the lithium ions. Estimates of the current flow on this assumption give reasonable values of the parameters.

The impurity diffusion along a single dislocation satisfies the formula

$$D = D_0 \exp(-E/kT)$$
$$D_0 = 0.012\ \text{cm}^2/\text{sec}$$
$$E = 0.3\ \text{eV}.$$

References

1 R. N. Tucker and P. Gibbs: J. Appl. Phys. **29** (1958) 1375.

DISCUSSION

Lazarus, D.: Did you measure the temperature dependence of the time constant of the transient in the ac measurement? Unless this dependence is the same as that of the magnitude of the augmented conductivity, some of it may be traceable to simple circuit considerations and not be attributable entirely to augmented pipe diffusion. If the entire effect is in fact due to pipe diffusion, the transient would presumably be traceable to diffusion-induced polarization, which should have the same activation energy as the augmented conductivity.

Thomson, R.: We did not measure the temperature dependence of the relaxation time. In our experiment, it is more difficult to measure than the peak value, and is subject to considerable uncertainty at the extremes of temperature. The simple capacitance effect you mention is very easy to distinguish from the diffusion current, and has been corrected for in the results quoted in the paper.

Kanzaki, H.: Do you have any suggestions from your experiments to the problem of which of two factors—charged dislocation and vacancy-dislocation association—are the predominant? In order to discriminate between these two, it is the most desirable to study the situation in the neighbourhood of dislocation core—the closer to the core, the better.

Thomson, R.: From our experiments, as they have been conducted, I cannot say. One might get information on this point by including the vacancy association energy as a parameter in the standard charged dislocation theoretical analysis. This would be a difficult problem, however, because the jog density on the dislocation enters the problem. If the jog density is small, then the dislocation acts as a simple trap and the vacancy association would be the important effect. If the jog density is high, then the energy of association as well as the vacancy formation energy must be used, and the solution of Poisson's equation becomes quite difficult. The cross-over between these two solutions would also have to be derived from a complex analysis. Experimentally, there might be a way to answer these questions, but the experiment would have to be more subtle than ours.

As to your comment regarding closeness to the core, it is our belief that the effect we obrseve *is* a core effect. The very small activation energy can only be explained by a core effect. In addition there are physical arguments which show that vacancy-impurity clustering cannot cause the effect. Essentially, this is to say that the only cluster which could transport the Na impurity toward the correct electrode in the field is too large to be a possible vehicles for diffusion.

Rabin, H.: Is there any possibility that your results could be connected either in whole or in part with electronic rather than ionic processes?

Thomson, R.: We carried out an elaborate set of experiments to check the charge flow against the mass flow as measured by radioactive tracers. Within a factor of two (the experimental error) these values were the same.