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Groping for a suitable force-distance relation between a dislocation and the impurity for KCl : Li$^+$ and KCl : Na$^+$ by the Blaha effect

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A strain-rate cycling test during the Blaha effect measurement was carried out at 80–300 K for KCl : Li$^+$ (0.5 mol % in the melt) and KCl : Na$^+$ (0.5 mol % in the melt). We attempted to select the most suitable force-distance relation between a dislocation and the monovalent cation impurity among the three models, which are a square force-distance relation, a parabolic one, and a triangular one taking account of the Friedel relation the groping for the most suitable force-distance relation was conducted by following three relationships: the relation between effective stress and temperature, the dependence of strain-rate sensitivity due to the impurities on temperature, and the proportionality of $\Delta H(T)$. The $\Delta H(T)$ is the activation enthalpy for the interaction between a dislocation and an impurity as a function of temperature. As a result, the square force-distance relation seemed to be the most suitable of the three for KCl : Na$^+$. However, it was difficult to select the most suitable relation of the three for KCl : Li$^+$. Furthermore, on the three force-distance relations, critical temperature, T_c, and $\Delta H(T_c)$ were obtained for both the specimens. © *1998 Kluwer Academic Publishers*

1. Introduction

It has been reported that a strain-rate cycling test during the Blaha effect measurement can separate the contributions arising from the interaction between a dislocation and impurities and that between the dislocations themselves during plastic deformation [1, 2]. The Blaha effect is the phenomenon where static flow stress decreases when an ultrasonic oscillatory stress is superimposed [3]. From a strain-rate cycling test during the Blaha effect measurement, we have obtained the relation curve of strain-rate sensitivity and stress decrement and useful information on the interaction between a mobile dislocation and impurities for KCl doped with divalent impurities [4–6]. It seems that the relation curve of strain-rate sensitivity and stress decrement reflects the influence of ultrasonic oscillation on the dislocation motion on the slip plane containing many impurities and few forest dislocations. In this paper, various force-distance relations which represent the interaction between a dislocation and an impurity are investigated with a view to selecting the most suitable one from the information given by the above-mentioned method for KCl doped with monovalent cation impurities. Furthermore, a critical temperature and the activation enthalpy for the interaction between a dislocation and the impurity are obtained for various force-distance relations.

2. Experimental procedure

Two kinds of single crystals used in this study, KCl doped with Li$^+$ (0.5 mol % in the melt) and KCl doped with Na$^+$ (0.5 mol % in the melt), were grown by the Kyropoulos method in air. The specimens, which were obtained from the ingots by cleaving to the size of $5 \times 5 \times 15$ mm^3, were annealed at 973 K for 24 h and were cooled to room temperature at the rate of 40 Kh^{-1} in order to reduce dislocation density as far as possible. Furthermore, the specimens were held at 673 K for 30 min, followed by quenching to room temperature immediately before the test, in order to disperse the impurities into them.

The two kinds of specimens were deformed by compression along the $\langle 1\,0\,0 \rangle$ axis at temperatures from 80–300 K. Each specimen was held at the test temperature for 30 min prior to the compression test and the stability of temperature during the test was kept within 2 K. The ultrasonic oscillatory stress was applied by a resonator in the same direction as the compression. The resonant frequency was 20 kHz. Because the wavelength, which is 225 mm, is 15 times as long as the length of the specimen, the strain of the specimen is considered to be homogeneous.

The stress drop due to superposition of oscillatory stress during plastic deformation is $\Delta\tau$, which increases with the stress amplitude at a given temperature and shear strain. 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. The strain-rate sensitivity, $\Delta\tau'/\Delta \ln \dot{\varepsilon}$, is given by $\Delta\tau'/1.609$, since the strain-rate cycling tests are made between the crosshead speeds of 20 and 100 μm min^{-1}. Schematic illustrations of the apparatus and the strain-rate cycling test during the Blaha effect measurement are shown in the previous paper [4]. The relation curve of $\Delta\tau'/\Delta \ln \dot{\varepsilon}$ against $\Delta\tau$ at a given temperature and shear strain, ε, is obtained from two graphs, $\Delta\tau - \varepsilon$ and $\Delta\tau'/\Delta \ln \dot{\varepsilon} - \varepsilon$, at various stress amplitudes and a given temperature.

