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Equilibrium of Vacancies with Dislocations in Alkali Halides

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Ionic conductivity in the extrinsic range of temperature was measured for specimens taken from various parts of single crystalline ingots of KCl obtained by zone purification. In the purest specimens (divalent impurities 10^{-6}), conductivity showed proportional increase against dislocation density between 5×10^6 and 5×10^7 cm⁻². Anisotropy of conductivity was also observed in bent and annealed purest crystals between electric fields parallel and perpendicular to oriented edge dislocations. Temperature dependence of the anisotropy ratio is consistent with predictions from charged dislocation theory and gives the value of 0.5 to 0.7 eV for the formation energy of positive ion vacancies. Observation of electric charge induced by movement of oriented edge dislocations shows that dislocation has positive charge of line density of 10^{-4} unit charge per atom when moving in the initial stage of plastic deformation below 200°C. Conclusion is that the behaviors of purest KCl agree well with predictions from charged dislocation theory.

1. Introduction

Previous results on the ionic conductivity of zone-refined KC1¹⁾ showed that the conductivity of the purest specimens (divalent impurity ions less than 10^{-8}) increased with increasing dislocation densities and that of impurer ones (divalent impurities 10^{-7} to 10^{-6}) decreased with increasing dislocation densities. Interpretation of these results in comparison with charged dislocation theory²⁾ led to the value of 0.7 eV for the formation energy of positive ion vacancies.

The experimental studies of the following three kinds have been undertaken in order to clarify further the nature of equilibrium distribution of vacancies around dislocations. They are: (1) dependence of conductivity upon dislocation densities, (2) anisotropy of conductivity due to oriented edge dislocation lines, and (3) electric charge induced by movement of oriented dislocations.

2. Experimental Procedures

Specimens of KC1 used in this study are taken from single-crystalline ingots obtained by zone purification. Details of purification and zone melting are described in the previous paper.¹⁾ Our recent results on quantitative spectroscopic analysis have shown that Na impurity as well as divalent impurities has been successfully removed by zonemelting. Concentration of Na in the purest specimens is estimated as low as 10⁻⁷ or less. The major impurities in the impurer specimens are Mg and Ca.

Bending deformation of cleaved specimens for introducing edge dislocations in the present study has been made at 200 to 300°C in air. Deformation in water is not used in any of deformations. It was found that high-temperature annealing of impurer specimens deformed in water reduced the number of divalent ions effective for low temperature conductivity.

The following experimental results, except otherwise stated, have been obtained for specimens annealed at 400°C in purified nitrogen atmosphere for 10 hrs after deformation.

3. Results and Discussion

3.1 Dependence of dc conductivity upon dislocation densities

Dc conductivity of specimens subjected to various degrees of plastic deformation are measured as a function of temperature and the results are compared with dislocation densities of the specimen obtained by etch pit counts. Fig.1 shows the results for the purest specimens (below) and impurer ones (above). The purest specimen with the lowest dislocation density (5×10^5 cm⁻²) has been obtained by annealing at 700°C. The specimens with dislocation density of 1×10^7 cm⁻² have been previously subjected to bending deformation. Etch pits of the bent and annealed specimens revealed clear evidence of oriented edge dislocation lines parallel to the bending axis.

As shown in Fig. 1, conductivity of the purest specimen shows proportional increase against dislocation densities between 5×10^6 and 5×10^7 cm⁻². Conductivity of the bent crystals shows anisotropy in relation to orientation of edge dislocation lines. In Fig. 1, // is the result where electric field is parallel to dislocations and \perp is that where electric field is perpendicular. The observed anisotropy effects will be further studied in 3.2 by using ac method.



Fig. 1. Specific conductance against dislocation density, for the purest KCl (below) and for the impurer one (above).

In the case of impurer ones, decrease of conductivity with increasing dislocation densities occurs rather discontinuously at dislocation densities around 5×10^7 cm⁻² and is sensitive to the mode of previous plastic deformation. This observation is consistent with the previous interpretation¹⁾ which suggested that formation of two-dimensional high-resistivity regions associated with dislocation walls are necessary, in reducing dc conductivity of impure specimens. The anisotropy effects due to oriented dislocations have not been found in impure specimens within experimental errors.

3.2 Anisotropy of ac conductivity due to oriented edge dislocation lines

Fig. 2 is a typical example of anisotropy



Fig. 2. Tan δ against frequency for the purest KCl previously bent and annealed. Electric field parallel (//) and perpendicular (\perp) to oriented edge dislocation lines.

of dielectric loss observed in bent and annealed pure specimens. // and \perp refer to parallel and perpendicular electric field relative to oriented edge dislocation lines, respectively. The ratio of parallel to perpendicular conductivity at low frequency is about 1.5 at 269°C and 2.0 at 320°C. The observed anisotropy is due to oriented edge dislocation lines and can be interpreted by existence of highly conducting pipes imbedded in perfect lattice.

