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Influence of a state of impurities on the interaction between a dislocation and impurities in KCl single crystals

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The strain-rate cycling test during the Blaha effect measurement at 80 to 240 K has been carried out for two kinds of single crystals: quenched and annealed specimens of KCl:Sr^{2+}. It was found that the force–distance profile, which expresses the interaction between a dislocation and impurities, cannot be approximated by the Fleischer's model when I–V dipoles turn into aggregates for KCl:Sr^{2+}, and that the activation energy for the break away of a dislocation from impurities becomes small for the annealed specimen, compared with the quenched one. Furthermore, the critical temperature, T_c, for the annealed KCl:Sr^{2+} is slightly smaller in comparison with that for the quenched one.

1. Introduction

It is well known that the state of impurities in a crystal affects its hardness. Green and Zydzik [1] reported that when a Kentron microhardness tester was used with a Knoop diamond indentor, the greatest hardness occurs for the highest concentration of isolated dipole and the decrease of hardness is then attributed to precipitation of the single crystals, KCl doped with Sr^{2+}. Dryden *et al.* [2] also reported that when a small amount of impurities diffuse into the matrix, or they aggregate, their state strongly influences the resistance to movement of the dislocations.

When alkali halide crystals are doped with divalent ions, the ions are expected to be paired with positive ion vacancies, to which they are strongly attracted [3], thus producing large tetragonal lattice distortions. The pairs are termed I–V dipoles. Assuming that a dislocation moves on a slip plane and interacts strongly with only those defects lying within one atom spacing of the slip plane, the relation between the effective stress and the temperature can be approximately explained by Fleischer's model [4].

It has been reported [5] that the relation between the strain-rate sensitivity and the stress decrement during the Blaha effect measurement gives information about the interaction between a dislocation and impurities. We therefore investigated the influence of the state of impurities in KCl:Sr^{2+} on the relation between temperature and the effective stress due to impurities, and on the activation energy for the break-away of a dislocation from weak obstacles such as I–V dipoles.

2. Experimental procedure

The crystals used in this work, KCl doped with Sr^{2+} (0.05 mol % in the melt), were grown by the Kyropoulos method in air. The specimens, which were obtained by cleaving to a size of $5 \times 5 \times 15$ mm^3, were annealed for 24 h at 973 K and were cooled to room temperature at a rate of 40 K h^{-1} in order to reduce dislocation density; the specimens were further held at 673 K for 30 min, followed by quenching to room temperature immediately before the test, in order to disperse the impurities in them. The quenched specimens stored at 370 K for 500 h, followed by gradual cooling in the furnace for the purpose of aggregating impurities in them [6]. This is termed the annealed specimen in this paper. The concentration of I–V dipoles was determined by dielectric loss measurement using an Andoh electricity TR-10C model.

Two kinds of specimen were deformed by compression along the $\langle 100 \rangle$ axis and the ultrasonic oscillatory stress was applied by a resonator in the same direction as the compression. The details of the tests during the plastic deformation were described elsewhere [7]. The strain-rate cycling tests during the Blaha effect measurement were performed at temperatures from 80–240 K.

3. Results and discussion

3.1. Dependence of the state of impurities for KCl:Sr^{2+} on heat treatment

Because an I–V dipole causes dielectric absorption, there is a peak on the tan δ–frequency relation. A relative formula which gives the proportionality between the concentration of I–V dipoles and a Debye peak height is expressed by the relation [8]

$$\tan \delta = 2\pi e^2 c / 3\varepsilon a k T \quad \text{(maximum)} \qquad (1)$$

where e is the elementary electric charge, c the concentration of the I–V dipole, ε the dielectric constant in

