

Effect of Plastic Deformation on the Electrical Conductivity of Silver Bromide*†

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Plastic deformation of AgBr at and below room temperature produces a conductivity increase that varies linearly with strain. The conductivity increase has a low activation energy, exhibits dispersion at low frequencies, and recovers slowly at room temperature. A small anisotropy in the conductivity increase can be produced which indicates that the increase is greater parallel to the slip planes than perpendicular to them. The conductivity increase is attributed to regions of disorder that are introduced by the deformation, and these regions of disorder appear to be piled-up groups of dislocations in the slip planes of the work-hardened crystal.

I. INTRODUCTION

REGIONS of disorder in crystals, such as grain boundaries, are known to have high-diffusion coefficients compared to the normal lattice.¹⁻³ It is reasonable to expect that the regions of disorder that are introduced by plastic deformation will act as similar paths of fast diffusion,^{4,5} and, in the case of ionic crystals, as paths of high electrical conductivity. The work of Hevesy and Obrutsheva⁶ on self-diffusion in lead, and the work of Matano⁷ on copper-zinc alloys is to be interpreted in this manner. In general it is difficult to measure directly the diffusion in cold-worked materials because at temperatures high enough to achieve measurable diffusion the effects of plastic deformation recover rapidly. However, in ionic crystals the effect of deformation on the conductivity can be studied, since the electrical conductivity and self-diffusion are both due to the motions of ions⁸; and the conductivity can be measured at low temperatures so that the effects of cold work recover slowly.

AgBr is an ionic crystal with the rock salt structure. The intrinsic conductivity is reasonably well understood as the result of the work of Teltow⁹ and Kurnick.¹⁰ The predominant lattice defect is the Frenkel defect, consisting of a silver interstitial ion and a silver ion vacancy.

The interstitial ion has the higher mobility, its mobility being about 10^3 greater than that of the vacancy at room temperature. Above 100°C all specimens of pure AgBr exhibit the same conductivity, but at lower temperatures, in the "structure-sensitive" region, the individual specimens exhibit conductivities that may differ appreciably. It is seen in Fig. 1 that above about 60°C all of the specimens have the same conductivity which is the same as the intrinsic conductivity extrapolated from the high temperature measurements of Kurnick.¹⁰ Below 60° the polycrystals have a higher conductivity than do the single crystals, and there is some variation among the individual single crystals. The specimens employed in this experiment were of almost constant purity so that the variation in the low-temperature conductivity is not due to impurities.¹¹ The most applicable explanation for this structure-sensitive conductivity is due to Smekal,¹² who suggested that it arises from the motions of ions along internal surfaces of abnormally low activation energy.

Plastic deformation produces two effects that might lead to an increase in the conductivity of an ionic crystal. First, large numbers of dislocations are formed which may well serve as the internal regions of low activation energy conceived by Smekal. Second, there will be vacancies and interstitial ions produced by the moving dislocations through mechanisms discussed by Seitz¹³ and Mott.¹⁴ These point defects are extra charge carriers which cause an increase in the conductivity. The work of Gyulai and Hartly¹⁵ on NaCl is to be interpreted in terms of the latter effect.¹⁶ In their work a 12 percent deformation of NaCl at 40°C produced a conductivity increase of a factor of 60. This increase decayed rapidly, falling to one-half maximum in 0.1 min and it had disappeared after 20 min. According to Seitz,¹⁶ the rapid recovery was due to the association of the positive and negative vacancies that were formed during the deformation. The rate of formation of the

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¹ A. LeClaire, *Progress in Metal Physics* (Interscience Publishers, Inc., New York, 1953), Vol. 4, p. 205.

² R. Smoluchowski, *Imperfections in Nearly Perfect Crystals*, edited by W. Shockley (John Wiley and Sons, Inc., New York, 1952), p. 451.

³ D. Turnbull, *Atom Movements* (American Society for Metals, Cleveland, 1951), p. 129.

⁴ A. H. Cottrell, *Theoretical Structural Metallurgy* (Edward Arnold and Company, London, 1948), Chap. XII.

⁵ C. Zener, *Imperfections in Nearly Perfect Crystals*, edited by W. Shockley (John Wiley and Sons, New York, 1952), p. 289.

⁶ G. Hevesy and A. Obrutsheva, *Nature* **115**, 674 (1925).

⁷ C. Matano, *Japan. J. Phys.* **9**, 41 (1934).

⁸ N. F. Mott and R. W. Gurney, *Electrical Processes in Ionic Crystals* (Oxford University Press, London, 1950), Chapter II.

⁹ J. Teltow, *Ann. Physik* **5**, 63, 88 (1950).

¹⁰ S. W. Kurnick, *J. Chem. Phys.* **20**, 218 (1952).

¹¹ E. Koch and C. Wagner, *Z. physik. Chem.* **38B**, 295 (1937).

¹² A. Smekal, *Handbuch der Physik* (Verlag Julius Springer, Berlin, 1933), Vol. 24/2, p. 878.

¹³ F. Seitz, *Advances in Phys.* **1**, 43 (1952).

¹⁴ N. F. Mott, *Phil. Mag.* **43**, 1151 (1952).

¹⁵ Z. Gyulai and D. Hartly, *Z. Physik* **51**, 378 (1928).

¹⁶ F. Seitz, *Phys. Rev.* **80**, 239 (1950).

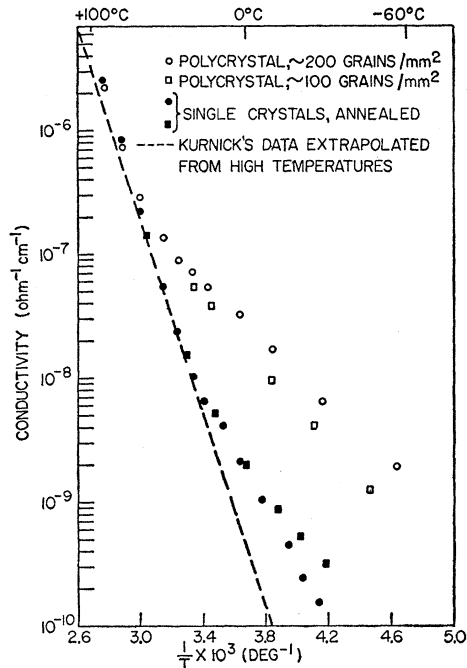


FIG. 1. Conductivity of annealed crystals of AgBr.

neutral vacancy pairs is controlled by the mobility of the sodium vacancy. It is to be expected that in AgBr there will be interstitial ions and vacancies formed during deformation; but the mobilities of the silver interstitial ions and vacancies near room temperature are so great that the point defects decay very rapidly. If the conductivity increase which is observed in the present experiment were due to silver interstitials or vacancies, it can be calculated from the mobilities¹⁰ that the conductivity would decay to half-maximum in less than 10^{-2} sec at 30°C . Actually, it is observed that the conductivity increase decays to half-maximum in about 10^5 sec, so that the effect which is studied here is not due to point defects created during the deformation.