3. Results

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

There are two bending points and two plateau regions on the relation curve of strain-rate sensitivity and stress decrement during the Blaha effect measurement for KCl doped with Li^+, as shown in Fig. 1. We denoted the first bending point at low stress decrement by τ_{p1} and the second one at high stress decrement by τ_{p2}. Fig. 1 concerns the relation between strain-rate sensitivity and stress decrement at various temperatures and a shear strain of 12% for $KCl:Li^+$. As the temperature increases, τ_{p1} and τ_{p2} shift in the direction of low stress decrement. The same phenomenon as Fig. 1 is also observed for $KCl:Na^+$. Note that τ_{p1} does not appear at a temperature above 221 K for $KCl:Li^+$ and at above 279 K for $KCl:Na^+$. The relation between strain-rate sensitivity and stress decrement for $KCl:Li^+$ at 299 K is shown in Fig. 2a and that for $KCl:Na^+$ at 279 K in Fig. 2b. For both the specimens, τ_{p1} does not appear on the relation curves of strain-rate sensitivity and stress decrement at various shear strains. These phenomena can be understood as follows. An application of ultrasonic oscillatory stress with low amplitude cannot influence the average length of the dislocation segment at low temperature as shown in Fig. 1, but even the stress with low amplitude can do so at such a temperature as Fig. 2a for $KCl:Li^+$ and b for $KCl:Na^+$, because τ_{p1} is considered to represent the effective stress due to only one type of the impurities which lie on the dislocation with the largest separation when the dislocation moves forward with the help of oscillation [4].

The strain-rate sensitivity becomes negative at shear strains of 24% and 28% ($\Delta\tau > 0.11$ MPa) for $KCl:Li^+$ and at shear strains of 8% ($\Delta\tau > 0.42$ MPa) and 14% ($\Delta\tau > 0.50$ MPa) for $KCl:Na^+$ as shown in Fig. 2a and b. The negative strain-rate sensitivity appears on the relation curves of strain-rate sensitivity and stress decrement above 216 K for $KCl:Li^+$ and above 246 K for $KCl:Na^+$.

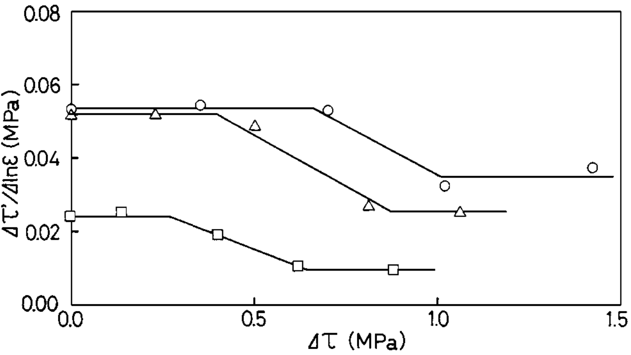

Figure 1 Relationship between the strain-rate sensitivity and the stress decrement for $KCl:Li^+$ (0.5 mol % in the melt) at a shear strain of 12% and various temperatures: (○) 122 K, (△) 146 K, (□) 177 K.

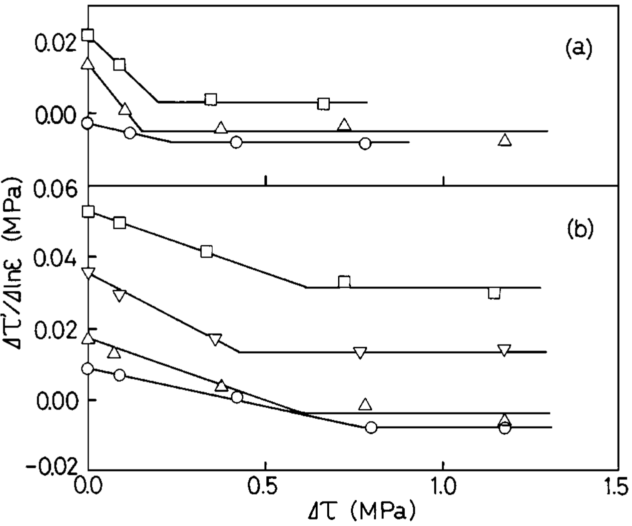

Figure 2 Relationship between the strain-rate sensitivity and the stress decrement for (a) $KCl:Li^+$ (0.5 mol % in the melt) at 299 K and ε: (○) 24%, (△) 28%, (□) 32% and (b) $KCl:Na^+$ (0.5 mol % in the melt) at 279 K and ε: (○) 8%, (△) 14%, (▽) 20%, (□) 26%.

3.2. Dependence of τ_{p1}, τ_{p2} and τ_y on the temperature

Fig. 3a for $KCl:Li^+$ and Fig. 3b for $KCl:Na^+$ show the dependence of τ_{p1}, τ_{p2} and the critical resolved shear stress, τ_y, on temperature. The plots of τ_{p1} and τ_{p2} in Fig. 3a and b are the mean value at a given temperature because τ_{p1} and τ_{p2} vary little with shear strain. The τ_y is determined at the intersection of the tangent to the easy glide region at a stress-strain curve and the straight line extrapolated from the elastic region at the curve. The curve of τ_{p1} is fitted to the data by using the least

