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Influence of Dislocation on Diffusion Rate of *F* Centers in KCl

Hiroyuki Mizuno and Shigeko Miyamoto
Matsushita Electronics Corporation, Takatsuki, Osaka, Japan

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An experimental confirmation of the *F*-center diffusion along disordered interfaces in KCl single crystals is given. KCl single crystals were exposed to potassium vapor after (a) they had been bent around the [100] crystal axis yielding only one slip system, or (b) had been compressed along a [100] direction yielding a single pair of mutually perpendicular slip systems. The crystal showed a distinct anisotropy of *F*-center diffusion. The explanation for this anisotropy can be based on the crystal dislocations.

INTRODUCTION

It is a well-known fact that when an additively colored crystal is irradiated with light in the wavelength region of the *F* band at room temperature, it shows a gradual increase of other absorption bands such as R_1, R_2, *M*, and *N* bands with a decrease of the *F* band. Seitz gave an interpretation of this change by assuming an aggregation of *F* centers. It seems reasonable to suppose that the mobility of *F* centers plays a very important role in such a transformation process. From this point of view it becomes desirable to investigate the behavior of the diffusion of *F* centers more exactly and to get a better insight concerning the divergent results obtained so far.

Since Pohl and his co-workers submitted the coloration of alkali halide crystals to an extensive series of experiments, a great number of investigations on the same subject have been published.[1] Comparing the results, however, there seems to be a lack in conformity, some crystal specimens coloring more easily than others. The main reason for this difference is believed to arise from uncontrolled dislocations, impurities, and other defects contained in an individual crystal. It would be interesting therefore to study the additive coloration of a perfectly pure, dislocation free specimen of an alkali-halide single crystal, but as it is extremely difficult to realize such conditions it would, on the other hand, be equally interesting to study the coloration of crystals containing controlled kinds and densities of defects.

In a previous paper[2] it was suggested that at temperatures below 500°C the diffusion of *F* centers in a KCl crystal might take place predominantly along disordered interfaces, and an experimental method was described. In the present paper a confirmation of this "diffusion along disordered interfaces" will be given. The basic idea underlying our method is the following: If in a crystal an abnormally high density of dislocations along a definite orientation is created, e.g., by macroscopic deformation, then the crystal should show a distinct anisotropy of *F*-center diffusion during additive coloring.

EXPERIMENTAL PROCEDURE

The KCl crystals used in our experiments were grown from synthetically produced KCl powders[3] and were purified by crystallizing them twice by the Kyropoulos method. Much attention was paid to remove various kinds of imperfections and impurities, especially divalent ions included in the KCl. Etching[4] revealed that the crystals contain dislocations of densities of 7×10^4 cm^{-2}. Spectral analysis showed that the total impurity content of the crystal is less than approximately 2 parts per million. From a single lot of crystals thus obtained, thin slices of $1.0\times2.0\times0.5$ cm^3 and rectangular blocks of $1.0\times1.5\times2.0$ cm^3 were cut in order to subject them, respectively, to two different methods of deformation:

(1) Bending the slices, which were cut along [010], with a radius of 3 cm around the [100] axis of the crystals (Hereafter we will indicate this deformation by *D*1.)

(2) Compressing the blocks in an elastic clamp (hereafter indicated by *D*2).

These deformations should be executed carefully over a sufficiently long interval of time in order to prevent the production of cracks in the crystal. The two situations are schematically shown in Figs. 1 (a) and (b).

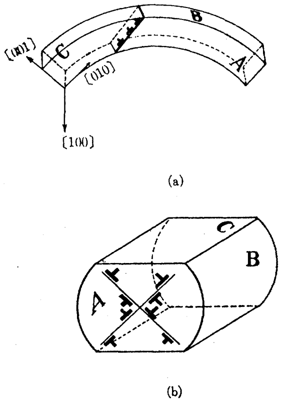

FIG. 1. Crystals employed for the experiment. (a) Bent crystal. (b) Deformed crystal.

