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Interaction between a dislocation and various divalent impurities in KCl single crystals

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The strain-rate cycling test during the Blaha effect measurement at 77–254 K was carried out for four kinds of single crystals: KCl doped with Mg^{2+}, Ca^{2+}, Sr^{2+} or Ba^{2+} as a weak obstacle. It was found that the critical temperature, at which the effective stress is zero, increases when the divalent ionic size approaches increasingly that of the K^+ ion. Furthermore, the activation energy for the interaction between a dislocation and the divalent ion-vacancy dipole was determined. The activation energy increases with the divalent ionic size. Fleischer's model attributes this to the difference of tetragonality around the dipole for each specimen.

1. Introduction

It has been reported previously that the strain-rate cycling test during the Blaha effect measurement can separate the influence of impurities and forest dislocations on dislocation motion at room temperature [1, 2]. The Blaha effect is the phenomenon whereby static flow stress decreases when an ultrasonic oscillatory stress is superimposed. Subsequently, the temperature dependence of the effective stress due to monovalent impurities in KCl single crystals doped with Br^- and I^- at temperatures of 77–420 K were discussed, and it was reported that the measurement of strain-rate sensitivity under application of ultrasonic oscillatory stress during plastic deformation finishes useful information on the interaction between a mobile dislocation and impurities [3]. Recently, we have measured the strain-rate sensitivity and the stress decrement due to oscillation for three kinds of single crystals: KCl, KCl doped with Sr^{2+}, and KCl doped with various impurities in the temperature range 77–220 K, and information was obtained on the interaction between a dislocation and weak obstacles [4].

It is well known that aliovalent cation impurities are a much more potent source of solution strengthening in ionic crystals than are isovalent cations. The phenomenon has been known for many years in alkali halides [5–7]. In order to determine if the divalent ionic size is an important factor in solution hardening, the interaction between a dislocation and various divalent impurities was investigated in KCl single crystals doped with Mg^{2+}, Ca^{2+}, Sr^{2+} or Ba^{+2} in the same way as described elsewhere [4]. The aim of the present work was to investigate the effect of various divalent impurities on the critical temperature, T_C, at which the effective stress due to a weak obstacle lying on the dislocation with the largest separation, is zero.

2. Experimental procedure

The single crystals used in this study were KCl doped with Mg^{2+} (0.035 mol % in the melt), Ca^{2+} (0.035 and 0.065 mol % in the melt), Sr^{2+} (0.035, 0.050 and 0.065 mol % in the melt) or Ba^{2+} (0.050 and 0.065 mol % in the melt) as divalent impurities, all of which were grown by the Kyropoulos method in air. The specimens, which were obtained by cleaving the ingots into $5 \times 5 \times 15\ mm^3$ crystal blocks, were annealed at 973 K for 24 h in order to reduce the dislocation density as far as possible, followed by cooling to room temperature at the rate of $40\ K\,h^{-1}$. Furthermore, the specimens were held at 673 K for 30 min and quenched to room temperature immediately before the test, in order to disperse the impurities into them. The specimens were deformed by compression along the $\langle 100 \rangle$ axis and the ultrasonic oscillatory stress was applied by the reasonator in the same direction as the compression. The reasonant frequency was 20 kHz. Strain-rate cycling tests made between the crosshead speeds of 20 and 100 $\mu m\ min^{-1}$ during the Blaha effect measurement were carried out at 77–254 K. The stress drop due to superposition of oscillatory stress during plastic deformation is $\Delta\tau$ and the stress change due to the strain-rate cycling is $\Delta\tau'$, when the strain-rate cycling is carried out keeping the stress amplitude constant. We obtained $\Delta\tau'/\Delta \ln \dot{\varepsilon}$ as the strain-rate sensitivity from the value of $\Delta\tau'$. The details of the tests during the plastic deformation were described elsewhere [4].