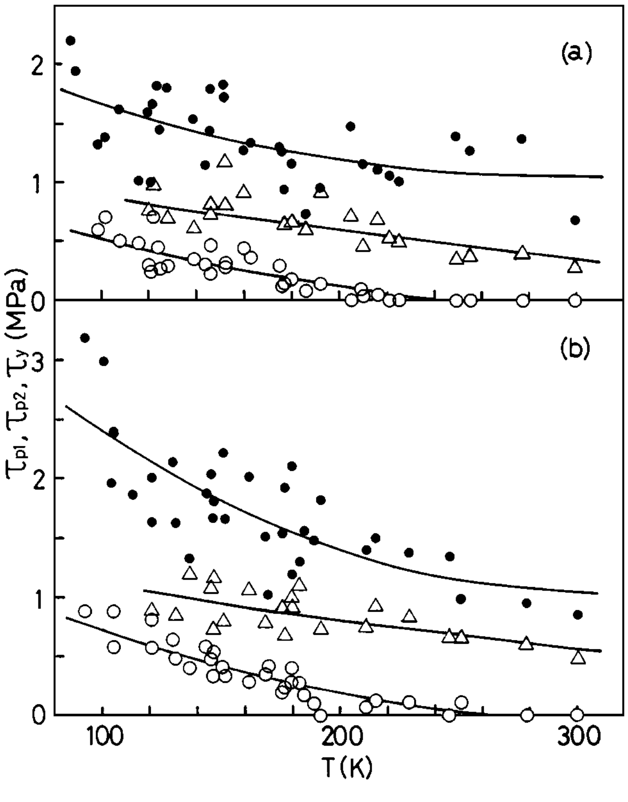

Figure 3 Dependence of (○) τ_{p1}, (△) τ_{p2}, and (•) τ_y on the temperature for (a) $KCl:Li^+$ (0.5 mol % in the melt) and (b) $KCl:Na^+$ (0.5 mol % in the melt).

squares method, assuming that the force-distance profile is a square [7] and the two curves of τ_{p2} and τ_y are to guide the reader's eye. τ_{p1} and τ_{p2} decrease with increasing temperature as the variation of τ_y within the temperature for both the specimens. At high temperature, the critical temperature, T_c, at which τ_{p1} is zero can be estimated to be around 250 K for $KCl:Li^+$ and 270 K for $KCl:Na^+$ from Fig. 3a and b. τ_{p2} for $KCl:Li^+$ and $KCl:Na^+$ increases with decreasing temperature and gradually approaches the τ_{p1} curve, which is the same phenomena for $KCl:Br^-$ and $KCl:I^-$ [8], as shown in Fig. 3a and b. From the description in previous papers [5, 8], this result for both the specimens may reveal that the distribution of dislocation segments becomes narrow with decreasing temperature.

4. Discussion

4.1. Relation between effective stress and temperature

The separation of various models between a dislocation and an impurity for a particular case has been conducted from the effect of the impurity concentration on the flow stress at 0 K and the variation of the thermal component of the flow stress with temperature [9]. In this section, the three models [7], which are a square force-distance relation, a parabolic one, and a triangular one, taking account of the Friedel relation [10] are examined on the basis of the relation between τ_{p1} and temperature for both the specimens. As described in the previous paper [4], the relation between τ_{p1} and temperature reveals the force-distance relation which represents the interaction between a dislocation and an impurity. The square force-distance relation, the parabolic one, and the triangular one are termed the SQ, the PA, and the TR, respectively in this paper. Fig. 4a and b show that the interaction between a dislocation and the impurity for $KCl:Li^+$ and $KCl:Na^+$ can be approximated to the SQ. The relation formula of τ_{p1} and temperature, T, is given by

$$\tau_{p1}^{2/3} = 1 - T \tag{1}$$

The value of T_c at which the line intersects the abscissa is 254 K for $KCl:Li^+$ and 267 K for $KCl:Na^+$. T_c is not influenced by the impurity concentration [4, 8]. τ_{p0}, which is obtained by extrapolating the line to 0 K is 1.10 MPa for $KCl:Li^+$ (0.5 mol % in the melt) and 1.45 MPa for $KCl:Na^+$ (0.5 mol % in the melt). τ_{p0} is the effective stress due to the impurities without thermal activation. If the interaction between a dislocation and the impurity for both the specimens can be approximated to the another two models, that is, the PA or the TR, T_c and τ_{p0} are given in Table I. The SQ gives the following relation

$$(\tau_{p1}/\tau_{p0})^{2/3} = 1 - (T/T_c) \tag{2}$$

the PA gives

$$(\tau_{p1}/\tau_{p0})^{2/3} = 1 - (T/T_c)^{2/3} \tag{3}$$

and the TR gives

$$(\tau_{p1}/\tau_{p0})^{2/3} = 1 - (T/T_c)^{1/2} \tag{4}$$

TABLE I Value of T_c and τ_{p0} for the three force-distance relations between a dislocation and the impurity

The force-distance relation	Specimen[a]	T_c (K)	τ_{p0} (MPa)
Square	$KCl:Li^+$	254	1.10
	$KCl:Na^+$	267	1.45
Parabola	$KCl:Li^+$	256	1.73
	$KCl:Na^+$	266	2.29
Triangle	$KCl:Li^+$	257	2.44
	$KCl:Na^+$	271	3.16

[a] The concentration of Li^+ or Na^+ in KCl is 0.5 mol % in the melt.