Straightforward calculations are made based on the simple model shown in Fig. 3. Specific resistance of specimens R_{\parallel} and R_{\perp} measured by electric field parallel and perpendicular to dislocation lines can be expressed as follows:



Fig. 3. Highly conducting pipes (with [hatched cross sections) around dislocation lines imbedded in perfect lattice.

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	$R_{\perp}/R_{/\!\!/}$ for $r\!>\!1$	value of r for $R_{\perp}/R_{\parallel}\!=\!2$	R_{\perp}/R_{\parallel} for $r\!<\!1$
p = (1/10)d	1 + r/10	10	(0.2+r)/(0.1+r)
$p\!=\!d$	r/8	16	1.1
$p\!=\!10d$	$1.1 + 10^{-2}r$	102	1.2
p = 100d	$1 + 10^{-4}r$	104	1

Table I. Approximate formulas deduced from Eqs. (1) and (2).

$$R_{\parallel} = \rho_p \cdot \frac{1}{n} \frac{1}{(rnd^2 + ndp + p)} \tag{1}$$

$$R_{\perp} = \rho_p \cdot n \left(\frac{1}{(r+p/d)n} + p \right) \tag{2}$$

where ρ_p : specific resistance of perfect region

 ρ_d : specific resistance of dislocation pipe

$$r = \rho_p / \rho_d$$
 and $n = 1/(p+d)$.

Calculations of Eqs. (1) and (2) are made for various values of p/d and for r > 1 and r < 1 assuming that (p+d) is constant. The results are as shown in Table I.

In Table I, the case r > 1 corresponds to the present case where dislocation region has higher conductance than perfect lattice.

Firstly, the following two observations are discussed in relation to the calculations described above. a) The experimental value of R_{\perp}/R_{\parallel} is about 2 at 320°C as shown in Fig. 2. b) The value of R_{\perp} is nearly equal to the resistance of well-annealed specimens which can be assumed equal to ρ_p . These two observations combined with the above analysis suggest strongly that value of p/d is greater than 10. Then it follows from the Table I that,

$$R_{\perp}/R_{\parallel} \approx 1 + \frac{r}{\left(\frac{p}{d}\right)^2} \tag{3}$$

$$r \approx (p/d)^2$$
, for $\frac{R_\perp}{R_{\parallel}} = 2$. (4)

Secondly, the other important result is that the value of R_{\perp}/R_{\parallel} is larger at higher temperature than at lower temperature as seen in Fig. 2. In the following, it can be shown that this observation is consistent with predictions from charged dislocation theory. Number of positive ion vacancies along dislocation line (or at crystal surface) will change with temperature according to $\exp(-g_+/kT)$, where g_+ is the formation energy of positive ion vacancy. The value of r is approximately proportional to $\exp(-g_+/kT)$ in the extrinsic range of temperature. The value of g_+ estimated from temperature dependence of r is 0.4 to 0.6 eV. This value will increase by about 0.1 eV when change of mobility energy near dislocations is taken into account as suggested previously¹⁾.

Fig. 4 shows changes of perpendicular conductivity during measurement cycle for freshly bent pure specimens. Dielectric loss peak apparent in 262°C and 288°C data disappeared during annealing at 300°C as seen in 272°C data. The observed change is probably due to onset of polygonization process which is evident from etch pit count after 400°C annealing. These observations have never been found in measurements by parallel electric field.



Fig. 4. Change of $\tan \delta$ during measuring cycle (from ① to ④) for freshly bent pure crystal measured by electric field perpendicular to edge dislocations.

3.3 Electric charge induced by movement of oriented dislocations

Experimental arrangements shown in Fig. 5 is used to study electric charge induced during instantaneous loading or unloading of bent and annealed crystals without any applied electric field. The observed charge is due to displacement of electric charge associated with movement of oriented edge dislocations. Measurements are made between room temperature and 200°C.

In Figs. 6 and 7, values of induced voltage in the electrometer for each loading or unloading of a weight which corresponds to 13 to $18 g/mm^2$ are plotted against static dead stress applied on the specimen. In our experimental conditions, induced voltage of 100 mV corresponds to induced charge of 10^{-12} Coul. Figs. 6 and 7 show typical results obtained at 200°C, for pure specimen and for impure one, respectively.

