

## Diffusion of $F$ Centers into Potassium Chloride Single Crystals

HIROYUKI MIZUNO AND MORIO INOUE  
*Matsushita Electronics Corporation, Takatsuki, Osaka, Japan*  
 (Received June 13, 1960)

Diffusion of  $F$  centers into potassium chloride crystals during an additive coloring process has been measured at various temperatures. A diffusion process which can be explained by a simple theory of volume diffusion seems to be predominant at higher temperatures. At lower temperatures, however, the occurrence of a disordered interfacial diffusion with an  $F$ -center concentration decreasing exponentially with the first power of penetration depth is confirmed.

### INTRODUCTION

IT is a well-known phenomenon that an alkali-halide crystal acquires a dark color when it is heated in the vapor of its metallic constituent. The absorption band is called the  $F$  band. Mott and Gurney have proposed a mechanism by which  $F$  centers are formed.<sup>1</sup> According to their conception a vapor atom is adsorbed at the surface, after a certain time the atom loses its electron, a negative ion moves up from a layer beneath and takes its place at the side of the adsorbed positive ion. It is the same mechanism by which new layers of the crystal are built up.

Rexer<sup>2</sup> carried out a number of interesting experiments on crystals in which there was a concentration gradient of  $F$  centers as a result of additive coloring and came to the conclusion that Fick's law was not obeyed. He observed a variety of unusual phenomena. The experiments were, however, difficult to interpret.

If the mechanism of Mott and Gurney is correct, the migration of  $F$  centers must be determined by their own concentration gradient, neglecting mutual interactions of the vacancies in a first approximation. It appears that this model provides an accurate method for measuring the diffusion rate of negative ion vacancies

based on the concentration gradient of  $F$  centers in additively colored crystals.

The main purpose of this work is to clarify the behavior of negative ion vacancies by studying the migration of  $F$  centers.

### EXPERIMENTAL PROCEDURE

KCl crystals were grown from the melt by the Kyropoulos method. They were heated at various temperatures to form  $F$  centers exposing only one lateral face to the potassium vapor. In order to measure the diffusion rate of negative ion vacancies it was necessary to have crystals with a concentration gradient of  $F$  centers. An estimation of the  $F$ -center concentration at any distance  $x$  from the surface was made in the following way<sup>3</sup>:

(1) Assuming the oscillator strength to be 0.81 the  $F$ -center concentration in the crystal was derived from the absorption coefficient and bandwidth by Smakula's formula.<sup>4</sup>

(2) The absorption coefficient of the colored crystal was measured again after taking off 30 to 100 microns

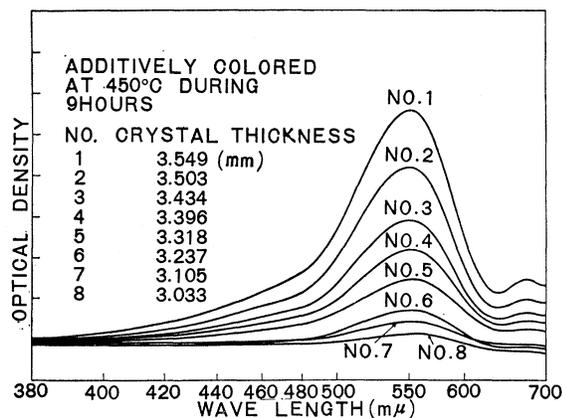


FIG. 1.  $F$ -center absorption at room temperature vs wavelength in an additively colored KCl crystal for different crystal thickness.

<sup>1</sup> N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, London, 1940).

<sup>2</sup> E. Rexer, *Physik. Z.* **32**, 215 (1931); *Z. Physik* **70**, 159 (1931).

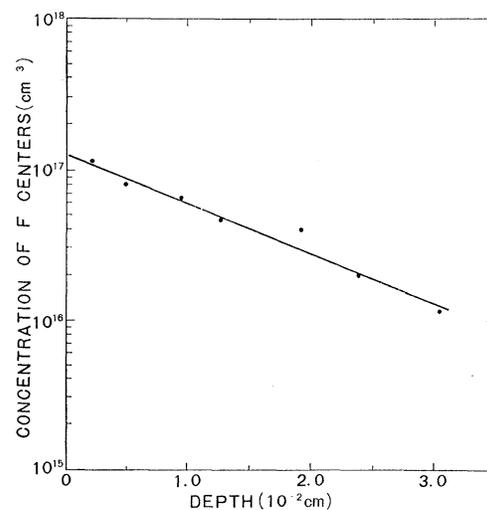


FIG. 2. Penetration curves of  $F$  centers additively colored at 450°C for 9 hours.