It has been pointed out that the dislocations produced during deformation may act as paths of high conductivity. The work of Turnbull and Hoffman¹⁷ on grain boundary self-diffusion in silver indicates that the high diffusion rate along small-angle grain boundaries is due to diffusion along the individual dislocation "pipes" that form the grain boundary. It has been suggested by Hart¹⁸ that the major enhancement of diffusion by cold-work is due to preferential diffusion along the dislocation pipes produced by the cold work.

An edge dislocation in an ionic crystal of the AgBr type is shown in Fig. 2 (after Seitz¹⁹). The plane shown is an (001) plane and the electrical charges alternate

on successive (001) planes. The slip plane, AC, is a (110) plane and the slip direction is $[\bar{1}\bar{1}0]$. The dislocation is formed by the insertion of two extra atomic half-planes which are enclosed by dotted lines. Beyond the edges of these half-planes there is an expansion of the lattice.²⁰ The stress in that region is relieved by the presence of interstitial ions or vacancies, both of which have a positive volume change associated with them.¹⁰ This leads to a lower activation energy for the creation of such point defects in that region. The activation energy for mobility along the dislocation is also lowered due to the dilation of the lattice. Calculations are not available for the activation energy for conduction along a dislocation. The work of Turnbull and Hoffman¹⁷ indicates that in silver the activation energy for self-diffusion along a dislocation is about 20 000 cal/mole, compared to 46 000 cal/mole in the normal lattice.

II. EXPERIMENTAL PROCEDURE

The AgBr was prepared by precipitation from Mallinckrodt HBr and AgNO_3 . Spectrographic analysis indicated the presence of about 0.001 percent of Cu, Mg, and Fe, with less than measurable amounts of other metallic impurities. The sulfur content was not appreciably greater than 0.0002 percent.

Single crystals were grown by withdrawal from the melt (Czochralski method) at the rate of 0.5 in./hr. After machining to size, the surface of the crystal was removed with a KCN solution. The crystals were annealed for 24 hr at 400°C , and cooled to room temperature at 25 deg/hr. The growth and anneal were in air atmosphere. Most specimens were $\frac{1}{4}$ in. diam and $\frac{3}{8}$ in. long; shorter specimens were used for high-frequency measurements, and longer specimens were used when accurate strain measurements were desired.

Specimens were deformed by compression in the apparatus shown in Fig. 3, by loading the ram with weights or with a compressed air piston, while the strain was measured with a displacement indicator in units

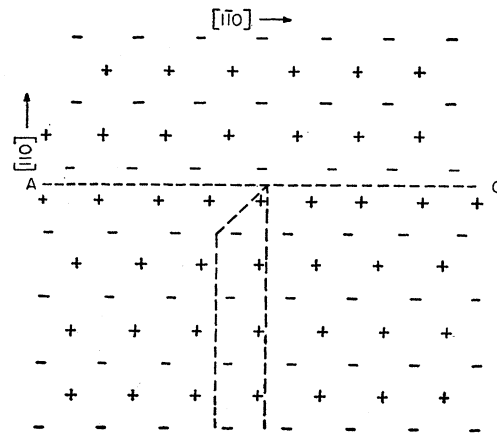


FIG. 2. Edge dislocation in AgBr-type crystal.

¹⁷ D. Turnbull and R. E. Hoffman, *Acta Metallurgica* 2, 419 (1954).

¹⁸ E. W. Hart, see reference 17.

¹⁹ F. Seitz, *Plastic Deformation Symposium*, Carnegie Institute of Technology (Office of Naval Research, Washington, D. C., 1950).

²⁰ A. H. Cottrell, *Dislocations and Plastic Flow in Crystals* (Oxford University Press, London, 1953), p. 57.

of 0.0001 in. Silicone oil served as a temperature bath, and to prevent moisture from condensing on the specimen. A thermocouple was placed within $\frac{1}{4}$ in. of the specimen and the apparatus was enclosed in a light-proof can.

Electrodes were applied with silver paint. The parallel resistance of the specimen was measured by placing it in parallel with an air condenser and measuring the capacity and dissipation factor of the combination with a General Radio Company capacitance bridge, type 716-C. Unless otherwise stated, the measurements were made at 30 cps or 100 cps. For a study of dispersion the range of 20 cps to 20 000 cps was used. Approximately 1 v/cm was applied to the crystals.

The specimen was loaded with increments of from 3 kg/cm² to 30 kg/cm². Usually the conductivity was measured after each load increment so that the deformation may have been spread out over a period of six or eight minutes. When the absolute value of the conductivity was of interest the deformation was limited to 8 or 10 percent, so that an accurate correction for change of geometry could be made.

III. EXPERIMENTAL RESULTS

A. Conductivity-Strain Dependence

In Fig. 4 are shown the conductivity increases produced in two single crystals that were $\frac{1}{4}$ in. square and $\frac{7}{8}$ in. long, and oriented so that the axis was in the [100] direction. The conductivity increased linearly with strain up to about 2.5 percent strain. This linearity extends down to 0.1 percent strain and, in some crystals, as high as 6 percent strain.

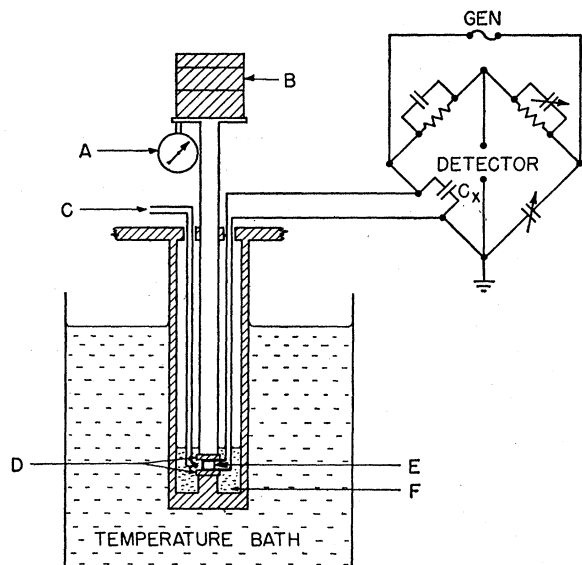


FIG. 3. Apparatus for deforming crystals and measuring ac conductivity. *A*—displacement gauge, *B*—deforming load, *C*—thermocouple, *D*—quartz insulating disks, *E*—specimen crystal, *F*—silicone oil bath.