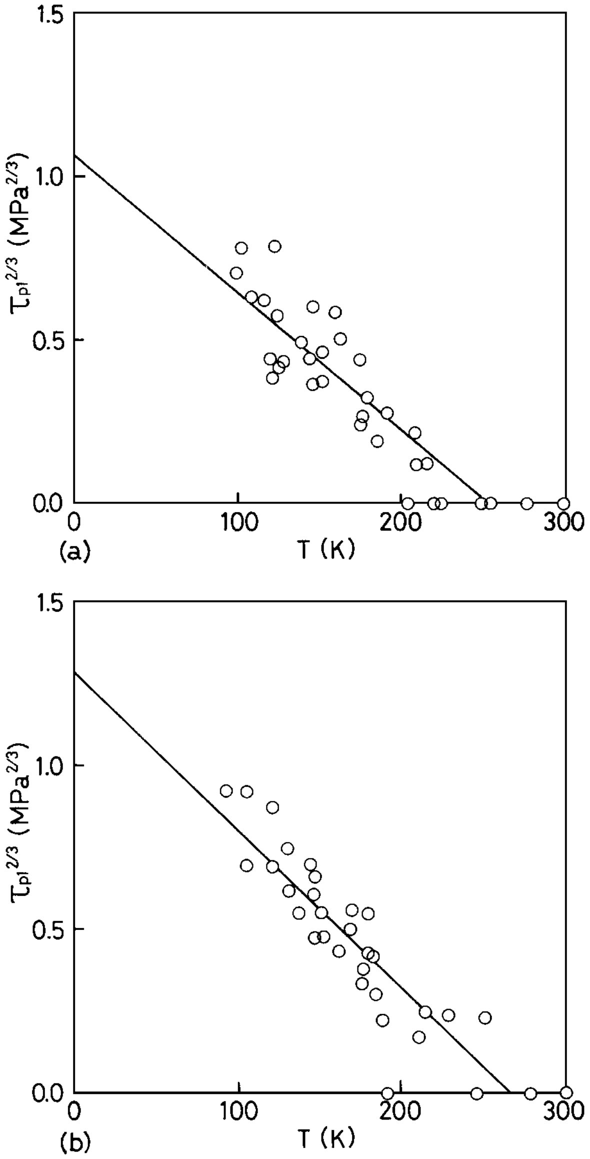

Figure 4 Linear plots of $\tau_{p1}^{2/3}$ and T for (a) $KCl:Li^+$ (0.5 mol % in the melt) and (b) $KCl:Na^+$ (0.5 mol % in the melt).

The results of Equations 2–4 are shown in Fig. 5a–c for $KCl:Li^+$ (0.5 mol % in the melt) and Fig. 6a–c for $KCl:Na^+$ (0.5 mol % in the melt). The slopes of straight lines in Fig. 5a–c and Fig. 6a–c are determined by the method of least squares. However as can be seen from Fig. 5a–c and Fig. 6a–c, there is no difference in the linear effective stress-temperature relation for the three models as 0no [11] described about the applied stress-temperature relation.