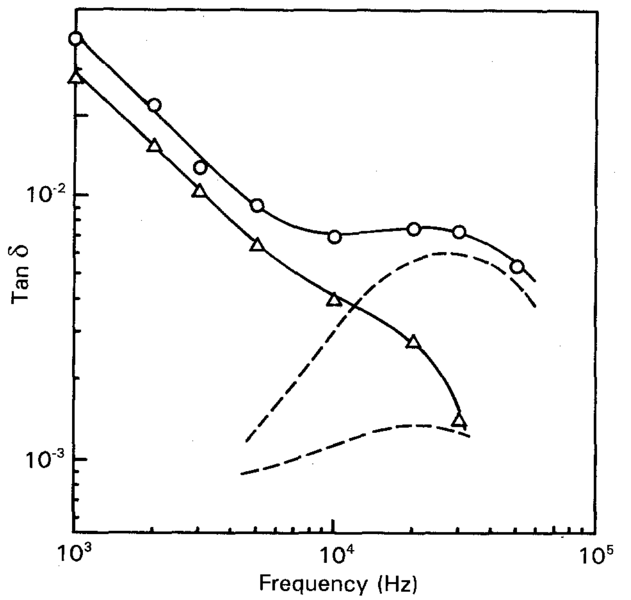

Figure 1 The dielectric loss in KCl containing Sr^{2+} ions at 393 K: (○) for the quenched specimen, (△) for the annealed specimen. (———) Losses coming from the dipoles.

the matrix, a the lattice constant, and kT has its usual meaning.

Influence of this heat treatment on the $\tan\delta$–frequency curves for $KCl:Sr^{2+}$ at 393 K is shown in Fig. 1. The upper solid and dotted curves correspond to the quenched specimen and the lower curves the annealed one. Dotted lines show Debye peaks obtained by subtracting the d.c. part which is obtained by extrapolating the linear part of the solid curves in the low-frequency region to the high-frequency region. Introducing the peak heights of the dotted curves into Equation 1, the concentration of the isolated dipole was determined to be 98.3 p.p.m. for the quenched specimen and 21.8 p.p.m. for the annealed one. On the other hand, the atomic absorption gave 121.7 p.p.m. for the Sr^{2+} concentration in the quenched specimen and 96.2 p.p.m. for the annealed one. Therefore, it should be considered that 71.9% of the I–V dipoles turn into the aggregates of $KCl:Sr^{2+}$ and they form at least trimers [6] by this heat treatment. The trimers have a structure in which three dipoles are arranged hexagonally head to tail in a (1 1 1) plane, as suggested by Cook and Dryden [6].

3.2. Relation between the strain-rate sensitivity and the stress decrement

The strain-rate cycling test during the Blaha effect measurement can separate the effective stress due to a weak obstacle such as an impurity from that due to dislocation cutting [7, 9]. The strain-rate sensitivity varies with stress decrement at a given strain, and the relation between the strain-rate sensitivity and the stress decrement provides information on the interaction between a dislocation and an impurity [5].

A general relation between strain-rate sensitivity, $\Delta\tau'/\Delta\ln\dot{\varepsilon}$, and the stress decrement due to oscillation, $\Delta\tau$, at a given strain is schematically drawn in Fig. 2 [5]. τ_{P1} corresponds to the effective stress due to the weak obstacles which lie on the dislocation with the largest separation when the dislocation moves forward [5]. τ_{P2} is the stress decrement at which the ultrasonic oscillatory stress helps the dislocation to break away from all weak obstacles, as reported elsewhere [7]. At the stress decrement of more than τ_{P2} the obstacles to the dislocation motion are only strong ones such as dislocation cuttings. $(\Delta\tau'/\Delta\ln\dot{\varepsilon})_P$ is defined in Fig. 2. The same phenomena as in Fig. 2 are expected for KCl single crystals doped with Sr^{2+} as weak obstacles.