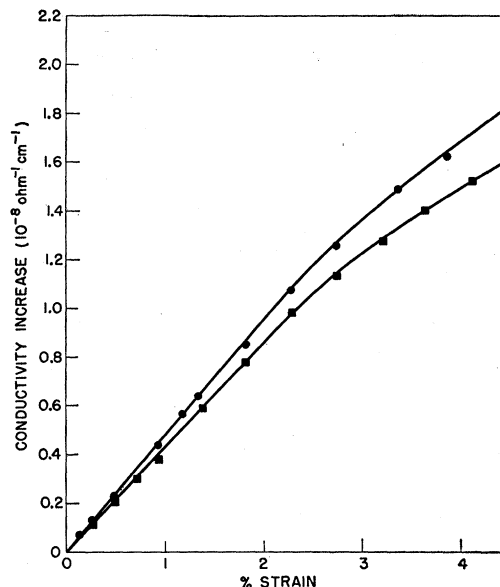


FIG. 4. Conductivity increase of two single crystals deformed at 30°C. The initial conductivity was 1.35×10^{-8} ohm⁻¹ cm⁻¹. Measured at 100 cps.

The departure from linearity at high strains appears to be associated with the fact that at the higher stresses there is transient creep during the time it takes to make the measurements. If the conductivity increases linearly with instantaneous strain but not with transient creep strain, the negative curvature of the plot of total strain *versus* conductivity is to be expected.

The conductivity increase shown in Fig. 4 is about 1.6×10^{-8} ohm⁻¹ cm⁻¹ at 30°C for a 4 percent strain. With extreme deformation of 75 percent in compression it is possible to produce increases as great as 50×10^{-8} ohm⁻¹ cm⁻¹.

B. Temperature Dependence of the Conductivity Increase

The temperature dependence of the conductivity increase of a deformed single crystal measured at 30 cps and 100 cps is shown in Fig. 5. The top curve indicates that the activation energy is 5800 cal/mole immediately after deformation. Low-frequency measurements soon after deformation characteristically give values of 5500 to 6500 cal/mole for the activation energy of the conductivity increase. The two lower solid curves show that the activation energy of the conductivity increase gets larger during recovery, approaching the behavior of the annealed crystal.

The activation energy of 5800 cal/mole can be compared with the 18 450 cal/mole that is characteristic of the intrinsic conductivity in AgBr.¹⁰ The value of 5800 cal/mole lies between the 4700 cal/mole for the mobility of silver interstitial ions and the 11 200 cal/mole for the mobility of silver vacancies.

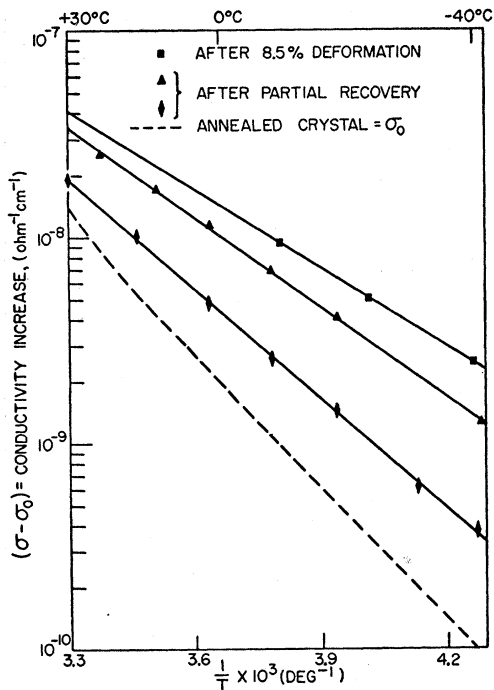


FIG. 5. Conductivity increase of a single-crystal specimen deformed in compression. Top curve was taken after deformation at -24°C . The second curve was taken after 2-hr recovery at 30°C , and the lowest solid curve was taken after 80-hr recovery at 30°C . Measured at 30 cps and 100 cps.

C. Frequency Dependence of the Conductivity Increase

At high temperatures, conductivity measurements of AgBr single crystals exhibit a dispersion that is characteristic of electrode polarization effects, and which has been studied by Friauf.²¹ Below 200°C these electrode polarization effects are small, and at 100°C there is no dispersion in the intrinsic conductivity between 20 cps and 20 000 cps. At still lower temperatures, however, a dispersion again appears which seems to be characteristic of the structure-sensitive conductivity, and which increases greatly with plastic deformation. Figure 6

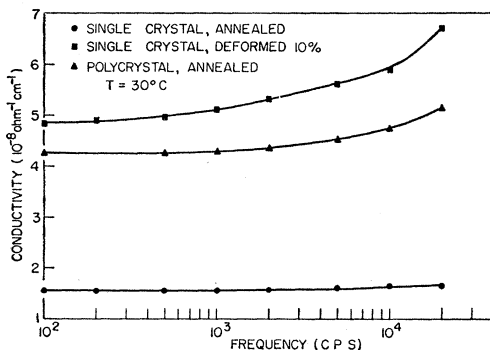


FIG. 6. Frequency dependence of conductivity.

²¹ R. J. Friauf, *J. Chem. Phys.* **22**, 1329 (1954).

shows the conductivity of an annealed single crystal that has very little dispersion at 30°C . After a 10 percent deformation the frequency dependence is pronounced. The behavior of an annealed polycrystal is more like that of the deformed single crystal than like the annealed single crystal.

As a result of this dispersion the activation energy of the conductivity increase produced by deformation appears to depend on the measuring frequency. This is seen in Fig. 7 where the conductivity increase of a single crystal after 10 percent deformation is shown as measured at several frequencies. For each frequency the points can be approximated by a straight line whose slope indicates an activation energy. The values obtained range from 4600 cal/mole at 20 000 cps to 6300 cal/mole at 100 cps.

