

Influence of Plastic Flow on the Electrical and Photographic Properties of the Alkali Halide Crystals

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The influence of plastic flow on the ionic conductivity and darkenability of the alkali halides is discussed on the basis of the assumption that vacant lattice sites are generated during lattice flow and condense to form clusters during a subsequent period of time. These assumptions appear to lead to a reasonable interpretation of the available experiments on the changes in properties of the alkali halides which accompany plastic flow. The bleaching action of plastic flow on colored crystals is also discussed, although the mechanism appears to be much less apparent in this case.

I. INTRODUCTION

IN the decade or so around 1930, there were carried out in continental Europe a number of experiments on the influence of plastic flow on the electrical conductivity and darkenability of the alkali halide crystals. This work, which centered in part about a controversy between Smekal¹ and Joffe² on the importance of imperfections in determining the properties of ionic crystals, takes on particular new meaning at the present time since it provides a close link between the properties of dislocations, positive- and negative-ion vacancies and color centers. These imperfections are finally beginning to be understood in a definite manner. It has been emphasized by a number of investigators³ in recent years that the behavior of atomic or ionic imperfections in solids should be conditioned by the presence of dislocations. The alkali halides appear to offer a new and somewhat spectacular example. The basic experimental facts and related interpretation seem to be as follows.

1. The Enhancement of Ionic Conductivity

The ionic conductivity of sodium chloride can be increased by a factor of 100 or so as a result of plastic flow with stresses above the yield point. This effect was observed initially by Gyulai and Hartly⁴ at 38°C. It was first questioned by Joffe,² who believed that it was the result of a type of piezoelectric effect. However, it was then confirmed by Stepanow,⁵ one of Joffe's co-workers, who observed the effect in a temperature range from 30° to 170°C. The conductivity immediately after plastic flow produced by stresses in the vicinity of 10⁸ dynes/cm² at 38°C rises from about 10⁻¹⁶ ohm⁻¹ cm⁻¹ to at least 10⁻¹⁴ ohm⁻¹ cm⁻¹. This additional conductivity gradually decreases with time and becomes negligible at the end of an hour or so. Stress below the

yield point does not produce a further rise of the same type, although Quittner⁶ has apparently found a transient effect for stresses as low as 1.5×10⁶ dynes/cm² that vanishes when the load is removed. Gyulai⁷ has observed far larger effects when pellets of sodium chloride powder are pressed under hydrostatic load. Such pellets show a conductivity as high as 7.4×10⁻⁷ ohm⁻¹ cm⁻¹ at 111°C after pressing. It seems likely that only a fraction of this increase in conductivity can be a volume effect; a large portion must originate in migration on surfaces or grain boundaries. The conductivity then drops with time and has been followed for a number of hours, at the end of which period it had reached a value of 1.6×10⁻¹⁰ ohm⁻¹ cm⁻¹. The normal value of the ionic conductivity of single crystals at this temperature is about 10⁻¹⁴ ohm⁻¹ cm⁻¹. Recrystallization also has the effect of increasing the conductivity by a large factor.

Most of the specimens of sodium chloride employed in the experiments described above probably had of the order of one part per million of divalent impurity atoms, which have positive-ion vacancies associated with them. Recent work of Etzel and Maurer⁸ shows that the heat of combination of the positive-ion vacancy and a divalent impurity is of the order of 0.3 ev in KCl, and presumably in NaCl, so that the vacancies spend an appreciable fraction of their time free at room temperature and contribute to the conductivity. It follows that the rise in ionic conductivity found by Gyulai and Hartly and by Stepanow in single crystals near room temperature arises from a density of about 10¹⁸ per cc of positive-ion vacancies which are produced during plastic flow. If we assume that the density of dislocation lines increases from about 10⁹ to 10¹¹ per cm² during the plastic flow, this corresponds to the production of at least one vacancy per atomic length of each line in the

¹ A. Smekal, *Zeits. f. Physik* **55**, 289 (1929); **93**, 166 (1934); *Physik. Zeits.* **33**, 204 (1932).