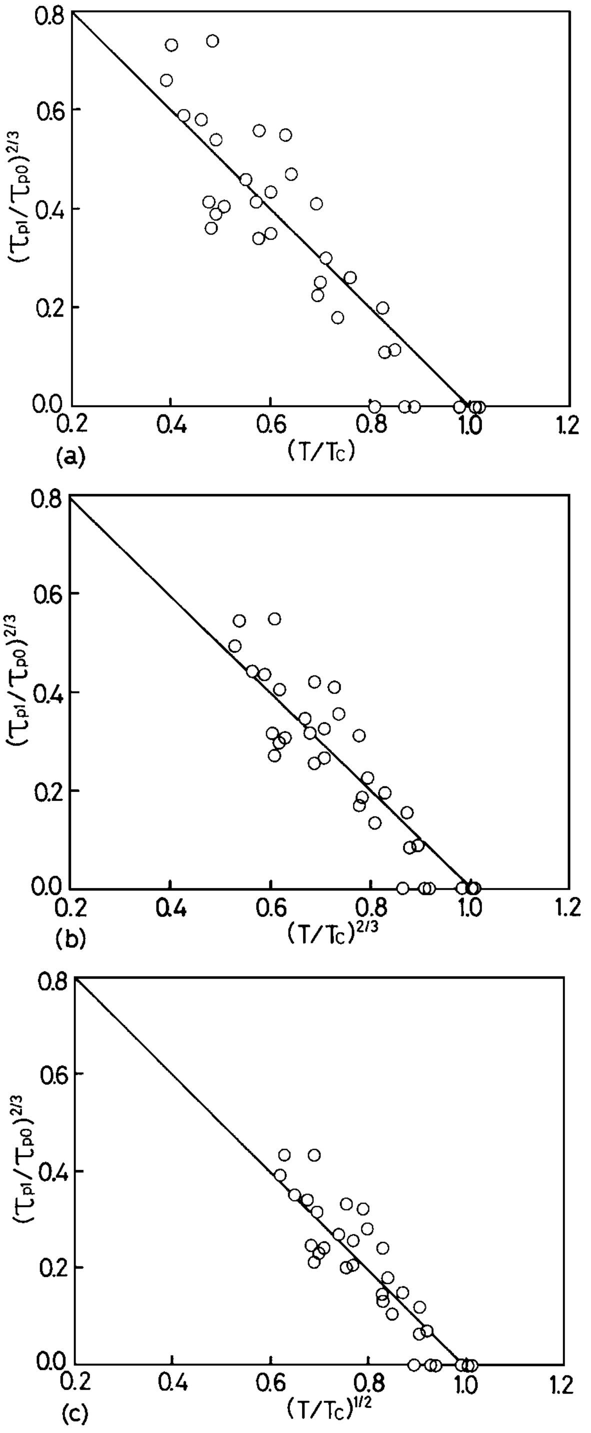

Figure 5 Relationship between the effective stress and the temperature for KCl : Li^+ (0.5 mol % in the melt) at various models: (a) the square force-distance relation, (b) the parabolic one, and (c) the triangular one.

On the three force-distance relations, the value of T_c is almost the same, irrespective of the kind of force-distance relation for both the specimens, and the value of T_c for KCl : Li^+ is obviously small in comparison with that for KCl : Na^+ from Table I. We have previously found that when the divalent cationic size is increasingly close to the K^+ ionic size, T_c tends to increase for KCl doped with Mg^{2+}, Ca^{2+}, Sr^{2+} or Ba^{2+} [6]. It may also be predicted for KCl doped with monovalent cation impurities that when the size of monovalent cation impurity is increasingly close to that of the K^+ from the small monovalent cationic size side, T_c tends to increase.

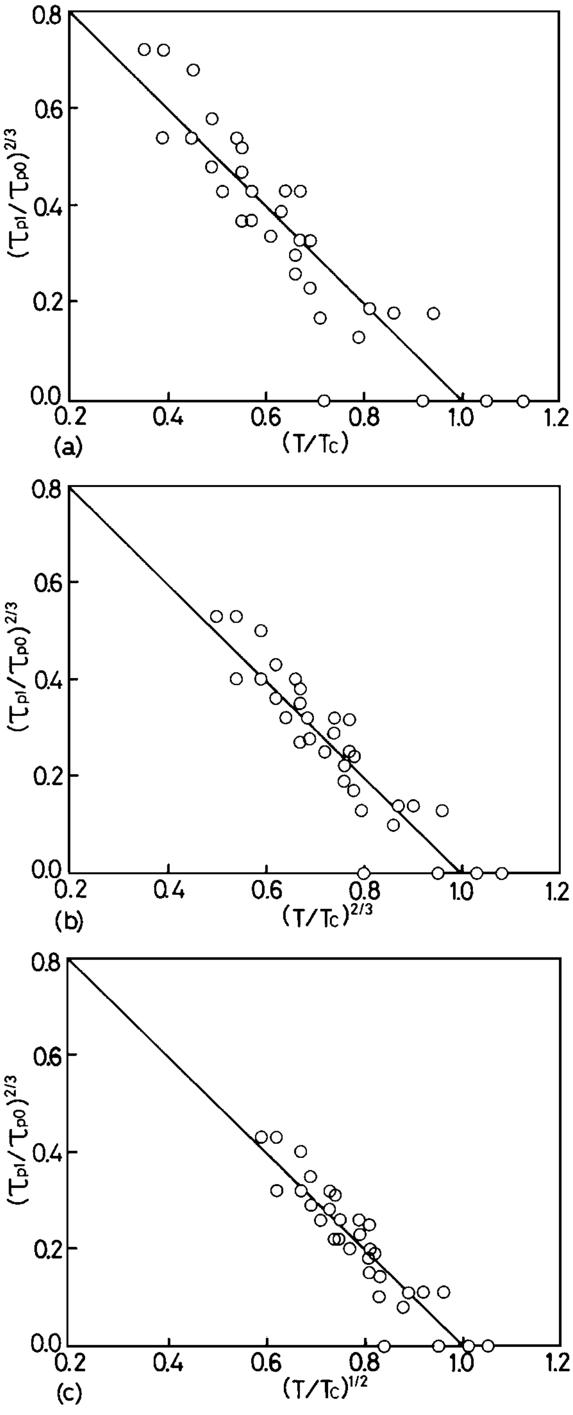

Figure 6 Relationship between the effective stress and the temperature for KCl : Na^+ (0.5 mol % in the melt) at various models: (a) the square force-distance relation, (b) the parabolic one, and (c) the triangular one.