3. Results and discussion

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

Fig. 1 shows the influence of temperature on the relation between the strain-rate sensitivity, $\Delta\tau'/\Delta \ln \dot{\varepsilon}$,

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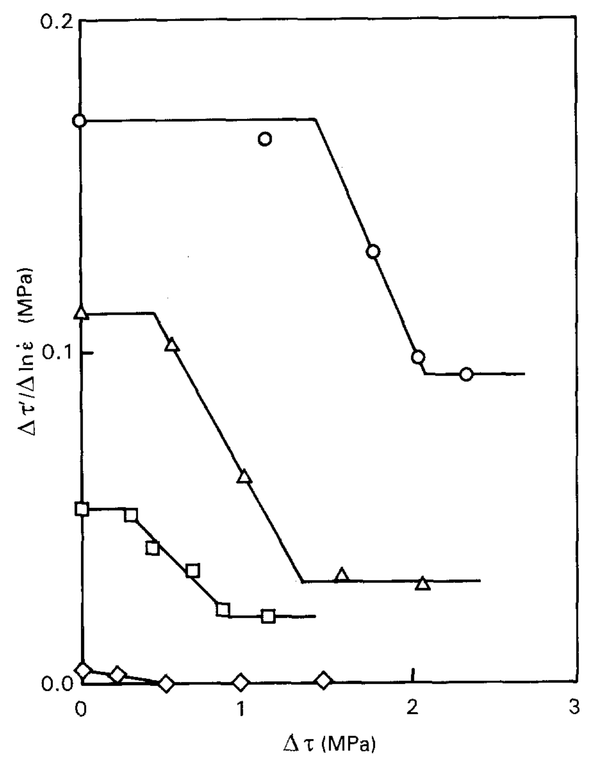

Figure 1 Relationship between the strain-rate sensitivity and the stress decrement at the shear strain of 10% for KCl: Sr^{2+} (0.050 mol %) at various temperatures: (○) 103 K, (△) 133 K, (□) 200 K, (◇) 225 K.

and the stress decrement, $\Delta\tau$, for KCl single crystals doped with Sr^{2+} as weak obstacles. As the temperature is high, the first bending point, τ_{P1}, shifts in the direction of low stress decrement and does not appear up to 225 K. The first plateau region indicates that the average length of the dislocation segment remains constant in that region [3, 4]. Thus, application of oscillation with low stress amplitude cannot influence the average length of the dislocation segment at low temperature, but even a low stress amplitude can do so at a temperature of 225 K. Such a phenomenon (Fig. 1) was also observed for the other specimens: KCl doped with Mg^{2+}, Ca^{2+} or Ba^{2+}. Generalization of the above phenomena gives Fig. 2. The phenomenon shown in the figure reflects the influence of ultrasonic oscillation on the dislocation motion on the slip plane containing many weak obstacles and a few strong ones during plastic deformation. The relationship between the strain-rate sensitivity and the stress decrement gives information of the interaction between a dislocation and an impurity, as mentioned above [3, 4, 8]. $(\Delta\tau'/\Delta \ln \dot{\varepsilon})_P$ due to weak obstacles is defined in Fig. 2. The reason for this will be described in a later section. In the previous paper [4], τ_{P1} was considered to represent the effective stress due to the weak obstacles which lie on the dislocation with the largest separation when the dislocation moves forward with the help of oscillation, and τ_{P1} should depend on temperature, and on the type and density of obstacles. Therefore, observation of τ_{P1} provides information on the interaction between a dislocation and weak obstacles.

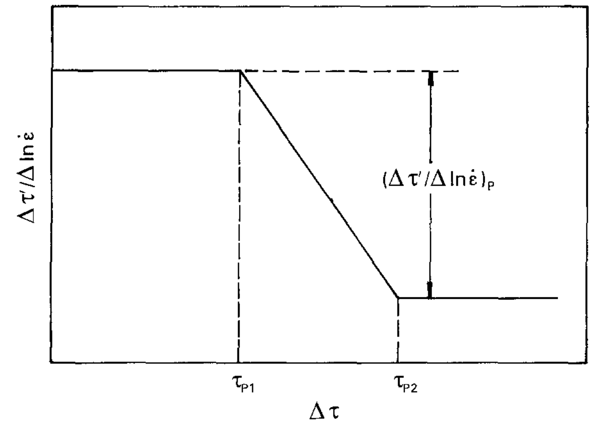

Figure 2 Illustration of relationship between the strain-rate sensitivity and the stress decrement at a given strain.