² A. Joffe, *Zeits. f. Physik* **62**, 730 (1936).

³ A. H. Cottrell, *Conference on the Strength of Solids* (The Physical Society, London, 1948), p. 30; J. R. Haynes and W. Shockley, *Conference on the Strength of Solids* (The Physical Society, London, 1948), p. 151; J. S. Koehler and F. Seitz, *J. App. Mech.* **14**, 217 (1947).

⁴ Z. Gyulai and D. Hartley, *Zeits. f. Physik* **51**, 378 (1928).

⁵ A. W. Stepanow, *Zeits. f. Physik* **81**, 560 (1933).

⁶ F. Quittner, *Zeits. f. Physik* **68**, 796 (1931); **56**, 597 (1929); **74**, 344 (1932); O. Beran and Quittner, *Zeits. f. Physik* **64**, 760 (1930).

⁷ Z. Gyulai, *Zeits. f. Physik* **78**, 630 (1932); **96**, 210 (1935); Z. Gyulai and J. Boros, *Zeits. f. Physik* **96**, 355 (1935); Z. Gyulai and P. Tomka, *Zeits. f. Physik* **96**, 350 (1935).

⁸ H. Etzel and R. J. Maurer (to be published). See also, C. Wagner and P. Hantelmann, *J. Chem. Phys.* **18**, 72 (1950); H. Kelting and H. Witts, *Zeits. f. Physik* **126**, 697 (1949).

final state. One need not look far to understand how the vacancies may be produced. Figure 1, which shows the cross-sectional pattern of an edge dislocation in an alkali halide, provides an explanation. The slip plane in the alkali halides appears⁹ to be the (110) plane and the slip direction is apparently $(\bar{1}\bar{1}0)$. Figures 1(a) and 1(b) represent cases in which the "extra" plane associated with the edge dislocation extends to two different heights in the vertical direction, the dotted lines correspond to the slip plane in the two instances. The dislocation line extends normal to the diagram. Neighboring planes possess the same pattern with the signs of the charges reversed. Suppose the pattern (a) is maintained for a number of rows and then changes abruptly to (b) so that planes (a) and (b) face one another at the point at which the slip plane jogs. The positive-ion a in Fig. 1(b) will then face the "incipient" halogen ion vacancy \square in Fig. 1(a). The jog will move one atomic spacing in opposite directions along the dislocation line if the positive ion a is replaced by a vacancy or if the incipient vacancy \square is replaced by a halogen ion. These are diffusion processes which allow¹⁰ the projection of the dislocation pattern in the plane normal to the displacement vector to alter.

Figure 1 shows the ease with which vacancies can be generated or absorbed at an edge dislocation in one of the alkali halides, so that that the surface of the crystal or large cracks are not needed, as Nabarro¹¹ has emphasized. It is not difficult to imagine that vacancies evaporate from jogs of the type shown in the figure if the dislocation is set in motion and if local heating occurs as the results of dissipation of energy by the dis-

location. The experiments of Taylor and Quinney¹² show that over 90 percent of the energy expended in plastic flow reappears as heat during flow. We may expect the heat generated to appear in the vicinity of the dislocations where it will be in the best possible state to evaporate dislocations from jogs of the type considered here.

It is also possible that the vacancies are generated as the result of collisions of dislocations. For example, two Taylor dislocations of opposite sign which are moving in opposite directions in neighboring slip planes and meet will produce either a row of vacancies or a row of interstitial atoms depending, respectively, upon whether the "extra" planes associated with the two dislocations are separated by one atomic spacing or overlap by this distance. Vacancies (or interstitial atoms) can be generated in this way by dislocations which are not purely of the Taylor type, provided they have at least a component of Taylor character, that is, are not pure Burgers dislocations.

It should be remarked that Stepanow⁵ appreciated the fact that the heat evolved during plastic flow could play a role of the type described here; however the theories of dislocations and of vacancies had not yet evolved so that these concepts were not available to implement Stepanow's intuitive ideas.