4.2. Dependence of the strain-rate sensitivity due to the impurities on the temperature

The dependence of the strain-rate sensitivity due to the impurities on the temperature was investigated about the above-mentioned three force-distance relations [7] for both the specimens.

When the thermally activated overcoming of the substitutional impurities controls the dislocation velocity [12], the strain rate, $\dot{\varepsilon}$, is assumed to be given by an Arrhenius equation [13]

$$\dot{\varepsilon} = \dot{\varepsilon}_0 \exp(-\Delta G/kT) \quad (5)$$

where $\dot{\varepsilon}_0$ is a frequency factor, ΔG is the change in Gibbs free energy of activation for the dislocation motion, and k is the Boltzmann constant. If the changes in entropy, ΔS, are neglected, ΔG of Equation 5 may be replaced by the activation enthalpy, ΔH. That is, ΔH is expressed by [14, 15]

$$\Delta H = \alpha k T \tag{6}$$

where α is a constant. ΔH can be calculated from the relation [14–17]

$$\Delta H = -kT^2(\partial \ln \dot{\varepsilon}/\partial \tau)_T(\partial \tau/\partial T)_{\dot{\varepsilon}} \tag{7}$$

Combining Equations 6 and 7, we find

$$(\partial \tau/\partial \ln \dot{\varepsilon})_T = -(\partial \tau/\partial T)_{\dot{\varepsilon}} T/\alpha \tag{8}$$

The $(\partial \tau/\partial T)_{\dot{\varepsilon}}$ of Equation 8 can be obtained from the differentiation of Equation 2 with respect to the temperature for the SQ as follows

$$\partial \tau_{p1}/\partial T = -3(1 - T/T_c)^{1/2}\tau_{p0}/(2T_c) \tag{9}$$

In the same way, the $(\partial \tau/\partial T)_{\dot{\varepsilon}}$ of Equation 8 for the PA can be obtained from Equation 3 as follows

$$\partial \tau_{p1}/\partial T = -\left\{(T_c/T)^{2/3} - 1\right\}^{1/2}\tau_{p0}/T_c \tag{10}$$

and also from Equation 4, that of Equation 8 for the TR is given by

$$\partial \tau_{p1}/\partial T = -3\left\{(T_c/T) - (T_c/T)^{1/2}\right\}^{1/2}\tau_{p0}/(4T_c) \tag{11}$$

Further substituting of Equation 9 in Equation 8, the strain-rate sensitivity due to the impurities for the SQ yields

$$(\partial \tau/\partial \ln \dot{\varepsilon}) = \{(3\tau_{p0})/(2T_c)\}\{1 - (T/T_c)\}^{1/2}T/\alpha \tag{12}$$

Similarly from Equations 8 and 10, the strain-rate sensitivity due to the impurities for the PA is expressed by

$$(\partial \tau/\partial \ln \dot{\varepsilon}) = (\tau_{p0}/T_c)\left\{(T_c/T)^{2/3} - 1\right\}^{1/2}T/\alpha \tag{13}$$

and also from Equations 8 and 11, that for the TR is expressed by

$$(\partial \tau/\partial \ln \dot{\varepsilon}) = \{(3\tau_{p0})/(4T_c)\}\left\{(T_c/T) - (T_c/T)^{1/2}\right\}^{1/2}T/\alpha \tag{14}$$