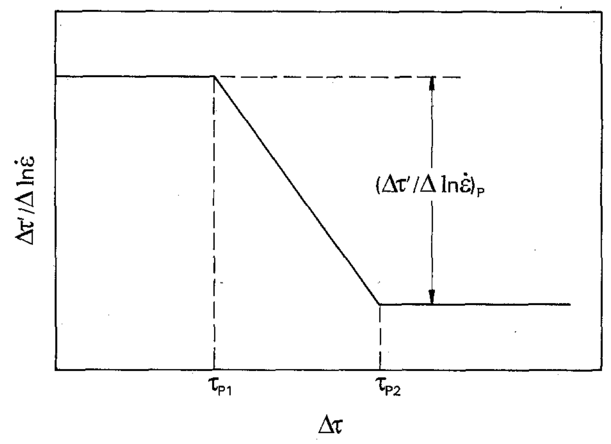

Figure 2 Illustration of relation between the strain-rate sensitivity and the stress decrement at a given strain.

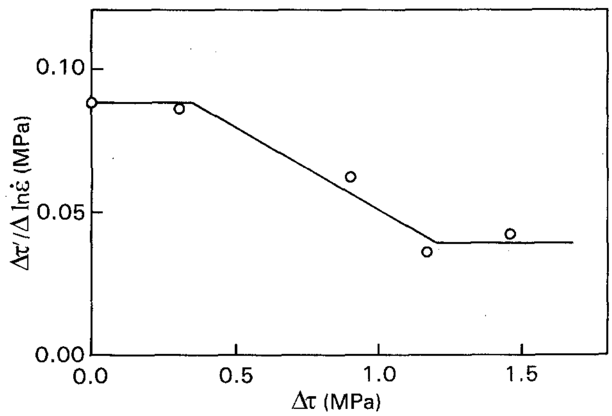

Figure 3 Relation between the strain-rate sensitivity and the stress decrement at a shear strain of 8% for the annealed $KCl:Sr^{2+}$ (0.05 mol % in the melt) at 125 K.

Fig. 3 shows the variation of strain-rate sensitivity with stress decrement at a shear strain of 8% for the annealed $KCl:Sr^{2+}$ at 125 K. There are two bending points and two plateau regions and the strain-rate sensitivity decreases with stress decrement between two bending points, as expected. The same phenomena were observed for the quenched specimens.

3.3. Influence of the state of impurities on the temperature dependence of τ_{P1} and τ_{P2} for $KCl:Sr^{2+}$

The dependence of τ_{P1} and τ_{P2} on temperature for quenched $KCl:Sr^{2+}$ is shown in Fig. 4a, while that for the annealed specimen is shown in Fig. 4b. It is clear

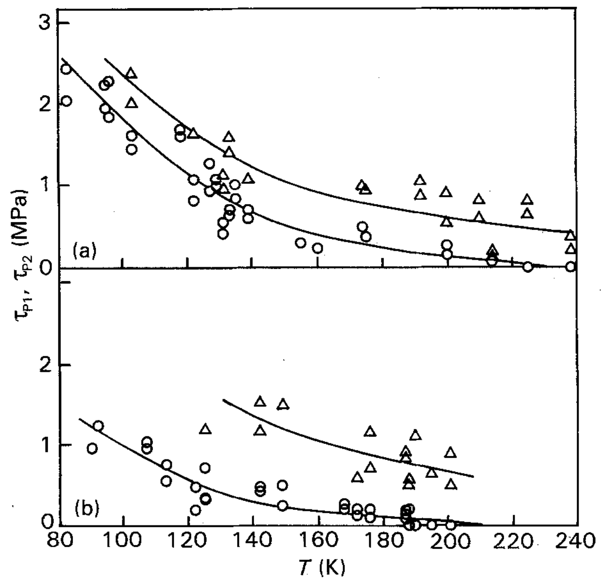

Figure 4 Dependence of (○) τ_{P1} and (△) τ_{P2} on temperature for $KCl:Sr^{2+}$: (a) for the quenched specimen and (b) for the annealed specimen.

