Study on the interaction between a dislocation and impurities in KCl : Sr^{2+} single crystals by the Blaha effect

Part I *Interaction between a dislocation and an impurity for the Fleischer's model taking account of the Friedel relation*

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It has been previously reported for KCl : Sr^{2+} (0.035, 0.050, 0.065 mol% in the melt) single crystals that the interaction between a dislocation and the impurity can be approximated to the Fleischer's model. From the values of ϕ_0 for the specimens, however, it was confirmed that the Friedel relation can be taken into the Fleischer's model. The ϕ_0 is the bending angle at which the dislocation embraces the impurities under the effective shear stress at 0 K. Furthermore, the interaction between a dislocation and the impurity could be approximated to the Fleischer's model taking account of the Friedel relation. This was examined on the basis of the dependence of strain-rate sensitivity due to the impurities on temperature at about 100–200 K. Then, the critical temperature, at which the effective shear stress is zero, was determined to be 289 K. In addition, the values of the enthalpy and the Gibbs free energy of activation for the breakaway of the dislocation from the impurity were obtained for the specimen.

1. Introduction

When alkali halide crystals are doped with divalent ions, the ions are expected to be paired with positive ion vacancies. The pairs are termed I-V dipoles and strongly interact with screw as well as edge dislocations. It has been previously reported for KCl single crystals doped with Mg^{2+}, Ca^{2+}, Sr^{2+} or Ba^{2+} that the interaction between a dislocation and the various divalent impurities can be approximated to the Fleischer's model [1]. This investigation was conducted on the basis of the relative curve of strain-rate sensitivity and stress decrement, which is obtained from the strain-rate cycling test during the Blaha effect measurement [2]. The curve reflects the influence of ultrasonic oscillation on the dislocation motion on the slip plane containing many impurities and a few dislocations [3, 4]. So far, however, we have not discussed whether the Friedel relation [5] can be taken into the Fleischer's model. Accordingly, the interaction between a dislocation and the impurities in KCl : Sr^{2+} is examined for the Fleischer's model taking account of the Friedel relation in this paper. This model is hereafter termed the F–F.

2. Experimental procedure

The KCl : Sr^{2+} (0.035, 0.050, 0.065 mol% in the melt) single crystals, which are the size of about $5 \times 5 \times 15$ mm^3, were kept at 973 K for 24 h and were cooled to room temperature at a rate of 40 Kh^{-1} in order to reduce dislocation density. Furthermore, the specimens were held at 673 K for 30 min and were cooled by water quenching in order to disperse the impurities immediately before the test.

Compression tests were carried out at temperatures from 80–240 K for the specimens along the $\langle 100 \rangle$ axis and the ultrasonic oscillatory stress of constant amplitude was applied by a resonator in the same direction as the compression during the strain-rate cycling test. Then, the stress change due to the strain-rate cycling is $\Delta\tau'$. The strain-rate sensitivity was obtained on the basis of the $\Delta\tau'$. The strain-rate cycling test during the oscillation has been described in the previous papers [4, 6].

3. Discussion

3.1. Relation between effective shear stress and temperature

Friedel [5] derived an expression for the average spacing, L, of impurities along the dislocation, namely

$$L = \left(\frac{2L_0^2 E}{\tau b} \right)^{1/3} \tag{1}$$

where L_0 is the average spacing of impurities on the slip plane, E is the line tension of the dislocations, τ is

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the effective shear stress and b is the magnitude of the Burgers vector. Fleischer [1] approximated the force-distance relation between a dislocation and the divalent impurity for LiF : Mg^{2+} (0.008 mol%) by

$$F = F_0 \Big/ \left(\frac{x}{b} + 1\right)^2 \tag{2}$$

and found the Gibbs free energy, ΔG, for the interaction between a dislocation and the divalent impurity by the following equation:

$$\Delta G = \int_0^B \left\{ F_0 \Big/ \left(\frac{x}{b} + 1\right)^2 - F \right\} \mathrm{d}x \tag{3}$$

where F is the force acted on the dislocation, F_0 is the F at the temperature of 0 K, x is the distance from the defect and B is the value of x at which F equals the defect force. Then, F and F_0 are expressed by using Equation 1 as follows

$$F = \left(2L_0^2 E\right)^{1/3} b^{2/3} \tau^{2/3} \tag{4}$$

$$F_0 = \left(2L_0^2 E\right)^{1/3} b^{2/3} \tau_0^{2/3} \tag{5}$$

where τ_0 is the effective shear stress at 0 K. From Equations 1 and 2, B in Equation 3 is given by

