

where the presence of accidental impurities affects the conductivity and diffusion coefficient of the silver ion. Accidental contamination of the samples during measurement may be the cause of this variation in their low-temperature behavior.

Since the mechanism of diffusion in the low-temperature impurity range is believed to be primarily due to silver ion vacancies, the data suggest that the failure of the Einstein-Nernst relation in the high-temperature intrinsic range is associated with the mechanism by which interstitial silver ions contribute to conductivity and diffusion.⁵

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¹ C. Tubandt, *Handbuch der Experimental Physik* (Akademische Verlagsgesellschaft M.B.H., Leipzig, 1932), Vol. 12, Part 1, p. 402.

² N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, New York, 1950), p. 63.

³ Each of the indicated points has an accuracy of better than $\pm 10\%$.

⁴ E. Koch and C. Wagner, *Z. physik. Chem.* **B38**, 295 (1937-1938).

⁵ I. Ebert and J. Teltow, *Ann. Physik* **15**, 268 (1955).

Ratio of Ionic Conductivity to Tracer Diffusion in Interstitialcy Migration

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THE experimental results of Compton¹ suggest that, for that part of the ionic migration in AgCl crystals which is due to the presence of interstitial silver ions, the ratio of ionic conductivity to tracer diffusion considerably exceeds the Einstein value. It will be shown here that a value of this ratio about three times the Einstein value is to be expected for migration by the *interstitialcy* mechanism discussed by Koch and Wagner² and so described by Seitz.³ In this mechanism an interstitial ion moves by pushing a neighboring lattice ion into an interstitial site and itself taking the place of the displaced lattice ion. The lattice site and the two interstitial positions involved are supposed collinear. If the jump distance of each of the two ions involved in such a jump is d , the interstitialcy, and so the charge, jumps a distance $2d$. Consideration of this point gives the main contribution to our result. A correlation effect of the type discussed by Bardeen and Herring⁴ for vacancy diffusion also contributes.

If D_i is the diffusion constant and ν_i the jump frequency for the interstitialcies, the familiar device of comparing the results of point-source diffusion and random-walk calculations gives

$$D_i = \frac{1}{6} \nu_i (2d)^2.$$

To obtain a corresponding expression for the tracer diffusion constant D_t , we suppose that there are N silver lattice positions and N_i interstitial silver ions. Since two silver ions are displaced in each interstitialcy jump, there will be $2N_i \nu_i$ ion jumps per second. Consequently a given tracer ion will make a jump $(2N_i/N) \nu_i$ times per second. The Bardeen-Herring correlation effect has to be considered here because successive jumps of a tracer ion, unlike successive jumps of an interstitialcy, are not independent. If the tracer has just jumped to an interstitial position the subsequent jump will indeed be random, but if it has just jumped to a lattice position the interstitialcy is so positioned that there is a relatively high probability of its causing the tracer to jump back in the direction from which it came. If $\langle \cos\theta \rangle_{AV}$ is the mean cosine of the angle between two consecutive jumps of a tracer ion when the first jump is into a lattice position, we find

$$D_t = \frac{1}{6} (1 + \langle \cos\theta \rangle_{AV}) (2N_i/N) \nu_i d^2.$$

Thus

$$D_t/D_i = \frac{1}{2} (1 + \langle \cos\theta \rangle_{AV}) (N_i/N).$$

The interstitialcies will themselves satisfy the Einstein relation since they will distribute themselves in an applied field according to the Boltzmann law⁵: that is

$$\sigma/D_i = N_i e^2 / kT,$$

and so

$$\sigma/D_t = 2(1 + \langle \cos\theta \rangle_{AV})^{-1} N e^2 / kT.$$

Our estimate of $\langle \cos\theta \rangle_{AV}$ is about -0.33 . Thus, if the migration were entirely by the interstitialcy mechanism, the observed ratio would be about three times the Einstein value. For vacancy diffusion, a Bardeen-Herring type correction alone operates and multiplies the Einstein value by only about 1.25. If we assume equal numbers of interstitialcies and vacancies, and use the values given by Ebert and Teltow⁶ for the ratio of mobilities, the expected value of σ/D_t at 350°C turns out to be about 2.5 times the Einstein value; this is to be compared with Compton's experimental factor of 1.7. Both factors decrease somewhat with increasing temperature. Departures from collinearity in the two ion displacements in an interstitialcy jump, or the presence of any of several other diffusion mechanisms, could account for Compton's factor being smaller than our estimate. It is difficult to assess how likely these various possibilities are.