3.2. Relation between the temperature and τ_{P1}

Fig. 3a–d show the dependence of τ_{P1} on the temperature for KCl doped with Mg^{2+} (0.035 mol % in the melt), Ca^{2+} (0.065 mol % in the melt), Sr^{2+} (0.050 mol % in the melt) or Ba^{2+} (0.065 mol % in the melt). τ_{P1} decreases with increasing temperature for the four kinds of specimens. The critical temperature, T_C, at which the curves intersect the abscissa and τ_{P1} is zero, is around 180, 220, 230 and 260 K for KCl:Mg^{2+}, KCl:Ca^{2+}, KCl:Sr^{2+}, and KCl:Ba^{2+}, respectively. When alkali halide crystals are doped with divalent ions, the divalent cations are mostly associated with cation vacancies in the form of a dipole for crystals quenched from a high temperature. A dislocation moves on a single slip plane and interacts strongly only with those defects lying within one

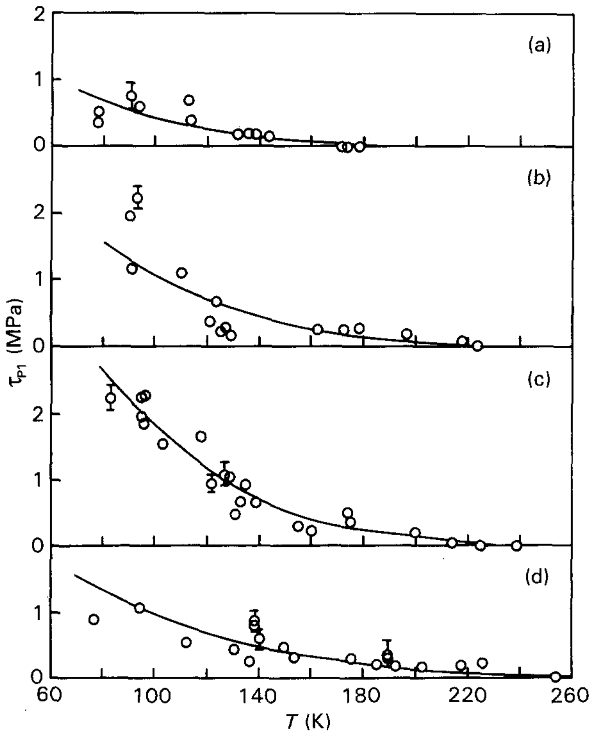

Figure 3 Dependence of τ_{P1} on the temperature for (a) KCl:Mg^{2+} (0.035 mol %), (b) KCl:Ca^{2+} (0.065 mol %), (c) KCl:Sr^{2+} (0.050 mol %), and (d) KCl:Ba^{2+} (0.065 mol %).