$$B = b\left\{ \left(\frac{\tau_0}{\tau}\right)^{1/3} - 1 \right\} \tag{6}$$

Substituting of Equations 4–6 in Equation 3, we find

$$\Delta G = \Delta G_0 \left\{ 1 - \left(\frac{\tau}{\tau_0}\right)^{1/3} \right\}^2, \ (\Delta G_0 = F_0 b) \tag{7}$$

and also from an Arrhenius equation for the thermally activated deformation rate, $\dot{\varepsilon}$, the Gibbs free energy of activation is expressed as

$$\Delta G = \alpha k T, \ \left(\alpha = \ln\left(\frac{\dot{\varepsilon}_0}{\dot{\varepsilon}}\right)\right) \tag{8}$$

where kT has the usual meaning and $\dot{\varepsilon}_0$ is a frequency factor. From the substitutional equation of Equation 8 in Equation 7, the relation of effective shear stress and temperature for the F–F is expressed in the form:

$$\left(\frac{\tau}{\tau_0}\right)^{1/3} = 1 - \left(\frac{T}{T_c}\right)^{1/2}, \ \left(T_c = \frac{\Delta G_0}{\alpha k}\right) \tag{9}$$

Therefore, the relative formula of the effective shear stress, τ_{p1}, due to the impurities and temperature for the F–F is

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

The τ_{p1} depends on temperature and on the type and density of impurities [4]. The result of Equation 10 is shown in Fig. 1 for KCl : Sr^{2+} (0.050 mol% in the melt).

TABLE I Values of τ_{p0} for the F–F

KCl : Sr^{2+} (mol%)	τ_{p0} (MPa)
0.035	11.44
0.050	25.47
0.065	36.31

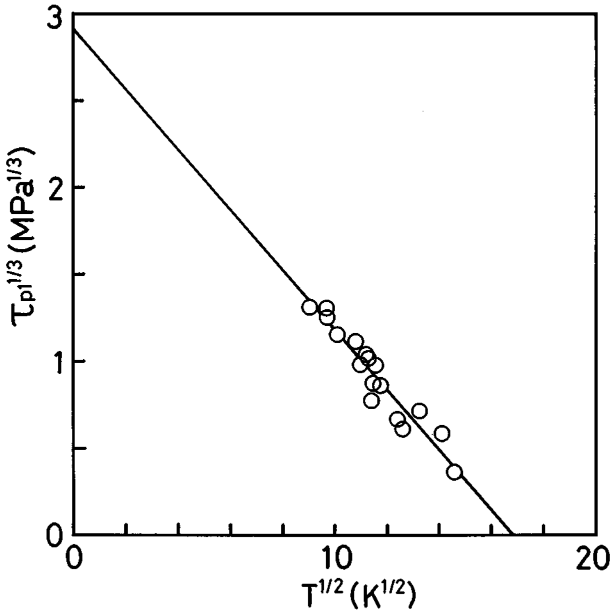

Figure 1 Linear plots of the effective shear stress and the temperature for KCl : Sr^{2+} (0.050 mol% in the melt) at the F–F.

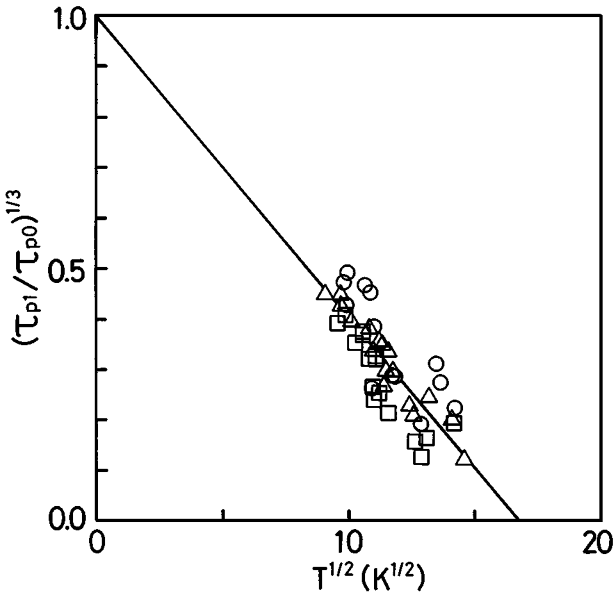

Figure 2 Linear plots of $(\tau_{p1}/\tau_{p0})^{1/3}$ and $T^{1/2}$ for KCl : Sr^{2+}: (○) 0.035 mol%, (△) 0.050 mol%, (□) 0.065 mol%.