Since processes such as sintering and recrystallization probably involve the motion of dislocations and diffusion of vacancies, we may expect them to be accompanied by an augmentation of ionic conductivity, just as in the simple case described here. In fact, the experiments of Gyulai⁷ with pressed pellets show that the

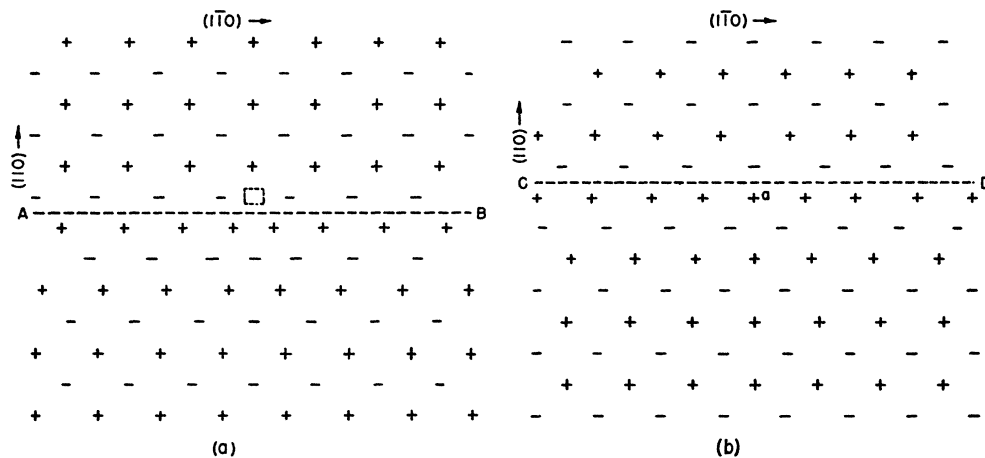


FIG. 1. Cross section through a Taylor dislocation in an alkali halide crystal at a point where the dislocation jogs from one slip plane to a neighboring plane. The slip plane is normal to the (110) direction and the slip direction is $(\bar{1}\bar{1}0)$. Figures (a) and (b) represent (100) planes which face one another at the position of the jog, so that the slip plane moves upward from the dotted line AB to CD. Planes beyond those shown in (a) and (b), along the continuous parts of the dislocation, resemble (a) and (b) although the sign of the charges alternate in neighboring planes. The incipient halogen-ion vacancy \square in Fig. (a) faces the positive ion a in Fig. (b).

⁹ E. Schmid and W. Boas, *Kristallplastizität* (Verlag. Julius Springer, Berlin, 1936).

¹⁰ See, for example, F. Seitz, "Review of the plastic properties of single crystals" (Conference on Plastic Deformation of Crystalline Solids, Pittsburgh, 1950).

¹¹ F. R. N. Nabarro, Conference on the Strength of Solids (The Physical Society, London, 1948), p. 75.

¹² G. I. Taylor and H. Quinney, Proc. Roy. Soc. 143, 307 (1934); 163, 157 (1937).

effects may be relatively enormous in the case of finely divided materials which contain relatively vast quantities of dislocations.

It is to be expected that vacancies can be generated in the same way in metals, however it would be far more difficult to detect their influence in the same, relatively unambiguous, manner. It is possible that the changes in density which accompany the production of vacancies could be detected, although there are at least two difficulties in evaluating such results quantitatively. First, the generation of new dislocations which accompany plastic flow should bring about density changes; second, it is possible, as mentioned above, that interstitial atoms as well as vacancies are produced so that the net change in density is smaller than if the vacancies alone were produced. The density changes associated with the generation of new dislocations could possibly be separated from those associated with the production of vacancies and interstitial atoms by annealing the specimens after cold working in such a way as to remove the vacancies without decreasing the additional hardening associated with the generation of new dislocations.