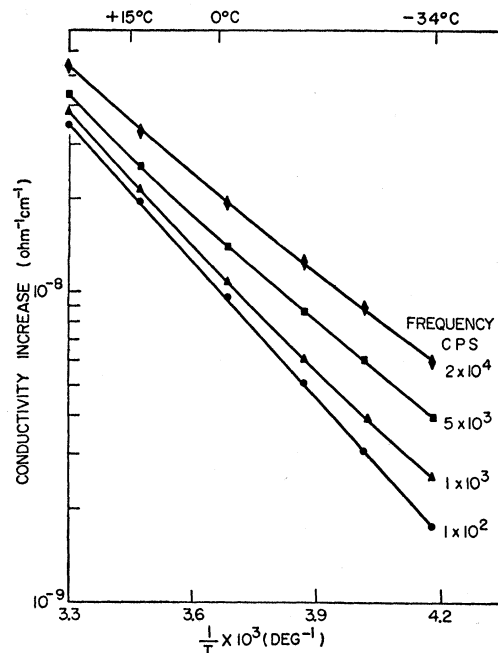


FIG. 7. Conductivity increase of a deformed single crystal measured at several frequencies. Measurements were made after 2-hr recovery at $+30^{\circ}\text{C}$.

In Fig. 8 the normalized conductivity increase at each temperature is seen to level off at low frequencies. This is a true leveling-off since dc measurements at 0°C yield the same results as do measurements at 100 cps. At the lower temperatures the dispersion sets in at lower frequencies.

D. Recovery

The conductivity increase produced by plastic deformation recovers slowly near room temperature. Figure 9 shows the recovery of a single crystal that was deformed 8.5 percent at 29.6°C and allowed to recover with the load removed. The experimental points can

be fitted with the expression

$$\Delta\sigma = \Delta\sigma_0 - a \log(t/t_0 + 1), \quad (1)$$

where t is the recovery time, a and t_0 are constants. This is the equation for recovery that Kuhlmann, Masing, and Raffelsieper,²² and Cottrell and Aytakin²³ have used to fit data for the recovery of yield stress in aluminum and zinc, respectively. The yield stress of AgBr recovers at a rate comparable with the recovery of conductivity as shown in Fig. 10.

The activation energy for the recovery of a single crystal deformed 8.5 percent with a load of 110 kg/cm² was determined. The recovery rate at 29.6°C was compared with the recovery rate when the temperature was changed to a new value in the range of 14°C to 60°C. The conductivity measurements were all made at 29.6°C. The relative recovery rates obtained in this manner are plotted in Fig. 11, and the slope corresponds to an activation energy of 18 500 ± 1500 cal/mole. This value is the same as the activation energy for conductivity by silver interstitial ions in the intrinsic range.¹⁰

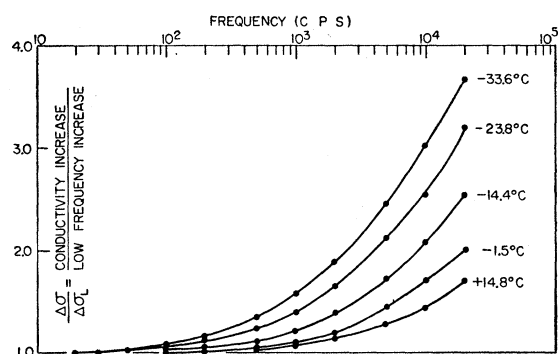


FIG. 8. $(\Delta\sigma/\Delta\sigma_L)$ = conductivity increase divided by the low-frequency increase to give a normalized curve at each temperature.

The plot is linear although the measurements for the various points were made at different stages of recovery. The uppermost point was measured while the conductivity recovered from 53 percent to 63 percent of total recovery, and the data for the bottom point was obtained while the conductivity recovered from 25 percent to 35 percent. This implies that the activation energy for recovery does not depend on the stage of recovery. In this connection, there is some question as to whether the activation energy for recovery of yield stress is a function of the yield stress.^{24,25}

The conductivity recovers also when there is no recovery of yield stress, i.e., when the deforming stress is left on the specimen. Figure 12 shows the transient creep of a specimen that was deformed 4 percent in

²² Kuhlmann, Masing, and Raffelsieper, *Z. Metallkunde* **40**, 241 (1949).

²³ A. H. Cottrell and V. Aytakin, *J. Inst. Metals* **77**, 389 (1950).

²⁴ P. A. Beck, *Advances in Phys* **3**, 245 (1954).

²⁵ Drouard, Washburn, and Parker, *Trans. Am. Inst. Mining Met. Engrs.* **197**, 1226 (1953).

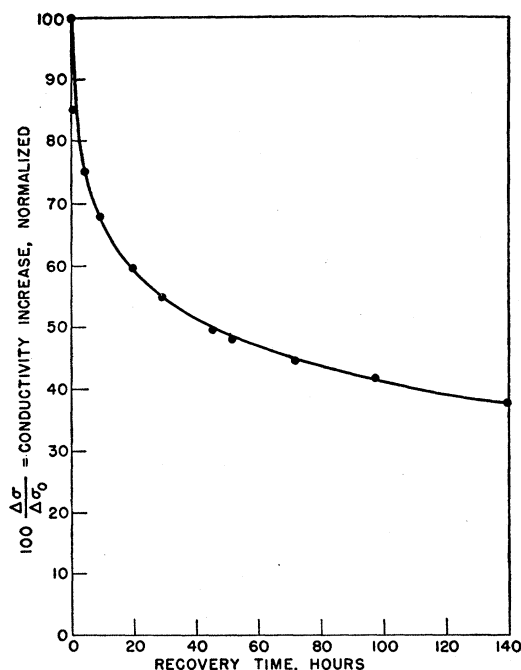


FIG. 9. Recovery of conductivity increase of a deformed single crystal. $\Delta\sigma_0$ is the conductivity increase after the instantaneous deformation, when $t=0$. The solid curve is $100(\Delta\sigma/\Delta\sigma_0) = 100 - 11.4 \log(t/0.57 + 1)$. Measured at 100 cps.

instantaneous deformation, and the applied stress kept constant thereafter. The creep initially followed the Andrade $t^{1/2}$ law. The conductivity of the specimen recovered during the transient creep, although not as rapidly as did a specimen from which the load was removed after a 4 percent instantaneous strain (dotted curve). Equation (1) fits the data for recovery with load on or with load off quite well, as is shown in Fig. 13. If anything, it fits the data for recovery with the load on

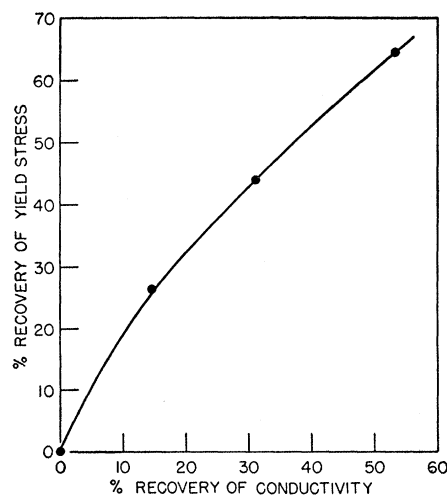


FIG. 10. Recovery of yield stress vs recovery of conductivity of a single crystal after 8.5 percent deformation at 29.6°C. Measured at 100 cps.