In all cases, electric signal has been greatly reduced in the second run of loading and unloading compared with the first run. This reduction corresponds to the irreversible motion of dislocations in the first run. The



Fig. 5. Experimental set-up to measure electric charge induced by instantaneous stressing.



Fig. 6. Induced voltage for each 18 g/mm² against static dead stress for pure KCl at 200°C.



Fig. 7. Induced voltage for each 13 g/mm² against static dead stress for impure KCl at 200°C.

amount of strain per loading is about 1×10^{-3} expressed in reduction of thickness.

In the Figs. 6 and 7, the sign of induced voltage is chosen as such that movement of positively charged dislocation will give positive voltage in loading. It has been found that electric signals in loading at first run correspond to movement of positively charged dislocations for both pure and impure crystals in the range of temperature studied.

In the following, it will be shown that line density of electric charges along moving dislocation lines can be estimated by comparing the value of induced charge with the amount of deformation accompanied. Firstly, amount of induced charge is proportional to number of moving electric charges times average distance moved. Number of moving charges can be expressed as total length of dislocations times charge density along them. Secondly, deformation during loading can also be expressed by length of dislocations times distance moved. Lastly, the

Table II. Line density of charge along dislocation line expressed in number of unit charge per atom.

Temperature (°C)	pure crystal	impure crystal
25	0.93×10^{-4}	0.28×10^{-4}
200	0.61×10^{-4}	3.2×10^{-4}

ratio of induced charge to deformation is proportional to charge density along dislocations with proportionality factor given by specimen geometry. The results obtained are shown in Table II.

These values of charge densities, however, are those for dislocations moving irreversibly in the lattice and should be distinguished from those for static dislocations in equilibrium with lattice which are considered in charged dislocation theory.

4. Conclusion

The present results on ionic conductivity, especially those described in 3.1 and 3.2 on the purest crystals of KC1, show satisfactory agreements with predictions from charged dislocation theory. These are convincing evidences for the situation in which positively charged edge dislocations are surrounded by atmosphere of excess positive ion vacancies.

On the other hand, understanding of the situation in impurer crystals is not conclusive at present although our experimental results so far did not show any serious contradictions to predictions from the theory.

References

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DISCUSSION

Smoluchowski, R.: Professor Royce at Princeton has observed a small difference in the activation energies in the directions parallel and perpendicular to the dislocations. How big differences do you find?

Kanzaki, H.: In dc measurements on freshly bent pure KC1 we observed the difference of activation energies between parallel and perpendicular electric field. In this case, the energy for parallel was a little (0.1 eV or less) smaller than the one for perpendicular. On the other hand, in ac measurments on bent and annealed pure KC1, the difference of activation energies between parallel and perpendicular was also observed. The difference in this case is reverse in sign compared with the above case as seen in Fig. 2. This observation was reproducible and we put main emphasis on low frequency data of conductivity in ac experiments in our discussions.

Howard, R.: (1) Have you considered the possibility that the decrease in conductivity of the impure specimens upon deformation may be due to impurities precipitating at dislocations?

(2) For the pure crystals, what density of vacancies at dislocations do you need to explain the increase in conductivity? Also what is the change in activation energy of a vacancy at a dislocation?

Kanzaki, H.: (1) In the experiments described in the previous paper (Northwestern Conference), the decrease in conductivity of impure KC1 was observed only in dc measurements and not in ac where we observed only change of slope in the log tan δ vs. log ω plot. This means that the decrease is mainly due to heterogeneity rather than decrease in carrier concentrations such as the case in precipitation at dislocations.

(2) We need about 3×10^7 vacancies per unit length of dislocations, neglecting mobility change. In the compressed and annealed pure KC1 (reported in the previous paper), we had to consider changes of both numbers and mobility at a dislocation. In the bent and annealed pure KC1 (as in Fig. 2), the predominant factor is change of numbers and not change of mobility.

Johnston, W.G.: Dr. Kanzaki may recall that several years ago he and I independently investigated the effect of plastic deformation on the electrical conductivity of silver bromide. Deformation produced large conductivity increases in that material, but I found that the conductivity increase was greater at higher frequencies. I found this behavior to be consistent with the behavior of a material in which the high conductivity paths ("pipes") are discontinuous. Would the speaker care to comment on the difference in frequency behavior observed in silver bromide and in the present experiments?

Kanzaki, H.: There are several differences between anisotropy observed here im 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*

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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 $0.3 \, \text{eV}$ for both edge and screw dislocations, and $D_0=0.01 \, \text{cm}^2/\text{sec}$. 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 Tucker¹⁾ 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, Na²⁴, 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 processestaking 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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