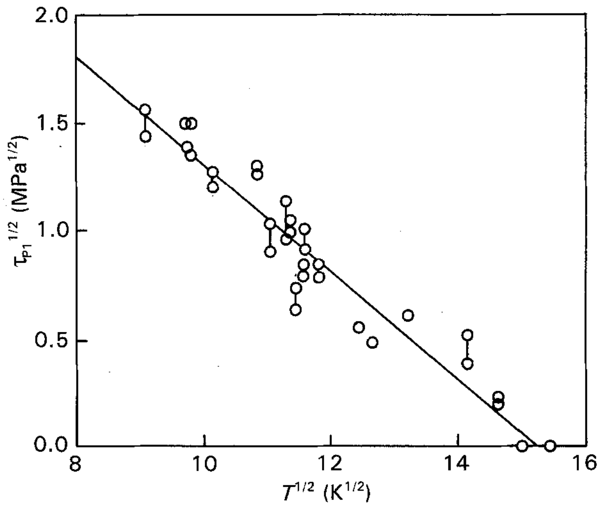

Figure 5 Linear plots of $\tau_{P1}^{1/2}$ and $T^{1/2}$ for the quenched $KCl:Sr^{2+}$ (0.05 mol % in the melt).

that τ_{P1} becomes small at low temperature as the I–V dipoles form aggregates. This is considered to be the reason why the separation between the weak obstacles lying on the dislocation becomes wider as the I–V dipoles turn into aggregates. In addition, we supposed that a decrease of τ_{P1} due to aggregation of I–V dipoles, i.e. softening, is attributable to the loss of tetragonality in terms of the Fleischer's model, as suggested by Chin *et al.* [10]. At high temperature, the critical temperature at which τ_{P1} is zero, T_c, for the annealed specimens is around 210 K and is slightly smaller in contrast with that for the quenched specimens, as shown in Fig. 4. For τ_{P2}, no great difference is seen between the quenched specimens and the annealed ones. Consequently, as I–V dipoles turn into the aggregates of $KCl:Sr^{2+}$, the difference between τ_{P1} and τ_{P2} obviously becomes wider in comparison with that of the quenched specimens. This suggests that the distribution of dislocation segments for the annealed specimen is wider than that for the quenched one.

3.4. Influence of the state of impurities on the interaction between a dislocation and impurities

Fig. 5 shows that the relation between the effective stress, τ_{P1}, and temperature for the quenched $KCl:Sr^{2+}$ can be approximated as Fleischer's relation [4]

$$(\tau_{P1}/\tau_{P0})^{1/2} = 1 - (T/T_c)^{1/2} \qquad (2)$$

where τ_{P0} is the effective stress due to weak obstacles without thermal activation. Then, τ_{P0} which is obtained by extrapolating the curve of τ_{P1} to 0 K is 14.5 MPa and T_c is 227 K.

When a dislocation can overcome weak obstacles dispersed in the lattice with the aid of thermal fluctuations, the values of the activation energy, H, are given by the relation [11]

$$H = -kT^2(\partial \ln\dot{\varepsilon}/\partial \tau_{P1})(\partial \tau_{P1}/\partial T) \qquad (3)$$

where $(\partial \ln\dot{\varepsilon}/\partial \tau_{P1})$ is obtained from $(\Delta\tau'/\Delta\ln\dot{\varepsilon})_P$ in Fig. 2. $(\partial \tau_{P1}/\partial T)$ can be obtained from the differentiation of Equation 2 as follows

$$\partial \tau_{P1}/\partial T = [1 - (T/T_c)^{-1/2}]\, \tau_{P0}/T_c \qquad (4)$$

The values of the activation energy obtained from Equation 3 are plotted as a function of temperature in Fig. 6. If a dislocation moves at a fixed velocity, the activation energy is expressed by the formula [11]

$$H = \alpha kT \qquad (5)$$

where α is a constant. It is seen from the figure that the activation energy is proportional to the temperature in accordance with the requirements of Equation 5. The value of $H(T_c)$ for the quenched specimen taken from Fig. 6 is 0.63 eV.