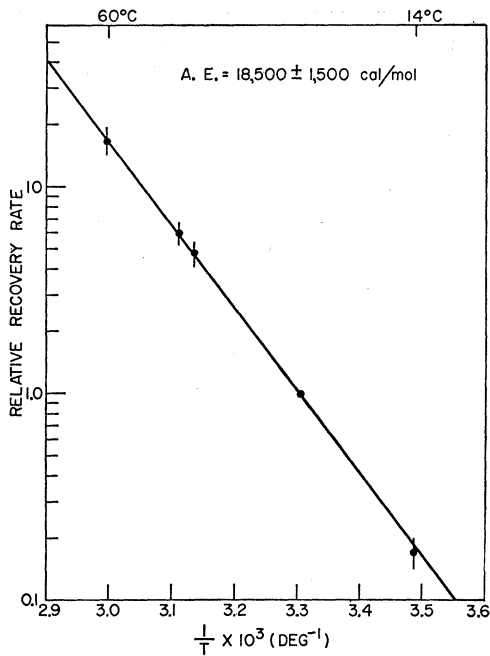


FIG. 11. Temperature dependence of recovery rate of conductivity of a deformed single crystal. Measurements made at 100 cps.

better, the difference being more obvious for small recovery times when a log plot is made of the data.

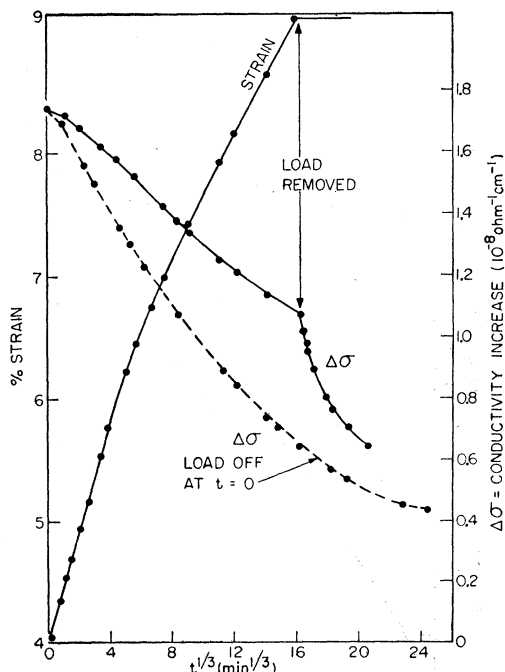


FIG. 12. Strain curve shows the transient creep of a single crystal with the stress kept constant after a 4 percent instantaneous deformation. Upper recovery curve, $\Delta\sigma$, shows the recovery of conductivity during transient creep. Dotted curve shows the recovery of conductivity of a single crystal that was deformed 4 percent and the load removed at once. $T=29.6^\circ\text{C}$.

E. Anisotropy of the Conductivity Increase

In order to compare the conductivity increase parallel to the slip plane with the increase perpendicular to the slip plane it is desirable to obtain slip on a single slip system. Single-crystal shear specimens were machined to 0.250 in. by 0.375 in. by 0.090 in., with the (011) plane parallel to the large faces. These (011) faces were fastened with Duco cement to the apparatus shown in Fig. 14, so that the shear would be along the (011) planes and in the $[0\bar{1}1]$ direction. Although the motion of the apparatus was constrained to a pure shear displacement, the crystals did not deform in pure shear on a single slip system. There was evidence of some slip on intersecting slip systems, but most of the slip was

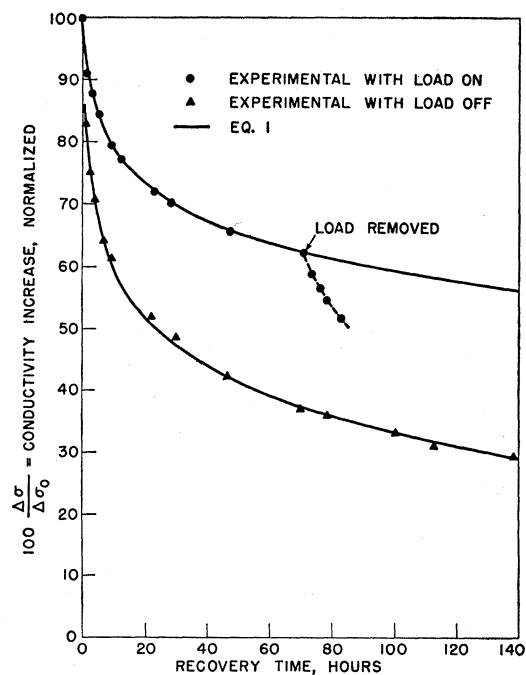


FIG. 13. Recovery of conductivity of single crystal with load on (upper curve), and recovery with load off (lower curve). The calculated curves are $100(\Delta\sigma/\Delta\sigma_0) = 100 - a \log(t/t_0 + 1)$, with $a=9.13$ and $t_0=1.13$ hr for the upper curve, and $a=11.8$ and $t_0=0.34$ hr for the lower curve.

on the desired system. Measurements made after a 10 percent shear strain indicated that the conductivity increase was about 40 percent greater parallel to the slip plane than perpendicular to it. There appeared to be no anisotropy in the slip plane. The results for three crystal deformed in this manner are shown in Table I. The large estimated errors resulted from the relatively small conductivity increase that could be produced, and from the contamination of the surfaces of the crystals in removing and reapplying electrodes.