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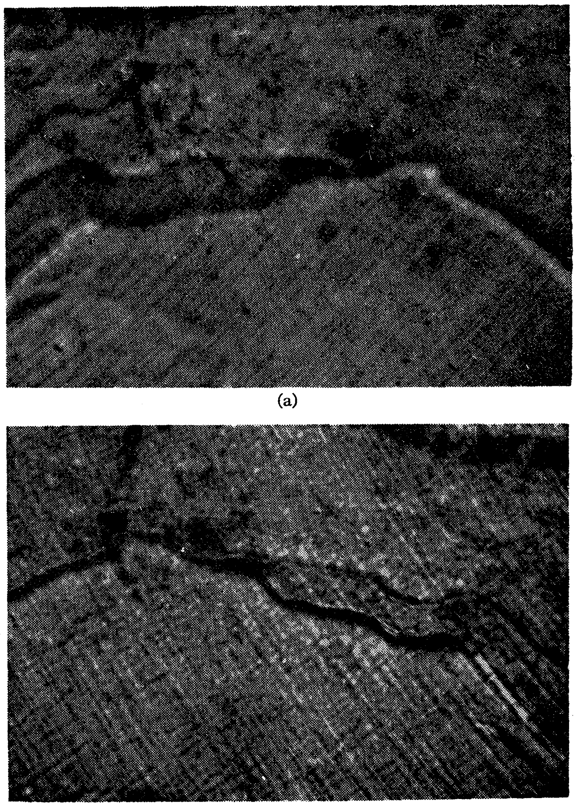
[1] For a good review of this work see F. Seitz, Revs. Modern Phys. **18**, 384 (1946); **26**, 7 (1954).

[2] H. Mizuno and M. Inoue, Phys. Rev. **120**, 1226 (1960); H. Mizuno and S. Miyamoto, Phys. Rev. Letters **6**, 410 (1961).

[3] K. Kobayashi and T. Tomiki, J. Phys. Soc. Japan **15**, 1982 (1960).

[4] Reagent: acetone+0.5 mole $HgCl_2$/liter. There is a strong evidence that both edge and screw dislocations can be detected by this reagent. See M. Inoue and H. Mizuno, Nat. Tech. Rept. **6**, 237 (1960) (in Japanese).



(a)

(b)

FIG. 2. Etch pits of bent crystal. (a) Etch pits on face *A* in Fig. 1. (b) Etch pits on face *C* in Fig. 1.

Etch pits on the (100) face *A* of the sliced crystals deformed by *D*1 lay in rows only along [011] as shown in Fig. 2(a), indicating that in the simple plastic bending only one slip system was operative. Figure 2(b) shows etch pits on the (100) face *C* at the opposite side of *A*. Etch pits on *C* lay in rows along [0$\bar{1}$1]. Hence it is obvious that most dislocations passed through the crystals from one face *A* to the opposite face *C* in parallel arrays of edge-type dislocations. The deformation *D*2 of the crystals resulted in a single pair of mutually perpendicular slip systems as indicated in Fig. 1(b). After 60 min exposure to the pressure, the rate of compression along [100] was 7.3%. Although various kinds of dislocations depending upon the degree of compression and the sample size can be expected, visual observation of the deformed crystals used in the experiments indicated that up to this limit of 7.3% deformation, only slip lines corresponding to a single pair of slip systems were present. As pointed out by Vaughan *et al.*,[5] at higher deformations double or, in general, complex multiple slips will occur.

The deformed crystals were annealed for 10 hr at 600°C in order to check the stability of the induced dislocations during the additive coloring process. The dislocation density of the crystals was determined with the etching technique. Although this technique may not give a very accurate absolute value of the dislocation density, it can be relied upon for relative measurements. The etch pits developed have shown that the deformed crystals have sufficient anisotropic dislocation contents:

(1) For the sliced crystals deformed by *D*1 with bending radius of 3 cm, the dislocation concentration through the face *A* is 5×10^6 cm^{-2} whereas through the face *B* it is 10^5 cm^{-2}.

(2) For the rectangular crystals deformed by *D*2 with 7.3% compression, the dislocation concentration through the face *A* is approximately 10^9 cm^{-2} while through the face *C* it is 10^5 cm^{-2}.