We now discuss the case of the annealed $KCl:Sr^{2+}$. Two models will be considered. One is Fleischer's model and the other is the model [12] in which the force–distance profile is a triangle. The triangle profile

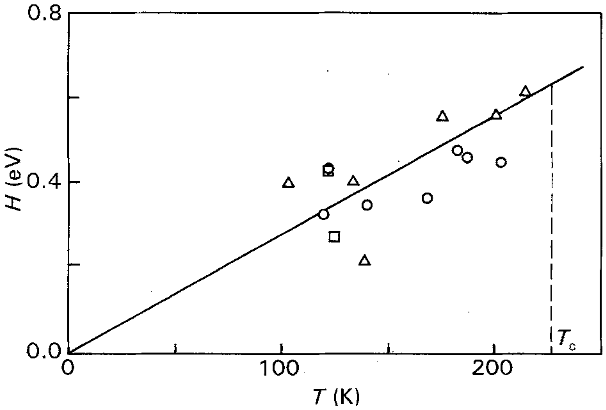

Figure 6 Relation between temperature and activation energy for the quenched $KCl:Sr^{2+}$. Sr^{2+} concentration: (○) 0.035, (△) 0.050, and (□) 0.065 mol % in the melt.

gives the following relation

$$(\tau_{P1}/\tau_{P0})^{2/3} = 1 - (T/T_c)^{1/2} \quad (6)$$

Fig. 7 shows whether Equations 2 and 6 satisfy the data. If the interaction between a dislocation and aggregates for $KCl:Sr^{2+}$ can be approximated to Fleischer's model, τ_{P0} is 8.9 MPa and T_c 223 K. However, if the force–distance profile is a triangle, τ_{P0} is 5.3 MPa and T_c is 211 K. As can be seen from the figure, it is difficult to determine whether the relation between the effective stress and temperature for the annealed $KCl:Sr^{2+}$ can be approximated to Fleischer's model within the temperature range. Therefore, we investigated the relation between the temperature and activation energy for the annealed $KCl:Sr^{2+}$ in Fig. 8. Assuming the interaction between a dislocation and weak obstacles for the aggregates can be approximated by Fleischer's model, the temperature and activation energy relation corresponds to the solid circles in Fig. 8. However, the data do not appear to be satisfied by Equation 5. On the other hand, plots of open circles in Fig. 8 show the activation energy obtained using Equation 6. The activation energy is then nearly proportional to temperature for plots of open circles, compared to plots of solid circles as shown in Fig. 8. In this case, the value of $H(T_c)$ for the annealed specimen taken from Fig. 8 is 0.37 eV. Thus the force–distance profile between a dislocation and aggregates for $KCl:Sr^{2+}$ can be approximated by a triangle rather than Fleischer's model. Consequently, the interaction between a dislocation and aggregates for $KCl:Sr^{2+}$ cannot be approximated by Fleischer's model.

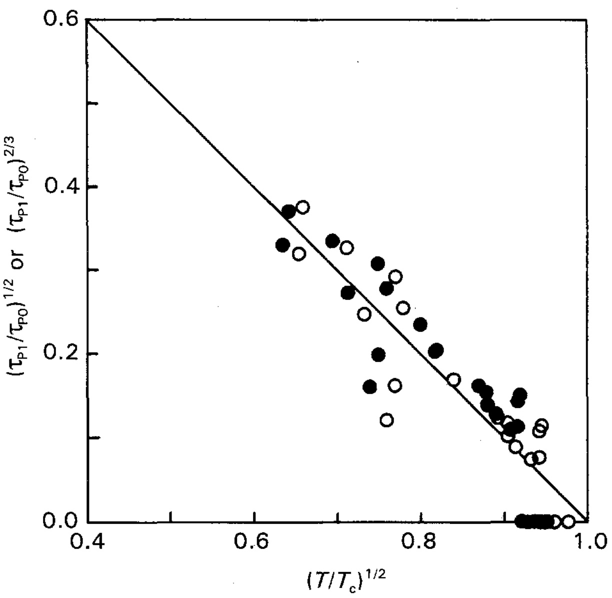

Figure 7 The relation between effective stress and temperature for the annealed $KCl:Sr^{2+}$. (●) $(\tau_{P1}/\tau_{P0})^{1/2}$–$(T/T_c)^{1/2}$; (○) $(\tau_{P1}/\tau_{P0})^{2/3}$–$(T/T_c)^{1/2}$.