Fig. 7a and b show the results for KCl : Li$^+$ (0.5 mol % in the melt) and KCl : Na$^+$ (0.5 mol % in the melt), that is, the each curve corresponds to the relation between temperature and the strain-rate sensitivity calculated from Equation 12 for the SQ, Equation 13 for the PA, and Equation 14 for the TR. The relation curve of temperature and the strain-rate sensitivity due to the impurities for the SQ, that for the PA, and that for the TR are represented as a solid line, a dashed line, and a dash-dotted line, respectively. The open circles in Fig. 7a and b correspond to the dependence of temperature and the strain-rate sensitivity due to impurities which is given by the difference between those at the first plateau region and at the second one on the relation curve of strain-rate sensitivity and stress decrement for KCl : Li$^+$ (0.5 mol % in the melt) and KCl : Na$^+$ (0.5 mol % in the melt) and is denoted by $(\Delta \tau'/\Delta \ln \dot{\varepsilon})_p$. The $(\Delta \tau'/\Delta \ln \dot{\varepsilon})_p$ is considered to be the strain-rate sensitivity due to the impurities from the following experimental results: the $(\Delta \tau'/\Delta \ln \dot{\varepsilon})_p$ is independent of the strain [4, 8] and is proportional to the square root of impurity concentration, which is related to the inverse of the average length of the dislocation segment, at a given temperature [6]. As can be seen from Fig. 7a and b, it is difficult to determine which force-distance relation is appropriate to the relation between temperature and $(\Delta \tau'/\Delta \ln \dot{\varepsilon})_p$ for both the specimens within the present temperatures. However, if the relation between temperature and $(\Delta \tau'/\Delta \ln \dot{\varepsilon})_p$ can be obtained below about 100 K, it will be possible to select the most suitable force-distance relation of the three for both the specimens on the basis of the dependence of the strain-rate sensitivity due to the impurities on the temperature. There is a great distinction in the strain-rate sensitivity due to the impurities for the three force-distance relations at the constant temperature below 100 K in comparison with that above 100 K, as shown in Fig. 7a and b.

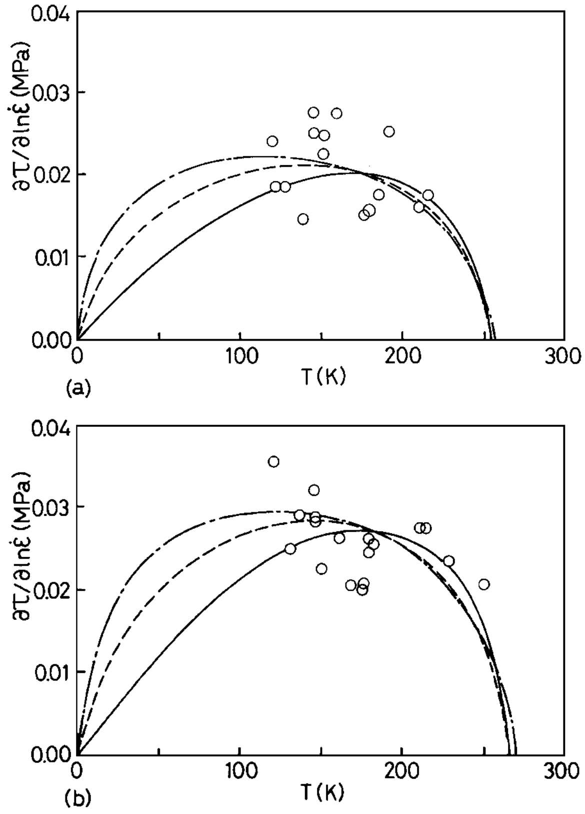

Figure 7 Dependence of the strain-rate sensitivity due to the impurities on the temperature for (a) KCl : Li$^+$ (0.5 mol % in the melt) and (b) KCl : Na$^+$ (0.5 mol % in the melt). (○) $(\Delta \tau'/\Delta \ln \dot{\varepsilon})_p$ is predicted by various models: the square force-distance relation (——), the parabolic one (- - -), and the triangular one (– - –).

TABLE II Value of $\Delta H(T_c)$ for the three force-distance relations between a dislocation and the impurity

The force-distance relation	Specimen	$\Delta H(T_c)$ (eV)
Square	$KCl:Li^+$	0.69
	$KCl:Na^+$	0.72
Parabola	$KCl:Li^+$	0.70
	$KCl:Na^+$	0.72
Triangle	$KCl:Li^+$	0.71
	$KCl:Na^+$	0.73