These results justify strongly the previous conclusions that only one slip system and a single pair of mutually perpendicular slip systems are operative for the bending and compression, respectively. It appeared also by counting the etch pits that the annealing process decreased the number of induced dislocations through the face *A* of the deformed crystals by about 10%. The deformed crystal was colored by heating it in the presence of potassium metal vapor. In order to obtain colored crystals with a marked concentration gradient of *F* centers, heating times of 20 hr at 450°C and 30 min at 600°C were found to be sufficient. Two wafers, 0.5 mm thick, were cut from each colored crystal at the centers of two lateral faces, normal and parallel to the compressive or bending axis direction. The absorption coefficients of *F* centers in different regions of the wafers were obtained by point-by-point photoelectric transmittance measurements using a thin rectangular beam of $30\times150\,\mu^2$ of monochromatic light. Light

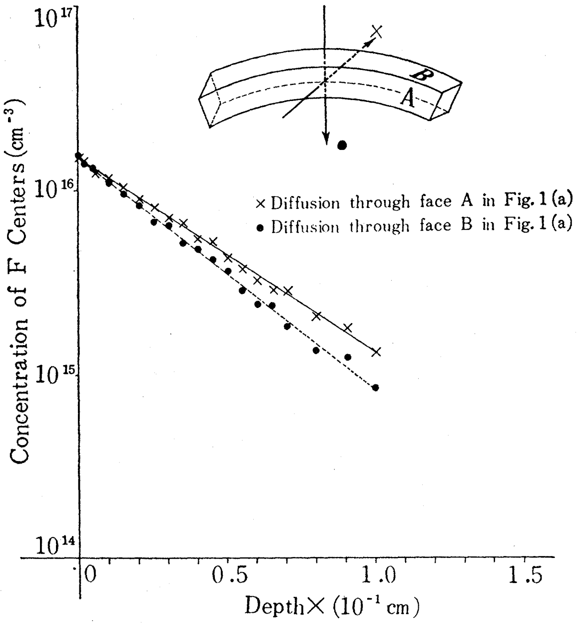


FIG. 3. Penetration curves of *F* centers in a bent crystal through different lateral faces additively colored at 450°C.

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[5] W. H. Vaughan, W. J. Leivo, and R. Smoluchowski, Phys. Rev. **110**, 652 (1958).

from a monochromator was focused on the sample by an objective lens and passed through the sample into a detector which was a photocell connected with a galvanometer of a high sensitivity. In order to calculate the concentration of F centers at each point of the wafers, Smakula's[6] formula was used. It should be mentioned that the measurements were carried out at the center of each exposed face in order to avoid interference from F centers which had penetrated through the other faces.

RESULTS

A. Sliced Crystals Deformed by D1

F-center concentrations after additive coloration at 450°C for 20 hours are plotted as a function of the penetration depth in Fig. 3. The solid curve in Fig. 3 shows F-center concentrations through the (100) face, perpendicular to the bending axis, that is, along the orientation of produced edge dislocations, whereas the dashed curve shows those through the (001) face, parallel to the bending axis. It is interesting to note that the rate of F-center diffusion at 450°C is strongly dependent on the orientation in the deformed crystal. As the dislocations are all parallel, it would be expected that the rate of F-center diffusion is highly anisotropic, with a maximum diffusion rate parallel to the dislocations. Figure 4 shows F-center concentrations at 600°C for 30 min as a function of the square of the penetration depth. It is remarkable that in this case there is no anisotropy of F-center diffusion. Such an anisotropy disappears above an additive coloring temperature of about 550°C even if the crystal contains a high density of dislocations. Hence in the high-temperature region there is no influence of dislocations upon the F-center diffusion in KCl crystals.

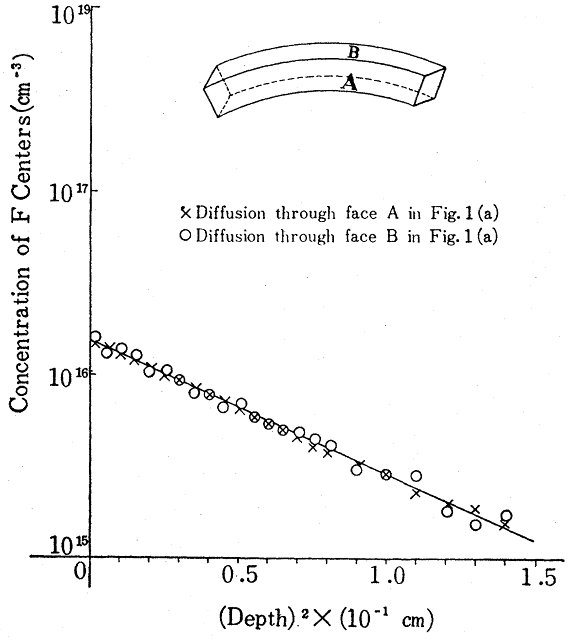

FIG. 4. Penetration curves of F centers in a bent crystal through different lateral faces additively colored at 600°C.