The value of τ_{p0}, which is obtained by extraporating the line to 0 K, increases with the concentration of impurities as given in Table I. Fig. 2 shows the relation between τ_{p1} and temperature for KCl : Sr^{2+} at the F–F. The critical temperature, T_c, at which the line intersects the abscissa in Fig. 2 and τ_{p1} is zero, is determined to be 289 K.

We examine whether the theory that the Friedel relation can be taken into the Fleischer's model is

TABLE II Values of ϕ_0

$KCl:Sr^{2+}$ (mol%)	ϕ_0 (degrees)
0.035	161
0.050	154
0.065	149

appropriate for the interaction between a dislocation and the impurity. The bending angle, ϕ_0, at which the dislocation embraces the impurities under the effective shear stress, τ_{p0}, at 0 K is obtained from

$$2E\cos(\phi_0/2) = \tau_{p0}Lb \tag{11}$$

and

$$L = \left(\frac{2L_0^2E}{\tau_{p0}b}\right)^{1/3} \tag{12}$$

namely,

$$\frac{\phi_0}{2} = \cos^{-1}\left(\frac{\tau_{p0}L_0b}{2E}\right)^{2/3} \tag{13}$$

where the line tension of the dislocations is calculated by μb^2. The shear modulus, μ, for [110] direction is assumed to be 1.01×10^{10} Pa at 0 K [7]. The average spacing of impurities on the slip plane is given by [8]

$$L_0 = b/(4c/3)^{1/2} \tag{14}$$

where the concentrations of the impurities, c, are 55.2, 98.3, 121.8 p.p.m. for $KCl:Sr^{2+}$ (0.035, 0.050, 0.065 mol% in the melt) from dielectric loss measurement. As a result, the values of ϕ_0 are given in Table II. Therefore, since the values of ϕ_0 for the specimens are above about 140 degrees [9], it was confirmed that the above-mentioned theory is appropriate for the interaction between a dislocation and the impurity in the specimens.

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

When a dislocation overcomes the impurity with the aid of thermal fluctuations, the activation enthalpy, ΔH, is given by the relation [10–13]:

$$\Delta H = -kT^2\left(\frac{\partial \ln\dot{\varepsilon}}{\partial\tau}\right)_T\left(\frac{\partial\tau}{\partial T}\right)_{\dot{\varepsilon}} \tag{15}$$

The $(\partial\ln\dot{\varepsilon}/\partial\tau)_T$ in Equation 15 is obtained from the $(\Delta\tau'/\Delta\ln\dot{\varepsilon})_p$ which is given by the difference between strain-rate sensitivity at first plateau region and at second one on the relative curve of strain-rate sensitivity and stress decrement [2, 6, 14]. The ΔH can also be expressed as the following equation on the assumption that the changes in entropy are neglected [10, 12]

$$\Delta H = \alpha kT \tag{16}$$

Combining Equations 15 and 16, we find

$$\left(\frac{\partial\tau}{\partial\ln\dot{\varepsilon}}\right)_T = -\left(\frac{\partial\tau}{\partial T}\right)_{\dot{\varepsilon}}\frac{T}{\alpha} \tag{17}$$

In Equation 17, the $(\partial\tau/\partial T)_{\dot{\varepsilon}}$ for the F–F can be expressed from the differentiation of Equation 10 with respect to the temperature by

$$\frac{\partial\tau}{\partial T} = \left(\frac{-3\tau_{p0}}{2T_c}\right)\left(\frac{T_c}{T}\right)^{1/2}\left\{1-\left(\frac{T}{T_c}\right)^{1/2}\right\}^2 \tag{18}$$

Thus, the strain-rate sensitivity due to the impurities for the F–F is given by substitution of Equation 18 into Equation 17 as follows

$$\frac{\partial\tau}{\partial\ln\dot{\varepsilon}} = \left(\frac{3\tau_{p0}T}{2T_c}\right)\left(\frac{T_c}{T}\right)^{1/2}\left\{1-\left(\frac{T}{T_c}\right)^{1/2}\right\}^2\Big/\alpha \tag{19}$$

and is represented as a solid line in Fig. 3a for $KCl:Sr^{2+}$ (0.050 mol% in the melt) and b for $KCl:Sr^{2+}$ (0.035 mol% in the melt). The open circles, which are measured for the specimens, is approximated to the solid line. Consequentry, the F–F seems to be a suitable model for the interaction between a dislocation and the impurity in the specimens.