The effects discussed here may be useful in distinguishing experimentally between interstitialcy and vacancy migration in other crystals.

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¹ W. D. Compton, preceding Letter [Phys. Rev. **101**, 1208 (1956)].

² E. Koch and C. Wagner, Z. physik Chem. **B38**, 295 (1937).

³ F. Seitz, Acta Cryst. **3**, 355 (1950).

⁴ J. Bardeen and C. Herring, in *Imperfections in Nearly Perfect Crystals*, edited by W. Shockley (John Wiley and Sons, Inc., New York, 1952). Professor Bardeen points out that a factor 2 is omitted from terms after the first on the right-hand side of Eq. (A.2) and the error persists through the paper.

⁵ The correction to the Einstein relation proposed by E. Katz [Phys. Rev. **99**, 1334 (1955)] is not consistent with this requirement and must in principle be zero.

⁶ I. Ebert and J. Teltow, Ann. Physik **15**, 268 (1955).

Photographs of the Stress Field Around Edge Dislocations

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PAST attempts to "see" individual dislocations in transparent crystals by means of polarized light have always been frustrated by the sheer density of these dislocations. However, such perfect silicon crystals are now grown that the dislocation density is low enough to make the inspection of individual dislocations possible by working in the near infrared where silicon is transparent. If one calculates from the stresses around dislocations¹ what the intensity distribution should be for observation between crossed Nicols, one gets, for an edge dislocation seen "end on" (assuming an isotropic medium), curves of equal intensity as shown in Fig. 1. Here it is assumed the slip vector of an edge dislocation makes an angle of 15° with the polarizer axis. Using measured values of the stress birefringence constants for the infrared, we find

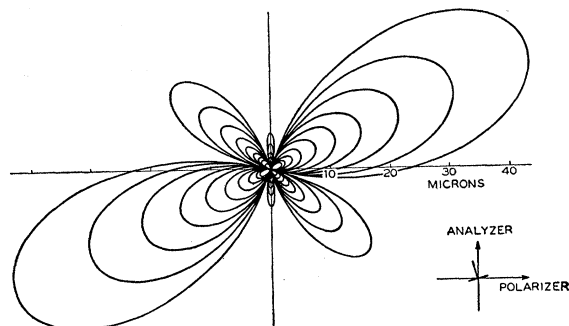


FIG. 1. Intensity of light around a dislocation the slip plane of which is turned 15° to the polarizer axis. The contour intervals are half-values.

that the intensity 50 microns from a dislocation is about one thousandth of what it would be in the absence of Nicol prisms. In the absence of Nicols, a picture of a metal screen requires an exposure of about

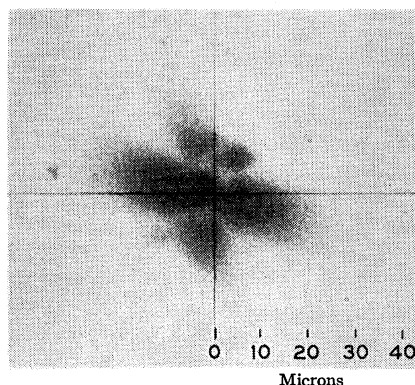


FIG. 2. Photograph in infrared through silicon.

one second when a carbon arc is used. Hence a dislocation could be photographed in about a quarter of an hour. Figure 2 is such a photograph taken on an Eastman I plate, sensitized for the infrared.

Figure 3 is a picture through a twinned specimen. The specimen is a 110 plate so the twin boundary, a 111, is seen "edge on." The contrast between the two parts is caused by an externally applied stress. A number of dislocations are seen "end on" along the twin boundary. A number of slip planes are to be seen, each with dislocations most of which are somewhat tipped. The slip planes make the correct angle with the twin



FIG. 3. Array of dislocations around a twin boundary.

boundary to be 111 planes as they should be. The dislocations repel each other so that the ones on the boundary are caused to stand erect, in which position they are most readily seen.

Computations also show that screw dislocations cannot be photographed along the axis and perpendicular photographs of either kind should take exposures of many days.

¹ W. T. Read, *Dislocations in Crystals* (McGraw-Hill Book Company, Inc., New York, 1953), p. 116.