F. Polycrystals

Small-grain polycrystals were prepared by casting, and annealed at 250°C for 24 hours. The temperature

dependence of the conductivity of a specimen with 200 grains/mm² is shown in Fig. 15. The annealed polycrystal has a higher conductivity with a lower activation energy than does the annealed single crystal. The effect of deformation on the polycrystal appears to be about the same as on the single crystal. The deformed single crystal behaves very much like the annealed polycrystal. In Fig. 6 the frequency dependence of the conductivity of a polycrystal was more like that of a deformed single crystal than an annealed single crystal. This similarity between grain boundary conduction and deformation conductivity is to be expected if both are characteristic of disordered regions of the crystal. The main difference in the two is that the grain boundary conductivity does not recover.

IV. DISCUSSION

An understanding of the mechanism whereby the conductivity of AgBr changes during plastic deformation should include the following main features of the experimental results: (a) Linear dependence of conductivity on strain; (b) low activation energy of the conductivity increase which changes as the crystal

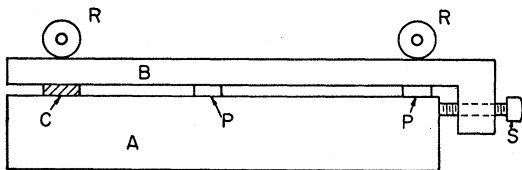


FIG. 14. Shear apparatus for thin crystal, *C*, which is glued to parts *A* and *B* of the apparatus. The rollers, *R*, and the spacers, *P*, constrain the motion of part *B* to a pure shear displacement. The screw, *S*, is used to provide the deforming force.

recovers; (c) frequency dependence of the conductivity increase; (d) time dependence of recovery; and (e) anisotropy of the conductivity increase.

It was pointed out in the introduction that the conductivity increase due to deformation cannot be attributed to interstitial ions or vacancies formed during the deformation because these point defects would decay much faster than the observed recovery. Further arguments are that the conductivity due to point defects would not exhibit the observed dispersion, and the activation energy of the conductivity increase cannot be correlated with the activation energy for the mobility of interstitial ions or vacancies.

The indefinite and variable activation energy and the dispersion of the conductivity increase point to an inhomogeneous mechanism in line with Smekal's¹² idea of internal regions of high conductivity, rather than to a change in the bulk conductivity. On the assumption that plastic deformation causes the introduction of regions of high conductivity into the crystal, one can devise a simple model that exhibits qualitatively the observed behavior.

Consider the undeformed crystal as depicted in Fig.

TABLE I. Anisotropy of conductivity increase in single crystals.^a

Crystal	$\Delta\sigma_e/\Delta\sigma_0$	$\Delta\sigma_s/\Delta\sigma_e$
A	1.48 ± 0.25	1.10 ± 0.35
B	1.42 ± 0.18	0.93 ± 0.25
C	1.38 ± 0.18	1.05 ± 0.25

^a $\Delta\sigma_0$ was measured perpendicular to the slip plane. $\Delta\sigma_e$ was parallel to the slip plane and perpendicular to the slip direction. $\Delta\sigma_s$ was parallel to the slip plane and in the slip direction.

16(a). Neglecting the parallel capacitance of the crystal, we can consider it as a simple resistance, R_0 in Fig. 16(b), when the electrodes are placed on the surfaces indicated by the arrows. The undeformed crystals behave as such simple resistances, showing little dispersion. In Fig. 16(c) the effect of the deformation has been to introduce a uniform region of high conductivity material, ab , that extends completely across the crystal. In Fig. 16(d) the increase in parallel conductance of the crystal is merely $1/R_d$, where R_d is the resistance of the high conductivity strip. The conductivity increase would exhibit the temperature dependence of R_d , and there would be no dispersion. However, such a model can be changed slightly to give a more realistic behavior.

Figure 16(e) depicts a deformed crystal in which the region of high conductivity does not extend completely through the crystal; but it has a gap, cd , the resistivity of the material in the gap being much higher than that in the regions ac and db . If the resistance of the high-conductivity material is R_d and that of the gap is R_g , the equivalent circuit can be depicted as in Fig. 16(f). The low-frequency or dc resistance of the lower branch

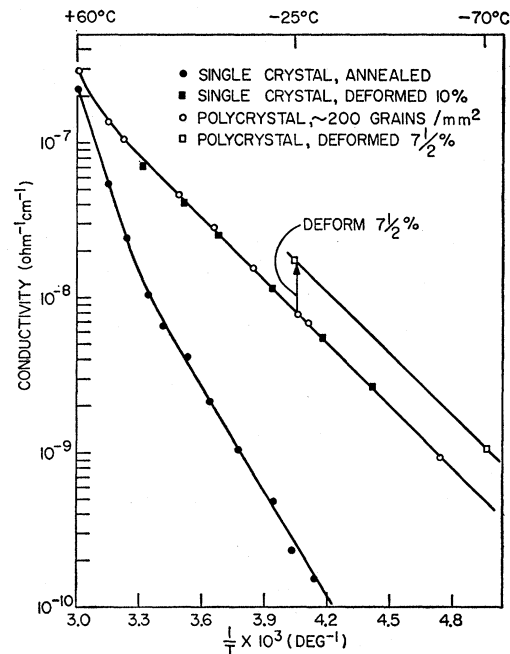


FIG. 15. Conductivity of a polycrystalline specimen before and after deformation. Single-crystal behavior is shown for comparison. Measurements were made at 30 cps and 100 cps.

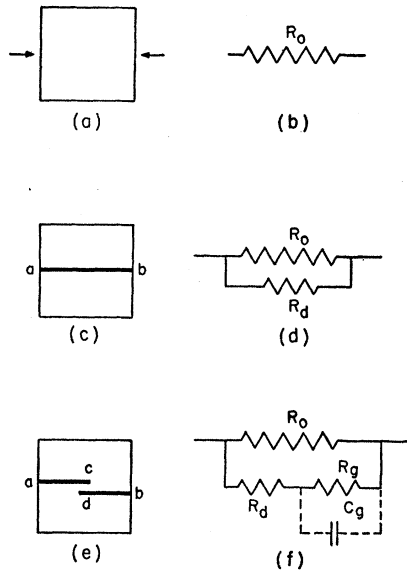


FIG. 16. (a)—Model of an annealed crystal. (b)—Equivalent circuit of (a), neglecting parallel capacitance. (c)—Deformed crystal with homogeneous region of high conductivity, ab , extending through the crystal. (d)—Equivalent circuit for (c). (e)—Deformed crystal with interrupted region of high conductivity material. (f)—Equivalent circuit for (e).

of the circuit is $R_d + R_g$, and the increase in conductance of the specimen is

$$\Delta G = 1/(R_d + R_g) = (1/R_d)/(1 + R_g/R_d). \quad (2)$$

If the gap is very small then $R_g/R_d \ll 1$, and the increase in conductance is $1/R_d$, which would exhibit the low activation energy characteristic of the high-conductivity region. As the ratio R_g/R_d increases, the temperature dependence of the conductivity increase would change from the low activation energy of R_d to some higher value, eventually approaching the activation energy of R_g . The recovery process in such a model can be viewed as one in which the quantity R_g/R_d increases as the gap gets larger, or as the gap gets larger and the amount of high conductivity material decreases.