Substituting of the differential equation of the following equation [4] with respect to the temperature into Equation 17, the strain-rate sensitivity due to the impurities for the Fleischer's model can be obtained.

$$\left(\frac{\tau_{p1}}{\tau_{p0}}\right)^{1/2} = 1-\left(\frac{T}{T_c}\right)^{1/2} \tag{20}$$

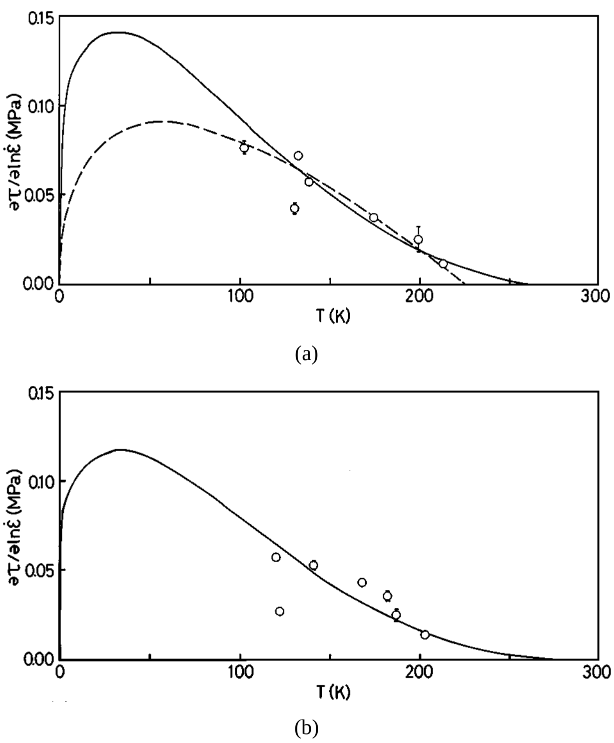

Figure 3 Relationship between the strain-rate sensitivity due to the impurities and temperature for $KCl:Sr^{2+}$: (a) 0.050 mol%, (b) 0.035 mol%. (——) corresponds to the dependence of temperature and strain-rate sensitivity due to the impurities for the F–F and (– – – –) that for the Fleischer's model. (○) : $(\Delta\tau'/\Delta\ln\dot{\varepsilon})_p$ for the specimens.

Namely,

$$\frac{\partial\tau}{\partial\ln\dot{\varepsilon}} = \left(\frac{\tau_{p0}}{T_c}\right)\left\{\left(\frac{T_c}{T}\right)^{1/2} - 1\right\}\frac{T}{\alpha} \qquad (21)$$

where τ_{p0} is 14.5 MPa and T_c is 227 K for $KCl:Sr^{2+}$ (0.050 mol% in the melt) [4]. The values of τ_{p0} and T_c for the Fleischer's model is small in contrast to those for the F–F. In addition, the strain-rate sensitivity due to the impurities obtained from Equation 21 is represented as a dashed line in Fig. 3a. Although the difference between the strain-rate sensitivity due to the impurities for the F–F and for the Fleischer's model is not almost observed above about 100 K, that for the F–F is large as against that for the Fleischer's model below 100 K for the specimen as shown in Fig. 3a.

3.3. The enthalpy and the Gibbs free energy of activation for the breakaway of the dislocation from the impurity

The activation enthalpy for the interaction between a dislocation and the impurity is calculated from the substitutional equation of Equation 18 in Equation 15, namely

$$\Delta H = -kT^2\left(\frac{\Delta\ln\dot{\varepsilon}}{\Delta\tau'}\right)_p \times \left(\frac{-3\tau_{p0}}{2T_c}\right)\left(\frac{T_c}{T}\right)^{1/2}\left\{1 - \left(\frac{T}{T_c}\right)^{1/2}\right\}^2 \qquad (22)$$

The values of the activation enthalpy derived from Equation 22 for the F–F are plotted as a function of temperature in Fig. 4. The value of $\Delta H(T_c)$ obtained from Fig. 4, which corresponds to the activation enthalpy for breakaway of the dislocation from the impurity at 0 K, is 0.79 eV.