<sup>3</sup> H. Mizuno and M. Inoue, *J. Phys. Soc. (Japan)* **15**, 211 (1960).

<sup>4</sup> A. Smakula, *Z. Physik* **59**, 603 (1930).

from the exposed surface by polishing it with red ochre on a silk cloth.

(3) The mean concentration of  $F$  centers included in the removed thin layer is determined by

$$n = \frac{l-dx}{dx} \{ \bar{C}_1 - \bar{C}_2 \} + \bar{C}_1,$$

where  $l$  = thickness of the crystal before polishing,  $dx$  = thickness of the removed layer,  $\bar{C}_1$  = mean concentration of  $F$  centers before polishing, and  $\bar{C}_2$  = mean concentration of  $F$  centers after polishing.

This procedure was repeated to a depth of 400 to 600 microns from the exposed surface. Figure 1 shows a typical example of decreasing absorption with decreasing thickness of the crystal. The absorption measurements were carried out on an automatic recording spectrophotometer and the corresponding values of the thickness were read on a micrometer with a direct reading to 1 micron. The temperatures of the additive coloring were controlled by an automatic regulator with a tolerance of 0.5%. The temperature range in the experiments was extended from 450°C to 600°C. Each measured value of  $F$ -center concentration was plotted in the middle of a thin layer.

### RESULTS

Plots of  $\log n$  versus depth are shown in Figs. 2, 3, and 4 corresponding to three temperatures from the range 450°C to 600°C. The crystals employed for these experiments were cut from one original single crystal. Figures 2 and 3 show straight lines whereas Fig. 4

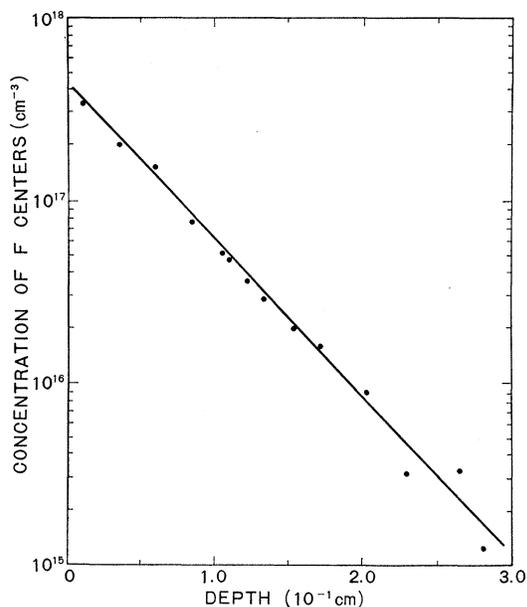


FIG. 3. Penetration curves of  $F$  centers additively colored at 500°C for 10 hours.

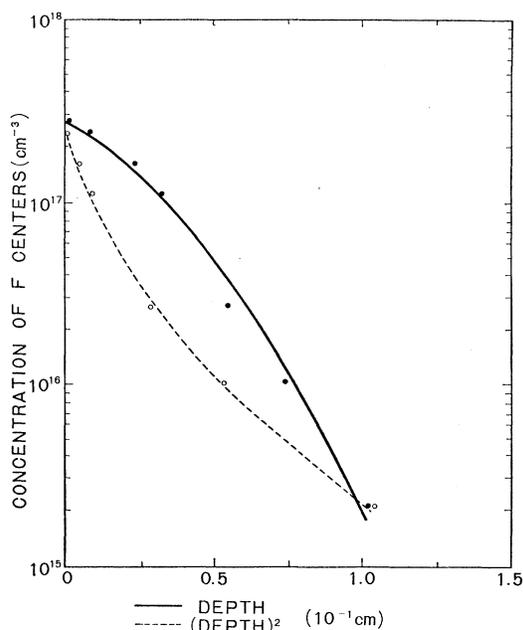


FIG. 4. Penetration curves of  $F$  centers additively colored at 600°C for 30 minutes.

shows a markedly different curve. In Fig. 4  $\log n$  is also plotted versus the square of the depth. These data show clearly that below 500°C the concentration of the  $F$  centers varies exponentially with the first power of the penetration depth while above 500°C for a small penetration depth the logarithm of the concentration shows a convex and a concave curves when plotted versus depth and depth square respectively.