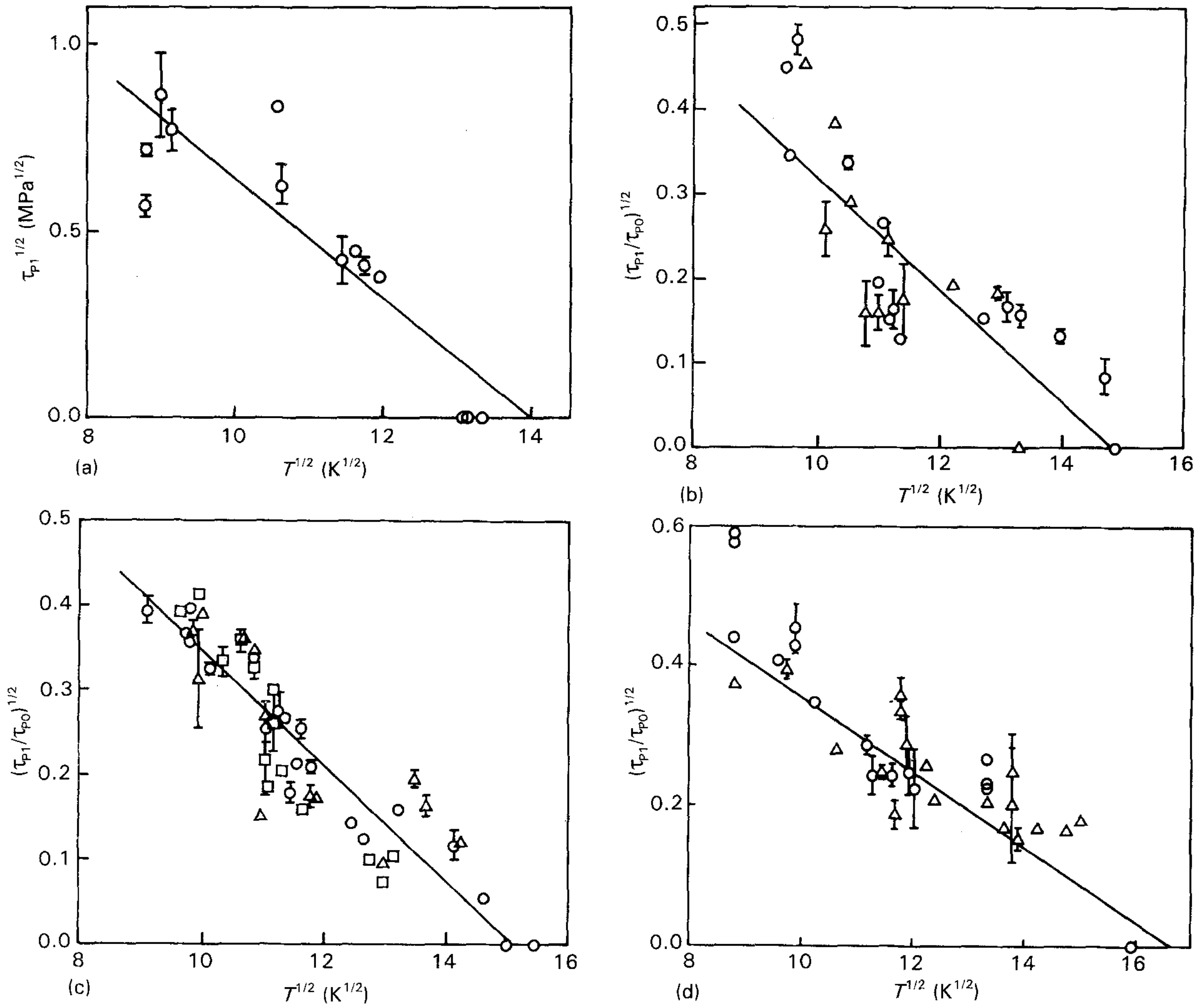

Figure 4 Linear plots of $\tau_{P1}^{1/2}$ and $T^{1/2}$ for (a) KCl:Mg^{2+} (○) 0.035 mol %, (b) KCl:Ca^{2+} (△) (0.035 mol % and (○) 0.065 mol %, (c) KCl:Sr^{2+} (△) 0.035 mol %, (○) 0.050 mol %, and (□) 0.065 mol %, and (d) KCl:Ba^{2+} (○) 0.050 mol % and (△) 0.065 mol %.

TABLE I Values of T_C

Specimen	T_C(K)
KCl:Mg^{2+}	191
KCl:Ca^{2+}	221
KCl:Sr^{2+}	227
KCl:Ba^{2+}	277

atom spacing of the glide plane. Then, the relation between the effective stress and the temperature can be approximated by [9]

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

where τ_{P0} is the effective stress due to the weak obstacles without thermal activation. The temperature dependence of τ_{P1} reveals the force–distance profile which expresses the interaction between a dislocation and weak obstacles. Fig. 4a–d shows that the relation between τ_{P1} and temperature agrees with Equation 1 for several specimens. We can then determine the critical temperature, T_C, from the intersection with the abscissa for each specimen, as shown in Table I. When the divalent ionic size is close to that of K$^+$, T_C tends to increase.