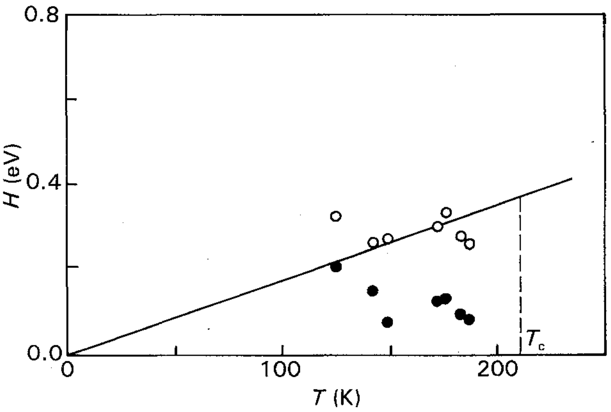

Figure 8 The relation between temperature and activation energy for the annealed $KCl:Sr^{2+}$. (●) $(\tau_{P1}/\tau_{P0})^{1/2}$–$(T/T_c)^{1/2}$, (○) $(\tau_{P1}/\tau_{P0})^{2/3}$–$(T/T_c)^{1/2}$.

4. Conclusion

As I–V dipoles turn into the aggregates for $KCl:Sr^{2+}$, the effective stress, τ_{P1}, becomes obviously smaller at low temperature, because the separation between the weak obstacles lying on the dislocation is wider. In addition, we supposed that the decrease of τ_{P1} is attributable to the loss of tetragonality in terms of Fleischer's model as I–V dipoles aggregate. Then the force–distance profile between a dislocation and aggregates for the annealed $KCl:Sr^{2+}$ cannot be approximated by Fleischer's model and the activation energy for the breakaway of a dislocation from weak obstacles becomes small for the annealed specimen, compared with the quenched one. Furthermore, the critical temperature, T_c, for the annealed $KCl:Sr^{2+}$ is slightly smaller in contrast to that for the quenched one.

References

1. M. L. GREEN and G. ZYDZIK, *Scripta Metall.* **6** (1972) 991.
2. J. S. DRYDEN, S. MORIMOTO and J. S. COOK, *Philos. Mag.* **12** (1965) 379.
3. H. PICK and H. WEBER, *Z. Phys.* **128** (1950) 409.
4. R. L. FLEISCHER, *J. Appl. Phys.* **33** (1962) 3504.
5. T. OHGAKU and N. TAKEUCHI, *Phys. Status Solidi (a)* **134** (1992) 397.
6. J. S. COOK and J. S. DRYDEN, *Proc. Phys. Soc.* **80** (1962) 479.
7. T. OHGAKU and N. TAKEUCHI, *Phys. Status Solidi (a)* **118** (1990) 153.
8. A. B. LIDIARD, Handbuch der Physik, Vol. 20 (Springer, Berlin, 1957) p. 246.
9. T. OHGAKU and N. TAKEUCHI, *Phys. Status Solidi (a)* **111** (1989) 165.
10. G. Y. CHIN, L. G. VAN UITERT, M. L. GREEN, G. J. ZYDZIK and T. Y. KOMETANI, *J. Am. Ceram. Soc.* **56** (1973) 369.
11. H. CONRAD, *Can. J. Phys.* **45** (1967) 581.
12. A. J. E. FOREMAN and M. J. MAKIN, *Philos. Mag.* **14** (1966) 911.

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