The general aspect of the curves is the same for crystals of different origin, apart from the fluctuation of the transition point.

### DISCUSSION

As previously mentioned the obvious way to describe the migration of  $F$  centers into the crystal during the additive coloring process is by solving a simple Fick's equation

$$\partial n / \partial t = D(\partial^2 n / \partial x^2), \quad (1)$$

where  $D$  is the diffusion constant. The solution of this equation is

$$n = n_0 \operatorname{erfc}[x/2(Dt)^{1/2}], \quad (2)$$

in which  $n_0$  is the constant concentration of metal vapor at the boundary  $x=0$ . Numerical values of Eq. (2) are plotted in Fig. 5. It is easily seen that the curve is very similar to that obtained experimentally in Fig. 4. It may be therefore safely concluded that in the high-temperature region a simple diffusion known as volume diffusion plays an important role. In the low-temperature region, however, the experimental results completely disagree with a conjecture based on the simple diffusion theory as may be seen in Figs. 2 and 3.

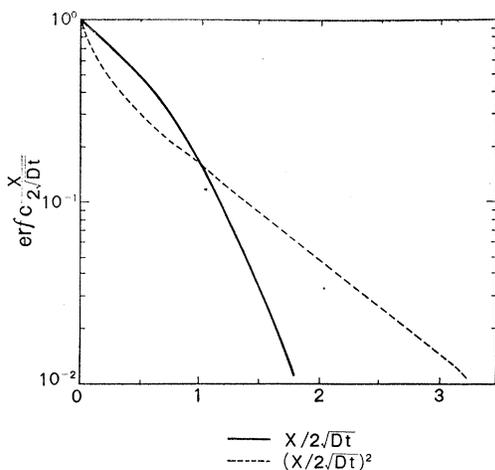


FIG. 5. Graphical solution of  $\text{erfc } x/2(Dt)^{1/2}$ . These curves were taken from H. S. Carslaw and J. C. Jaeger, *Conduction of Heat in Solids* (Clarendon Press, Oxford, 1958), Fig. 5, p. 61.

A specimen obtained by the simple solidification of molten salt will generally be composed of a large number of crystal grains and dislocations.<sup>5</sup> Etching reveals that the crystals before additive coloring contain subgrains of 0.7-mm average diameter and approximately  $3 \times 10^4$  dislocations/cm<sup>2</sup> within the subgrains. A typical example of this is shown in Fig. 6. The boundary regions of grains and disordered interfaces cannot possess the normal crystalline arrangement and are therefore highly disordered. It might therefore be expected that the  $F$  centers in these regions move with a lower activation energy than in the bulk of the crystal. Also, the smaller number of  $F$  centers in the grain boundaries and disordered interfaces confirms that diffusion along these disordered lattices takes place at lower temperatures.

Fisher<sup>6</sup> has indicated that a different solution of the diffusion equation would be more appropriate taking into account a diffusion along a disordered internal interface. In his solution the relation between the  $F$ -center concentration and penetration depth is described by

$$\log n \sim -2^{1/2}(D/D'\delta)^{1/2} \{ \log e / (\pi Dt)^{1/2} \} x + \text{const}, \quad (3)$$

where  $D'$  and  $\delta$  are the diffusion coefficient along the disordered interface and its width, respectively. According to Eq. (3) a plot of  $\log n$  versus the penetration depth should yield a straight line with the slope;

$$2^{1/2}(D/D'\delta)^{1/2} \log e / (\pi Dt)^{1/2}. \quad (4)$$

Seitz<sup>7</sup> has estimated the activation energy of the diffusion of negative ion vacancies in the high-temperature region for KCl and concluded that it is about 1 ev larger than that of a positive ion vacancies.