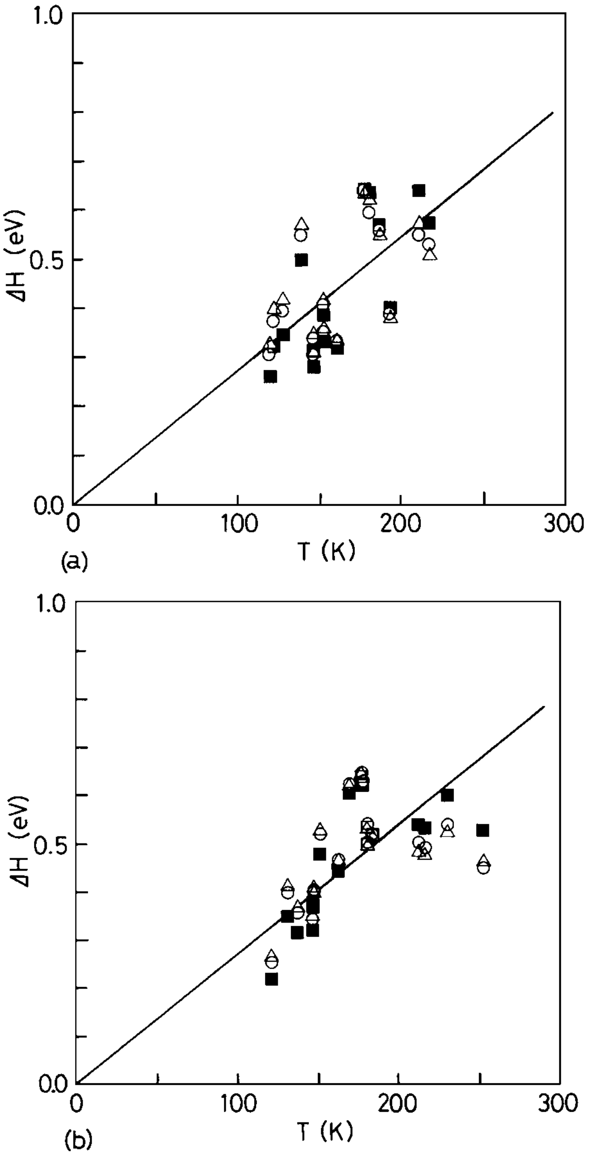

Figure 8 Proportional relationship between the temperature and the activation enthalpy for the interaction between a dislocation and the impurity for (a) $KCl:Li^+$ (0.5 mol % in the melt) and (b) $KCl:Na^+$ (0.5 mol % in the melt) at various models: (■) the square force-distance relation, (○) the parabolic one, and (△) the triangular one.

4.3. Relation between temperature and the activation enthalpy for the interaction between a dislocation and the impurity

The relation between temperature and the activation enthalpy for the interaction between a dislocation and the impurity was investigated for both the specimens about the above-mentioned three force-distance relations [7].

The activation enthalpy for the interaction between a dislocation and the impurity can be obtained from the substitution of Equation 9 for the SQ, Equation 10 for the PA, and Equation 11 for the TR in Equation 7. As for $(\partial \ln \dot{\varepsilon}/\partial \tau)_T$ in Equation 7, that is replaced by $(\Delta \ln \dot{\varepsilon}/\Delta \tau')_p$ as a reciprocal of the strain-rate sensitivity due to impurities. The results of calculations for ΔH against the temperature, $\Delta H(T)$, at the three force-distance relations are shown in Fig. 8a for $KCl:Li^+$ and Fig. 8b for $KCl:Na^+$. The slope of $\Delta H(T)$, which is determined by the method of least squares, is quite coincidental for the three force-distance relations for both the specimens. From the $\Delta H(T)$, the activation enthalpy for the SQ seems to be nearly proportional to the temperature in comparison with the cases of the PA and the TR for $KCl:Na^+$ as shown in Fig. 8b. However, it is difficult to select the most suitable model of the three for $KCl:Li^+$ from the proportionality of $\Delta H(T)$ in Fig. 8a. The value of $\Delta H(T_c)$ taken from the relation between temperature and the activation enthalpy for the interaction between a dislocation and the impurity is given in Table II. The value of $\Delta H(T_c)$ corresponds to the activation enthalpy for overcoming the strain field with cubic distortion around the substitutional impurity by a dislocation at 0 K. On the three force-distance relations, the value of ΔH (T_c) is almost the same, irrespective of the kind of force-distance relation for both the specimens and the value of $\Delta H(T_c)$ for $KCl:Li^+$ is nearly equal to that for $KCl:Na^+$ from Table II.

5. Conclusion

The force-distance relation, which represents the interaction between a dislocation and an impurity, is investigated for $KCl:Li^+$ and $KCl:Na^+$ with respect to three models [7], which are a square force-distance relation, a parabolic one, and a triangular one, taking account of the Friedel relation [10] by following three relationships: the relation between effective stress and temperature, the dependence of strain-rate sensitivity due to the impurities on temperature, and the proportionality of $\Delta H(T)$. As a result, the SQ seems to be the most suitable model of the three for $KCl:Na^+$ from the proportionality of $\Delta H(T)$ as shown in Fig. 8b. However, it is difficult to select the most suitable model of the three for $KCl:Li^+$ from the above-mentioned three relationships.

For the three force-distance relations, the values of T_c and $\Delta H(T_c)$ are almost the same, irrespective of the kind of force-distance relation for both the specimens. The value of T_c for $KCl:Li^+$ is obviously small in comparison with that for $KCl:Na^+$, whereas the value of $\Delta H(T_c)$ for $KCl:Li^+$ is nearly equal to that for $KCl:Na^+$ as summarized in Table I and II. As for T_c, it has been reported for KCl doped with various divalent cation impurities that when the divalent cationic size is increasingly close to that of the K^+ from the small divalent cationic size side, T_c tends to increase [6]. The same phenomenon as mentioned for KCl doped with divalent cation impurities may also be predicted for KCl doped with monovalent cation ones.

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