3.3. Activation energy for the interaction between a dislocation and the divalent impurities

The rate-controlling mechanism during plastic deformation of KCl doped with divalent impurities is thermally activated overcoming of the weak obstacles dispersed in the lattice by dislocation motion [10]. Then the strain rate, $\dot{\varepsilon}$, at low temperature is assumed to be given by an Arrhenius-type relationship [11]

$$\dot{\varepsilon} = \dot{\varepsilon}_0 \exp(-\Delta G/kT) \qquad (2)$$

where $\dot{\varepsilon}_0$ is a frequency factor which is unique for a particular dislocation mechanism, ΔG the change in Gibbs free energy of activation for the dislocation motion, and kT has the usual meaning. If changes in entropy, ΔS, are neglected, ΔG of Equation 2 may be replaced by the activation energy ΔH, and the activation energy is expressed by

$$\Delta H = \alpha kT \qquad (3)$$

where α is a constant. The value of the activation energy is given by [12]

$$\Delta H = -kT^2 (\partial \ln \dot{\varepsilon}/\partial\tau)(\partial\tau/\partial T) \qquad (4)$$

$(\partial\tau/\partial T)$ can be obtained from the differentiation of Equation 1

$$\partial\tau_{P1}/\partial T = [1 - (T/T_C)^{-1/2}]\,\tau_{P0}/T_C \qquad (5)$$

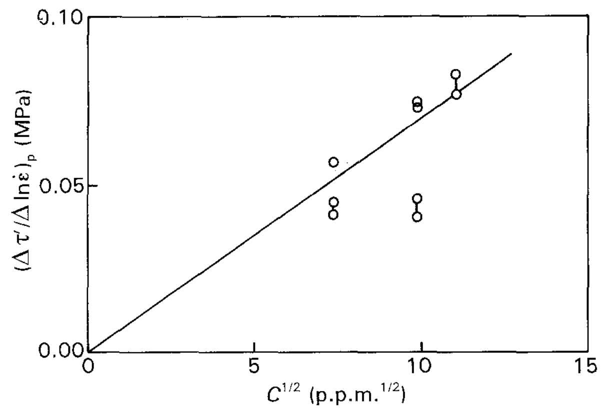

Figure 5 Relationship between $(\Delta\tau'/\Delta \ln \dot{\varepsilon})_P$ and $c^{1/2}$ for KCl : Sr^{2+} at 120–130 K.