<sup>5</sup> A. B. Lidiard, *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1957), p. 281.

<sup>6</sup> J. C. Fisher, *J. Appl. Phys.* **22**, 74 (1951).

<sup>7</sup> F. Seitz, *Revs. Modern Phys.* **16**, 7 (1954).

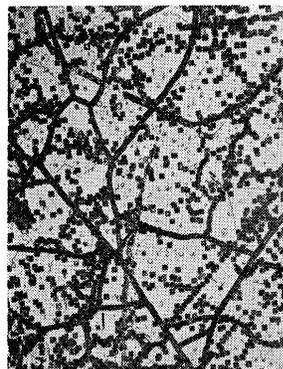


FIG. 6. Etch pits of KCl single crystal showing subgrains and dislocations. (Etchant; Acetone + 0.5 mole HgCl<sub>2</sub>/l); Magnification; 22.5 $\times$ .

Consequently the activation energy of the diffusion of negative ion vacancies is approximately 1.9 ev if the activation energy of positive ion vacancies are assumed to be 0.9 ev.<sup>8</sup> Applying this value, the diffusion coefficient of the negative ion vacancy is derived;

$$D = D_0 \exp(-1.9/kT), \quad (5)$$

where  $D_0$  may be of the order of 1.0 cm<sup>2</sup> sec<sup>-1</sup>. According to Eq. (4) the slope of the line together with the known value of  $D$  for the volume diffusion of Eq. (5) at 450°C and diffusion time  $t$ , fixes the value of  $D/D'\delta$  at

$$D/D'\delta = 1.34 \times 10^{-2} \text{ cm}^{-1}.$$

In order to obtain a value for  $D'$  a certain width of disordered interfaces must be assumed. It would be reasonable to put it at least of the order of two atom layers,

$$\delta \sim 10^{-7} \text{ cm}.$$

With this value of  $\delta$

$$D'/D \sim 10^9$$

is obtained as the ratio of the disordered interface diffusion coefficient to the volume diffusion coefficient at 450°C.

Moreover there is another difficulty in the simple diffusion theory; it follows from Eq. (1) that  $n = \frac{1}{2}n_0$  when  $x/2(Dt)^{1/2} = 0.477$ . With the value of  $D$  in Eq. (5), the time taken to reach this value of concentration at a depth of 1 cm is about  $10^8$  hours for  $T = 800^\circ\text{K}$ . This is incredibly long compared with the time derived from additive coloring experiments. It is, therefore, necessary to introduce some other diffusion mechanism of low activation energy for the explanation of the rapid penetration of  $F$  centers in the experiments. Laurence<sup>9</sup> has studied the diffusion in sodium chloride crystals containing added calcium ions. He comes to the conclusion that there is a strong possibility that the diffusion occurs by means of vacancy pairs at high

<sup>8</sup> Y. Haven (private communication) has pointed out that this value should be lowered to 1.4 ev. In this case the following values of  $D'/D$  and the time taken to reach  $n = \frac{1}{2}n_0$  at the depth of 1 cm must be revised to  $10^8$  and  $3 \times 10^6$  hours, respectively.

<sup>9</sup> N. Laurence, thesis, University of Illinois, Urbana, Illinois (unpublished). One of the authors (H.M.) is indebted to Professor Robert J. Maurer for communication on Laurence's thesis.

temperatures, that is, pairs of associated positive and negative ion vacancies. We agree with Laurence's point of view because we found that the diffusion behavior of negative ion vacancies could be explained by the simple volume diffusion theory in the high-temperature region and therefore the assumption of the existence of the diffusion along disordered interfaces was not necessary. On the other hand, we are inclined to believe that the diffusion along disordered interfaces is predominant at low temperatures.

It would be very interesting to continue these experiments on crystals of varying dislocation and grain boundary structures. The exact determination of the relationship between the behavior of the diffusion and the defects in the crystals is still left to future investigations.

*Note added in proof.* After this work was completed, a paper on Cl ion diffusion was published by Barr, Hoodless, Morrison, and Rudham, *Trans. Faraday Soc.* **56**, 697 (1960). The authors are indebted to Dr. Y. Haven for this information.