Across the gap, cd , there will be an associated capacitance, designated as C_g in Fig. 16(f). The parallel resistance of the circuit consisting of R_d , R_g , and C_g can be written as

$$R_p = R_g(ay^2 + 2y + 1)/(ay + 1), \quad (3)$$

where $y = R_d/R_g$, and $a = 1 + (R_g C_g \omega)^2$. ω is $2\pi \times$ frequency.

At low frequencies, $a = 1$ and the parallel resistance is the same as the low-frequency resistance written above. At very high frequencies $a \gg 1$, and the parallel resistance is $R_p = yR_g = R_d$, which has a low activation energy. At low frequencies there is some contribution from the high-resistivity material in the gap that results in a higher apparent activation energy. This accounts for the apparent change of activation energy with frequency as indicated in Fig. 7.

The model proposed, in which there are regions of high conductivity separated by regions of lower conductivity, will exhibit an activation energy that changes with recovery, and it will exhibit a dispersion such as is actually observed. The shortcomings of the model are clear. We have employed a single R_g and a single R_d , whereas a deformed crystal will have large numbers of such interrupted paths. If, indeed, we are to consider dislocations as regions of high conductivity, we may expect to find as many as 10^{11} or 10^{12} dislocations/cm² in a deformed crystal. Where we have employed a single gap in the high-conductivity material there will actually be many interruptions, ranging from very large gaps that have the conductivity of the normal material, to very small gaps which have a higher conductivity because the stress fields of nearby dislocations produce dilatation in those regions. Such a distribution of gap size means that the frequency dependence of a real crystal will be spread out over a much larger range of frequencies than would be the case for the model above.

With such a model one may calculate an approximate lower limit for the frequency at which dispersion should be observed. It is seen in Eq. (3) that when $R_g C_g \omega \ll 1$, the parallel resistance will be the same as the dc value. When $R_g C_g \omega \cong 1$, the parallel resistance will depart from the dc value. In the product $R_g C_g$, the geometric factors cancel out and

$$R_g C_g = k_0 / [\sigma(4\pi)(9 \times 10^{11})], \quad (4)$$

where k_0 is the low-frequency dielectric constant, and σ is the conductivity of the gap material in ohm⁻¹ cm⁻¹. The lowest conductivity that can occur in the gap is that of the undeformed crystal, σ_0 , so that the lowest value of the frequency for which $R_g C_g \omega = 1$ is

$$\omega_{\min} = 1/(R_g C_g)_{\max} = (4\pi)(9 \times 10^{11})\sigma_0/k_0. \quad (5)$$

There should be no dispersion at frequencies appreciably below this value. From the curves in Fig. 8 we can take the value of the observed frequency at which $\Delta\sigma/\Delta\sigma_L = 1.10$ as the lowest frequency at which dispersion is observed. In Table II this experimental value is compared with $\omega_{\min}/2\pi$ calculated in the above manner. The calculated lower limit for dispersion is in agreement with the observed dispersion.

A simple physical description of the cause of dispersion can be given. At low frequencies there will be a pile-up of charge at the boundaries of the high-conductivity regions since the motion out of these regions

TABLE II. Calculated and observed low-frequency limit for dispersion.

Temperature (°C)	f_{\min} (calc) (cps)	f_{obs} for $\Delta\sigma/\Delta\sigma_L = 1.10$ (cps)
+14.8	760	1200
-1.5	280	600
-14.4	140	280
-23.8	80	140
-33.6	46	100

restricted by the low conductivity of the gap material. The polarization due to such blocked charges will oppose the applied field and the conductivity of the disordered region will be lowered. At much higher frequencies the charges in the high-conductivity regions can move in phase with the applied voltage without causing appreciable pile-up of charge at the boundaries of these regions. The effect is similar to the high-temperature polarization of AgBr, where the blocking of charges occurs at the surface of the electrodes, rather than at internal boundaries.²¹

An upper limit of 4600 cal/mole can be placed on the activation energy for conduction in the disordered regions of the crystal. The value of 4600 cal/mole was observed at the highest frequency employed, and it should be more characteristic of the disordered regions than are the values obtained at lower measuring frequencies.

The foregoing discussion suggests that the conductivity in a deformed crystal is increased by the introduction of interrupted paths of high conductivity, or of low activation energy. The anisotropy of the conductivity increase indicates that these paths of high conductivity tend to lie parallel to the slip planes. Dislocations should behave as regions of low activation energy for conduction; and, after a deformation, the dislocations are distributed in the slip planes of the work-hardened crystal. It would appear that only those dislocations that are close enough together to form a well-connected path through the crystal can contribute to the low-frequency conductivity measurements on large crystals. Isolated dislocations are short segments of high-conductivity material imbedded in the normal crystal, so that their contribution to the low-frequency conductivity is small.

If the low-frequency conductivity increase is due to dislocations that are close enough together to form a fairly well connected path through the crystal, the model proposed by Mott^{14,26} for a work-hardened crystal can be employed to give a more detailed picture of the conductivity increase and the recovery after deformation. In this model dislocations are produced dynamically at Frank-Read sources in groups of n , where n may be as high as 1000. After moving some average distance, L , the dislocations become piled up at obstacles in the slip planes. L is on the order of 10^{-2} cm in metals. If N Frank-Read sources per unit volume have each produced n dislocations that move an average distance, L , the strain is

$$\epsilon = NnL^2b, \quad (6)$$

where b is the Burgers vector. The obstacles that stop the dislocations may be sessile dislocations that are formed by slip on intersecting slip systems.

In the crystals deformed in this experiment the deformation has been on more than one slip system, so that there would be the necessary obstacles for such

a model. The model predicts a parabolic law for work hardening, which is the type of work hardening that was observed in this experiment.