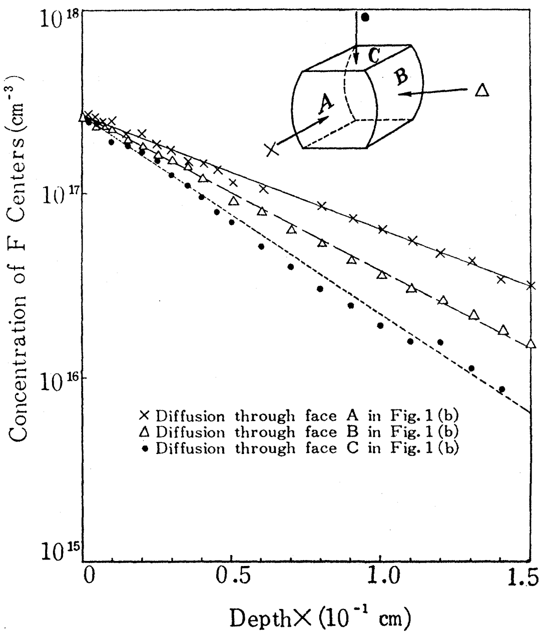

FIG. 5. Penetration curves of F centers in a deformed crystal through different lateral faces additively colored at 450°C.

B. Crystals Deformed by D2

F-center concentrations of crystals with a $D2$ deformation after additive coloration at 450°C for 20 hr are plotted as a function of the penetration depth in Fig. 5. The solid curve in Fig. 5 shows F-center concentrations through the swollen face A in Fig. 1(b), that is, along the orientation of produced edge dislocations, whereas the dashed curve shows those through the nondeformed plane C. F-center concentrations through face B are also shown in Fig. 5 as a broken curve. As will be discussed in the following section, it seems reasonable to conclude that these anisotropies are due to the pronounced orientation of edge and screw dislocations, respectively.

DISCUSSION

After establishing the fact that dislocations in general tend to accelerate the diffusion process of F centers, it is necessary to give a quantitative foundation of the effect and to examine more closely the influence of any particular form of dislocation on the penetration effect.

A. Crystals with a D1 Deformation

The dislocation theory of plastic bending has been discussed by Cottrell.[7] In simple bending, the disloca-

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[6] A. Smakula, Z. Physik **59**, 603 (1930).

[7] A. H. Cottrell, *Dislocations and Plastic Flow in Crystals* (Clarendon Press, Oxford, 1953), p. 29.

tions run parallel to the bending axis and the density N of dislocations is given by

$$N = 1/rb, \tag{1}$$

where b is the average component of the Burgers vector parallel to the neutral plane and r is the radius of bend. Applying the values of 10^{-7} cm and 3 cm for b and r, respectively in Eq. (1), the density of dislocations is given by 3.3×10^{6} cm^{-2}, which is in good agreement with the etch pit result of 5×10^{6} cm^{-2}. Variation in the radius of bend by two orders of magnitude, which according to Eq. (1) should vary the density of dislocations by two orders of magnitude, has given a corresponding variation in the density of etch pits. Thus, the etch-pit technique is believed to give a rather faithful representation of the order of dislocation density.

A phenomenological theory of diffusion through a disordered interface has been given by Fisher.[8] Following his theory, the relation between the F-center concentration n and penetration depth x from the crystal surface is described by

$$\log n \sim -2^{\frac{1}{2}}(D/D'\delta)^{\frac{1}{2}}[(\log e)/(\pi Dt)^{\frac{1}{4}}]x + \text{const}, \tag{2}$$

where D, D' are the diffusion coefficients through the bulk of the crystal and a disordered internal interface, respectively, and δ is the width of a disordered interface. According to Eq. (2) a plot of $\log n$ versus the penetration depth should yield a straight line with the slope:

$$2^{\frac{1}{2}}(D/D'\delta)^{\frac{1}{2}}[(\log e)/(\pi Dt)^{\frac{1}{4}}]. \tag{3}$$

Assuming a dislocation width of 10^{-7} cm for the bending of $r=3$ cm, and a volume diffusion coefficient of F centers of 3.9×10^{-9} cm^2 sec^{-1} at 450°C,[2,8] diffusion coefficients D' through the (100) face, perpendicular to the bending axis, that is, along the orientation of produced arrays of edge dislocations, and through the (001) face parallel to the bending axis are found to be 6.37×10^{-4} cm^2 sec^{-1} and 3.09×10^{-4} cm^2 sec^{-1} at 450°C, respectively. It appears that the diffusion coefficient of F centers through face A is nearly twice as high as that through face B, which is an indication of the close relation between the density of edge dislocations and the rate of F-center diffusion.