The vacancies produced during plastic flow will eventually recombine with one another to form clusters so that they will become immobile and cease contributing appreciably to the ionic conductivity.¹³ The first stable cluster of this type is probably a pair of vacancies having opposite signs, although these may have a sufficiently small dissociation energy that they have only a transient existence. Pairs of this type may play a very important role, however, in transporting negative ion vacancies to regions where larger and more stable clusters are formed.¹³ The positive-ion vacancy in sodium and potassium chloride probably^{8,13} has a jump frequency in the neighborhood of 10 sec.^{-1} at room temperature, whereas the free negative-ion vacancy has a value only about 10^{-5} as large, so that free negative-ion vacancies would not aggregate appreciably in 20 min. without assistance. On the other hand, pairs of vacancies probably have jump frequencies comparable to those for positive-ion vacancies¹⁴ and could cause appreciable coagulation in a time of the order of 20 min. The clusters formed would probably dissolve in a long period of time and be precipitated in more stable form at dislocations. However, this process may take far longer periods of time than those required to form the first stable clusters, such as neutral quartets or octets. Clusters of this type could dissolve rapidly during plastic flow as a result of the thermal action of dislocations which pass nearby.

It may be remarked here that the fact that dislocations can act as sources or sinks for vacancies makes it

¹³ This topic has been discussed by the writer, *Rev. Mod. Phys.* **18**, 384 (1936); see also, N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, London, 1940). See also Estermann, Leivo and Stern, *Phys. Rev.* **75**, 627 (1949).

¹⁴ G. J. Dienes, *J. Chem. Phys.* **16**, 620 (1948).

unnecessary to assume that vacancies originate at the surface of the crystal in cases in which densities above 10^{18} per cc are produced by electron bombardment or x-ray irradiation, as the writer assumed in reference 13. However, it apparently is still necessary to assume that the positive-negative pair can diffuse at least as fast as a positive-ion vacancy to explain such things as the rapid coagulation of *F*-centers when the crystal is irradiated with light in the *F*-band (see Section II below).

II. THE ENHANCEMENT OF DARKENABILITY

The extent to which crystals of the alkali halides may be darkened by x-rays, or cathode rays, or ultraviolet light, lying in the long wave-length tail of the fundamental absorption band, is strongly dependent upon the mechanical history¹⁵ of the specimen as well as upon other factors such as thermal treatment and impurity content. This fact appears to have been appreciated first by Przibram.¹⁵ Exposure to these radiations produces *F*-centers, which are now presumed¹³ with almost complete certainty to be halogen-ion vacancies to which electrons are bound, and *V*-centers which are believed to be positive-ion vacancies to which positive holes are bound. There is good evidence to suggest¹⁶ that the *V*-centers observed at room temperature consist of a closely bound pair of positive-ion vacancies to which one or two holes are attached.

A certain amount of plastic flow increases markedly the amount by which the crystal may be darkened although very large amounts to flow seem to lead to an eventual decrease. The long wave-length tail of the fundamental absorption band is broadened as a result of plastic flow. The enhancement of the darkenability for ultraviolet light lying in this range is undoubtedly connected with this effect. It may be remarked that Smakula¹⁵ has found that the quantum yield for darkening appears to be very close to unity during the early stages of darkening by ultraviolet light, although the yield eventually decreases. Photo-conductivity¹⁷ is not observed during such darkening if visible light is excluded.

The influence of plastic flow on the darkenability can probably be ascribed to the large density of clusters of positive- and negative-ion vacancies which are formed during plastic flow, as discussed in Section I. The x-rays and cathode rays produce free electrons and holes and these undoubtedly have a solvent action on the clusters, as described elsewhere by the writer,¹³ so that *F*- and *V*-centers are formed. These particles undoubtedly can also have a solvent action on the lines of incipient

¹⁵ See for example, K. Przibram, *Zeits. f. Physik* **41**, 833 (1927); **68**, 403 (1931) and many other papers by the same author; A. Smekal, *Zeits. f. Physik* **55**, 289 (1929); *Zeits. Ver. deut. Ing.* **72**, 667 (1928); E. Rexer, *Physik. Zeits.* **33**, 202 (1932); *Zeits. f. Physik* **75**, 777 (1932); A. Smakula, *Zeits. f. Physik* **59**, 603 (1929); **63**, 762 (1930).