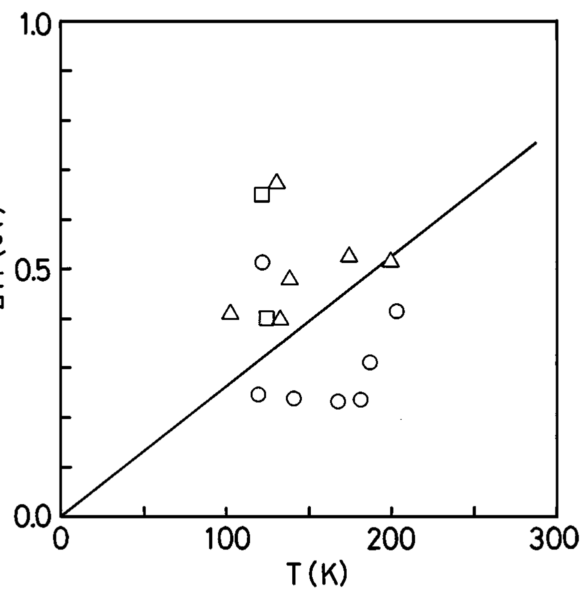

Figure 4 Proportional relationship between the temperature and the activation enthalpy for the interaction between a dislocation and the impurity in $KCl:Sr^{2+}$: (○) 0.035 mol%, (△) 0.050 mol%, (□) 0.065 mol%.

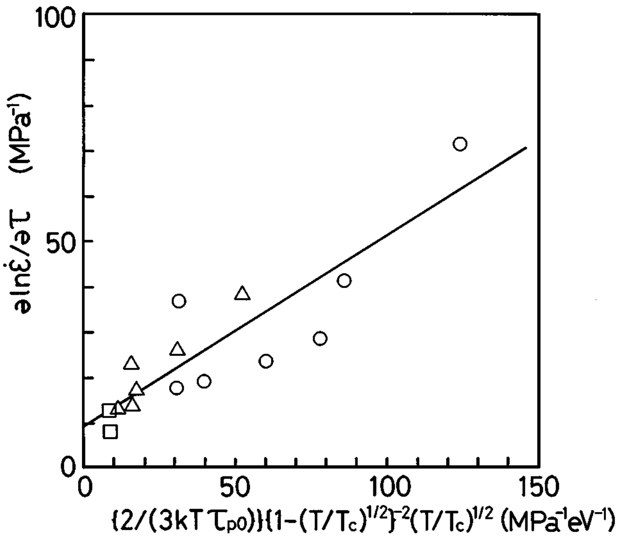

Figure 5 Linear plots of Equation 24 for $KCl:Sr^{2+}$: (○) 0.035 mol%, (△) 0.050 mol%, (□) 0.065 mol%.

The Gibbs free energy for the interaction between a dislocation and the impurity is obtained from the following way. Differentiating the combining Equations 7 and 8 with respect to the shear stress gives

$$\frac{\partial\ln\dot{\varepsilon}}{\partial\tau} = \left(\frac{2\Delta G_0}{3kT\tau_0}\right)\left(\frac{\tau_0}{\tau}\right)^{2/3}\left\{1 - \left(\frac{\tau}{\tau_0}\right)^{1/3}\right\} + \frac{\partial\ln\dot{\varepsilon}_0}{\partial\tau} \qquad (23)$$

Further substituting of Equation 9 in Equation 23 gives

$$\frac{\partial\ln\dot{\varepsilon}}{\partial\tau} = \left(\frac{2\Delta G_0}{3kT\tau_{p0}}\right)\left\{1 - \left(\frac{T}{T_c}\right)^{1/2}\right\}^{-2}\left(\frac{T}{T_c}\right)^{1/2} + \frac{\partial\ln\dot{\varepsilon}_0}{\partial\tau} \qquad (24)$$

where τ_0 is replaced by τ_{p0}. Fig. 5 shows the result of calculations of Equation 24 for the F–F. The open symbols correspond to the $(\Delta\ln\dot{\varepsilon}/\Delta\tau')_p$ for the specimens. From the slope of straight line, the Gibbs free energy is 0.39 eV.

4. Conclusion

For the interaction between a dislocation and the impurity in $KCl:Sr^{2+}$ (0.035, 0.050, 0.065 mol% in the melt), it was confirmed that the Friedel relation can be taken into the Fleischer's model from the values of ϕ_0. Furthermore, it can be found that the interaction between a dislocation and the impurity in the specimen can be approximated to the F–F on the basis of the dependence of strain-rate sensitivity due to the impurities on temperature as shown in Fig. 3a and b. Then, the T_c is 289 K for the specimen. The enthalpy and the Gibbs free energy of activation, which are obtained from Figs 4 and 5, for the interaction between a dislocation and the impurity are 0.79 eV and 0.39 eV respectively.

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