B. Crystals with a D2 Deformation

In KCl crystals, slip occurs on (110) planes in [1$\bar{1}$0] directions and, therefore, there should be at least two sets of planes in which the resolved shear stress is the same. As mentioned before, when KCl crystals are compressed about 7.3% at room temperature along the [110] direction, various kinds of deformations appear according to sample sizes. In order to obtain a deformed crystal including only a single pair of mutually perpendicular slip systems, it is necessary that the cross-sectional edge lengths of the compressed face of the cleaved crystal differ at least by a factor of 2. Instead, in a crystal having a nearly square cross section such slipping is rather fortuitous and depends upon various factors, especially upon the rate of compression. In our experiments this rate had to be as slow as possible in order to prevent cracking of the crystal. It follows that the dislocations are of the screw type if the slip lines are at 45° to the cube edge, whereas they are of the edge type if they are parallel to the cube edge. Closely spaced edge dislocations, therefore, together with the screw dislocations appear on one pair of parallelepiped faces perpendicularly crossed with each other. In other words, edge dislocations appear on face A while screw dislocations appear on face B in Fig. 1(b). It seems, therefore, reasonable to conclude that the difference between the F-center diffusion rate through A and that through C is due to the induced edge dislocations, while the difference between F-center diffusion rate through B and that through C is due to the induced screw dislocations. From the slopes of the curves in Fig. 5 together with Eq. (3) the diffusion coefficients D can be obtained to be 1.28×10^{-2}, 7.21×10^{-3}, 4.27×10^{-3} cm^2 sec^{-1}, respectively, for diffusion through the A, B, and C faces.[9]

CONCLUSIONS

A study of F-center diffusion in single crystals shows that the diffusion rate can be anisotropic if the crystals contain a high density of parallel arrays of edge dislocations or screw dislocations. Measurements of the diffusion rate in different directions of such crystals, where the anisotropy in dislocation density is a factor of 10 to 10^3, show that diffusion rates measured parallel to the array are 2 to 3 times larger than those measured perpendicular to the array.

Since it has been well established experimentally that there is preferential diffusion of F centers along dislocation lines, the question may arise of a quantitative correspondence between dislocation density and the rate of F-center diffusion. The exact solution of this problem is left for future work.

ACKNOWLEDGMENTS

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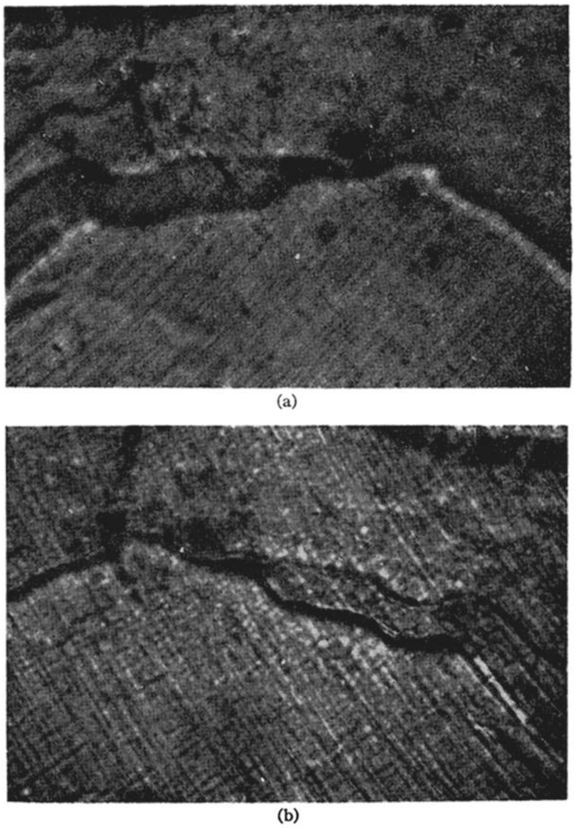
[8] J. C. Fisher, J. Appl. Phys. 22, 74 (1951).

[9] These large diffusion coefficients seem to indicate that most F centers move along the dislocations at any temperature. However, the smaller number of F centers situated in the dislocations makes this impossible at higher temperatures.



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