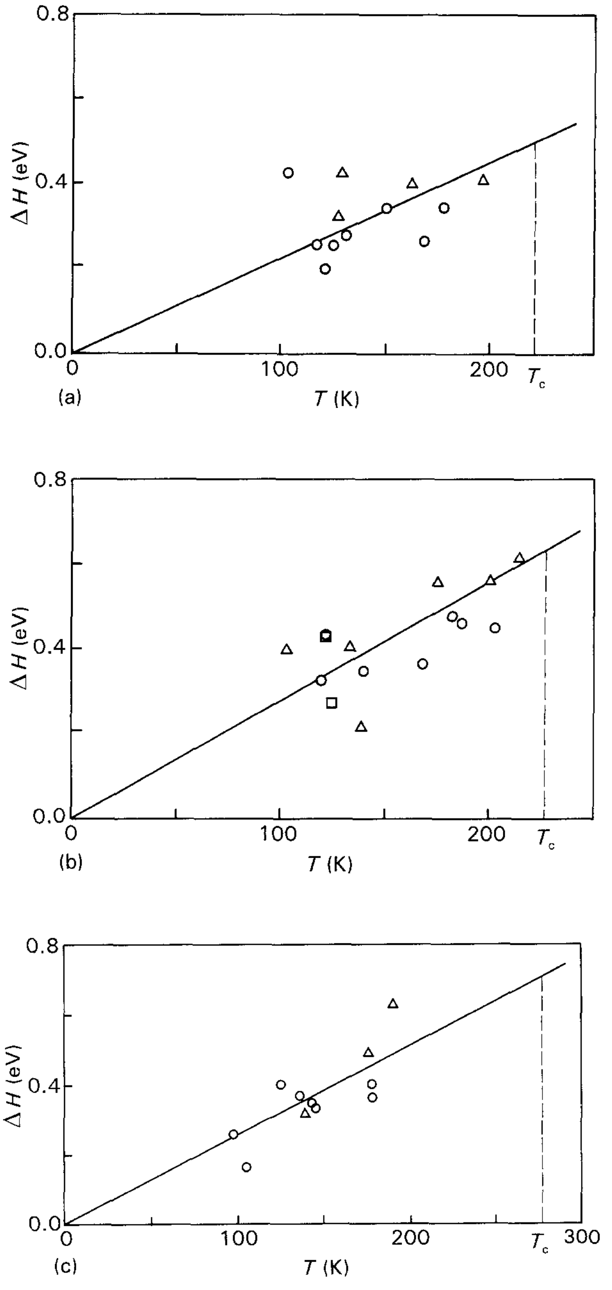

Figure 6 Relationship between the temperature and the activation energy for (a) KCl : Ca^{2+} (○) 0.035 mol % and (△) 0.065 mol %, (b) KCl : Sr^{2+} (○) 0.035 mol %, (△) 0.050 mol%, and (□) 0.065 mol %, and (c) KCl : Ba^{2+} (○) 0.050 mol % and (△) 0.065 mol %.

We assumed from two phenomena that $(\partial\tau'/\partial \ln \dot{\varepsilon})_P$ in Fig. 2 is the strain-rate sensitivity due to impurities. The first phenomenon is that the curve of Fig. 2 shifts upwards with increasing shear strain because the strain-rate sensitivity due to dislocation cuttings increases with increasing strain, while $(\Delta\tau'/\Delta \ln \dot{\varepsilon})_P$ is constant independently of the strain [3, 4]. The other phenomenon is that the strain-rate sensitivity, $(\Delta\tau/\Delta \ln \dot{\varepsilon})_P$, is proportional to $c^{1/2}$ at a given temperature. This is shown in Fig. 5. The concentration of the I–V dipole, c, is estimated by the dielectric loss measurement.

The values of the activation energy, ΔH, derived using Equation 4, are plotted as a function of temperature in Fig. 6a–c. It is seen from these figures that the relation between the temperature and the activation energy is satisfied by Equation 3. The value of $H(T_C)$, taken from Fig. 6a–c, corresponds to the activation energy for the overcoming of the defects by a dislocation at 0 K. The values are 0.50, 0.63, and 0.71 eV for KCl : Ca^{2+}, KCl : Sr^{2+}, and Kcl : Ba^{2+}, respectively. The values of the activation energy for KCl : Mg^{2+} could not be derived because the second bending point, τ_{P2}, in Fig. 2 did not appear in our experiment. The results that $H(T_C)$ increases with increasing divalent cation size, suggest that the tetragonality, $\Delta\varepsilon$, resulting from the formation of the I–V dipole for alkali halide doped with divalent cation, in Fleischer's model [9, 13] increases when the divalent ionic size increasingly approaches that of the K^+ ion.

4. Conclusion

T_C was derived from the relation between $T^{1/2}$ and $\tau_{P1}^{1/2}$ which reveals the force–distance curve with respect to Fleischer's model in Fig. 4a–d. In Table I, the results for each specimen are summarized. When the divalent cation size is increasingly close to the K^+ ionic size, T_C tends to increase. Furthermore, the values of the activation energy for the interaction between a dislocation and impurities, as obtained from Fig. 6a–c, are 0.50, 0.63, and 0.71 eV for KCl : Ca^{2+}, KCl : Sr^{2+}, and KCl : Ba^{2+}, respectively. The results suggest that the tetragonality around the dipole increases with H, T_C from Fleischer's model.

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