After the deformation there are groups of n dislocations piled up at obstacles throughout the crystal. These may form a network which provides high-conductivity paths throughout the specimen. Immediately after deformation all the dislocations are piled up so that they will all contribute to the conductivity. We may then write the conductivity increase as

$$\Delta\sigma \propto Nn. \quad (7)$$

From Eq. (6) and Eq. (7) it can be seen that if L is constant the conductivity will increase linearly with strain,

$$\Delta\sigma \propto \epsilon, \quad (8)$$

which is the relationship that is observed experimentally, for small strains, as is shown in Fig. 4.

As soon as the piled-up groups are formed, dislocations will begin to escape by climbing from the slip planes and moving to regions of the crystal where they are relatively isolated, eventually perhaps leading to a polygonization. Such escaping dislocations are lost to the low-frequency conductivity process. The rate of escape of piled-up dislocations from a group can be written as

$$dn/dt = -\nu \exp(-W/kT), \quad (9)$$

where ν is a frequency, and W is the activation energy for climb. Mott suggests that W is of the form

$$W = W_0 - \gamma sb^3n, \quad (10)$$

where W_0 is the activation energy for climb of a free dislocation, b is the interatomic distance, s is the yield stress, and γ is a constant of the order unity. The reasoning here is essentially that the work expended in moving a jog one atomic distance is the force on the jog, snb^2 , times the distance it moves, b .²⁷ If the load remains on the specimen, s is constant and

$$dn/dt = -\nu \exp\{-(W_0 - \gamma sb^3n)/kT\}. \quad (11)$$

This can be integrated to give

$$n = n_0 - (1/\beta) \log(t/t_0 + 1), \quad (12)$$

where n_0 is the initial number of dislocations in a piled-up group, and

$$\beta = \gamma sb^3/kT, \quad (13)$$

$$t_0 = (1/\beta\nu) \exp(W_0/kT - n_0\beta). \quad (14)$$

The experimental quantity plotted in Fig. 13 is a normalized conductivity increase, $(\Delta\sigma/\Delta\sigma_0) \times 100$. Since $\Delta\sigma$ is proportional to n , Eq. (12) can be written as

$$(\Delta\sigma/\Delta\sigma_0) \times 100 = 100 - (100/n_0\beta) \log(t/t_0 + 1). \quad (15)$$

This expression is the same equation that was used to fit the data for recovery in Fig. 13, and it is seen that

²⁶ N. F. Mott, Phil. Mag. 44, 742 (1953).

²⁷ See reference 21, p. 188.

$100/n_0\beta = 9.1$, when $s = 4 \times 10^7$ dynes/cm², $T = 303^\circ\text{K}$, and $b = 2.88 \times 10^{-8}$ cm. If one takes $\gamma = 1$, the number of dislocations initially present in a piled-up group can be calculated to give $n_0 = 480$. This value is in agreement with estimates of up to 1000 for this number in metals.

The calculation of recovery rate when the deforming load is removed is not as straightforward as the above calculation for the recovery of conductivity during transient creep. The reason is that during recovery with the load off the yield stress, s , changes, and it may be a function of n ; so Eq. (11) does not integrate to give the observed type of recovery equation. This is the same difficulty that arises in the calculation of recovery of yield stress with this model.²⁶

The activation energy for climb of a free dislocation can be calculated, using $t_0 = 1.13$ hr (Fig. 13), and $n_0 = 480$. We follow Mott in taking $\nu = 10^{12}$ sec⁻¹, and calculate from Eq. (14) that $W_0 = 26\,300$ cal/mole. This value of W_0 can be used to calculate the activation energy for recovery of the crystals for which data is presented in Fig. 11. The applied load was 110 kg/cm² and we may take s to be the maximum resolved shear stress of 55 kc/cm². Equation (10) indicates that

$$W = W_0 - \gamma s b^2 n_0 = 17\,100 \text{ cal/mole}, \quad (16)$$

which is in agreement with the observed activation energy for recovery of $18\,500 \pm 1500$ cal/mole. Equation (10) indicates that the activation energy for recovery is a function of s and n , so that it should change during recovery. The change of activation energy with recovery was not observed in the data presented in Fig. 11, but the experimental work has not been extensive enough to settle this point. It would appear that such a dependence of activation energy on recovery must be investigated quite carefully.²²⁻²⁵

The activation energy for climb of a free dislocation, W_0 , should be the activation energy for self-diffusion.²⁸ In AgBr this would be the activation energy for self-diffusion of bromine, which is the slower of the two ions. At high temperatures the work of Christy²⁹ on creep in AgBr indicates that the activation energy for diffusion of bromine is on the order of 60 000 cal/mole. The calculations of Dienes³⁰ for alkali halides suggest that the bromine vacancies in AgBr may be transported as vacancy pairs formed with silver vacancies. The mobility of such a pair would be on the order of the mobility of a single silver vacancy. It is also probable

that some of the transport of the bromine is along dislocations with a low activation energy. If the activation energy for diffusion of silver ions is as low as 4600 cal/mole in the disordered regions, as compared with 18 450 cal/mole in a normal crystal, it is not unreasonable to suppose that the energy for diffusion of bromine ions in such disordered regions can be 26 300 cal/mole as compared with 60 000 cal/mole in the normal crystal. The present interpretation of the experiment indicates that the activation energy for diffusion of bromine in a deformed single crystal of AgBr is on the order of 26 300 cal/mole.

VI. CONCLUSIONS

Plastic deformation of AgBr produces a conductivity increase, at and below room temperature, that varies linearly with strain for small strains, has a low activation energy, exhibits dispersion, and recovers slowly. An anisotropy in the conductivity increase indicates that it is greater parallel to the slip planes than perpendicular to them. The conductivity increase is due to the creation of regions of disorder in the crystal. The activation energy for conduction in the disordered regions is less than 4600 cal/mole, compared with 18 450 cal/mole for the intrinsic conductivity. The regions of disorder appear to be groups of dislocations that are piled-up in the slip planes of the work-hardened crystal. The indefinite and variable activation energy, and the dispersion are consequences of the inhomogeneous nature of the disordered regions. If the conductivity increase is proportional to the number of piled-up dislocations, Mott's model of a work-hardened crystal leads to a linear strain-conductivity relation, and to the proper time-dependence for recovery of conductivity during transient creep. The interpretation of the recovery on the basis of this model indicates that the activation energy for diffusion of bromine in deformed crystals of AgBr at low temperatures is on the order of 26 000 cal/mole.

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²⁸ N. F. Mott, Proc. Phys. Soc. (London) **B64**, 729 (1951).

²⁹ R. W. Christy, Acta Metallurgica **2**, 284 (1954).

³⁰ G. J. Dienes, J. Chem. Phys. **16**, 620 (1948).