## Dynamics of Radiation Damage\*

J. B. GIBSON, A. N. GOLAND,<sup>†</sup> M. MILGRAM, AND G. H. VINEYARD

*Brookhaven National Laboratory, Upton, New York*

(Received July 14, 1960)

Radiation damage events at low and moderate energies (up to 400 ev) are studied by machine calculations in a model representing copper. Orbits of knock-on atoms are found and the resulting damaged configurations are observed to consist of interstitials and vacancies. Thresholds for producing permanently displaced atoms (i.e., interstitials) are about 25 ev in the  $\langle 100 \rangle$  direction, 25 to 30 ev in the  $\langle 110 \rangle$  direction, and around 85 ev in the  $\langle 111 \rangle$  direction. Collision chains in the  $\langle 100 \rangle$  and  $\langle 110 \rangle$  directions are prominent; at low energies the chains focus, at higher energies they defocus. Above threshold, the chains transport matter, as well as energy, and produce an interstitial at a distance. The range of  $\langle 110 \rangle$  chains has been studied in detail. Localized vibrational modes associated with interstitials, agitations qualitatively like thermal spikes, ring annealing processes, and a higher energy process somewhat like a displacement spike have been observed. Replacements have been found to be very numerous.

The configurations of various static defects have also been studied in this model. The interstitial is found to reside in a "split" configuration, sharing a lattice site with another atom. The crowdion is found not to be stable, and Frenkel pairs are stable only beyond minimum separations, which are found to be very much dependent on orientation.

### 1. INTRODUCTION

THE initial event in the damaging of a crystal lattice by high-energy radiation is the sudden transfer of a rather large amount of kinetic energy (10 to perhaps  $10^5$  ev) to a single atom. The energized atom then ploughs through the lattice knocking other atoms from their sites and leaving a damaged region behind. From a theoretical standpoint this damaging event is a complex many-body problem, and it has been treated in the past only by making drastic approximations.<sup>1</sup> Generally it has been considered as a cascade of independent, two-body collisions between knock-on atoms and stationary atoms. The knock-on atoms have been assumed to move freely between collisions. The stationary atoms have been assumed to behave as though randomly located, and their binding in the lattice has been taken into account by the very

much simplified assumption that they will be displaced and enter the group of freely moving knock-ons if and only if endowed with energy above a certain threshold, generally in the neighborhood of 25 ev. On this cascade model the damage is predicted to be a set of interstitial atoms and an equal number of vacant lattice sites, distributed randomly over a small region. Other models have been proposed in which many-body effects are given prominence. Thermal spike and displacement spike models are of this character. In the former, the region around the site of a knock-on is assumed to behave as if suddenly heated, and its subsequent cooling is treated by the classical laws of heat conduction in a homogeneous medium. In the displacement spike models, qualitative arguments about the character of damage are advanced on the assumption that a kind of miniature "explosion" occurs around the site of the knock-on. These models are difficult to harmonize with one another, and each has obvious shortcomings. Patchwork attempts at improving the models in individual details have not yet been very impressive.

In the last few years a number of sophisticated radiation damage experiments have been made. In the most notable of these highly purified metals have been

\* Work supported by the U. S. Atomic Energy Commission.

<sup>†</sup> Guest Scientist from Ordnance Materials Research Office, Watertown, Massachusetts.

<sup>1</sup> For reviews see F. Seitz and J. S. Koehler, in *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1956), Vol. 2, p. 305; also G. J. Dienes and G. H. Vineyard, *Radiation Effects in Solids* (Interscience Publishers, Inc., New York, 1957).

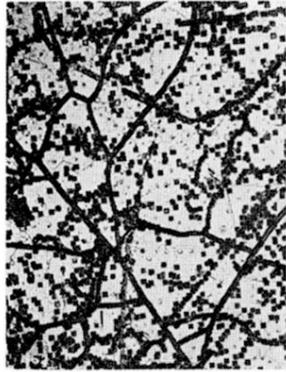


FIG. 6. Etch pits of KCl single crystal showing subgrains and dislocations. (Etchant; Acetone +0.5 mole  $\text{HgCl}_2/l$ ); Magnification;  $22.5\times$ .