¹⁶ F. Seitz, *Phys. Rev.* **79**, 529 (1950). E. Burstein and J. J. Oberly, *Phys. Rev.* **79**, 903 (1950).

¹⁷ R. Hilsch and R. W. Pohl, *Zeits. f. Physik* **68**, 721 (1931).

vacancies along the edge of a dislocation. It requires as much energy to free these vacancies as to generate vacancies by transferring ions from the interior to the surface of the crystal. As a result, we might expect the "solvent action" of electrons and holes on the incipient vacancies at dislocations to be somewhat weaker than the action on the vacancies in small clusters, which are less stable. This view is in general agreement with the fact that it is relatively difficult to darken a well-annealed crystal for the first time, although it darkens more easily either after plastic flow or after it has been darkened and bleached without a prolonged annealing process at elevated temperatures.

In this connection it should be remarked that Harten¹⁸ has recently described the results of darkening well-annealed single crystals of KCl with 60 kv x-rays and has found the following interesting facts, which duplicate almost exactly observations made on similar crystals by Estermann and Stern¹⁹ with electron bombardment.

(a) Darkening is much more difficult at low temperatures than at temperatures near room temperature or above. For example, the energy required to produce an *F*-center rises from 100 ev near room temperature to 2000 ev near liquid air temperatures. This indicates that a thermal step is required in the production of color centers. This step is presumably the freeing of incipient vacancies from dislocations, or from clusters of vacancies near dislocations.

(b) The saturation darkening that may be achieved at low temperatures is much higher than at room temperature or above. This implies that the equilibrium darkening is determined by a balance between a forward and a reverse reaction, and that the latter decreases more rapidly than the former at lower temperatures.

(c) The darkenability of specimens which have been darkened and then bleached by the action of light and heat is not the same as that of virgin specimens, being markedly greater. This implies that the vacancies freed during the initial darkening are less tightly bound after bleaching.

The manner in which ultraviolet light lying in the tail of the fundamental absorption band produces *F*-centers (and presumably *V*-centers) is somewhat more obscure, since excitons, rather than free electrons and holes are formed. A possible explanation is as follows.

The ultraviolet light produces excitons which are trapped at clusters of vacancies if the light lies in the central portions of the fundamental band, or it produces trapped excitons directly in the vicinity of the cluster if the wave-length lies in the tail of the band. We may expect the width of the forbidden region of the energy spectrum to be altered in the vicinity of the clusters of vacancies so that excitons, which must remain in the vicinity of the cluster, can be formed with less energy

there than in the center of the perfect crystal. The trapped exciton is probably metastable since irradiation in the fundamental absorption band does not appear to produce luminescent light.²⁰ We may assume that the electron becomes localized near a halogen-ion vacancy and the hole near a positive-ion vacancy. It is not easy to guess exactly what occurs next in the formation of *F*-centers and *V*-centers. It is possible that the positive-ion vacancy which has captured the hole wanders away immediately after the capture. This wandering would be aided by two factors. First, the negative charge of the vacancy would be neutralized by the hole so that it would not be so tightly bound, and, second, the thermal wave which is generated during readjustment of the nuclear coordinates to their new equilibrium positions may provide sufficient energy to supply the activation energy required. It is possible that once the positive-ion vacancy to which a hole is attached becomes free of the cluster it may wander about with an appreciable jump frequency carrying the hole with it. In fact, the experiments of Pringsheim²¹ and his co-workers on the properties of alkali halides which are irradiated at low temperature suggest that this is the case and that single positive-ion vacancies with holes attached form normal *V*-centers at room temperature by a migration process of this kind.

The halogen-ion vacancy to which an electron is attached may also move somewhat away from the cluster, although we can be certain that it will not move very far, for *F*-centers are very stable at room temperature when light is excluded.¹³

The beautiful experiments of Apker and Taft²² show almost conclusively that excitons formed by irradiation in the center of the fundamental absorption band of KI and RbI produce *F*-centers which act as the source of photoelectrons when the crystals are irradiated with light in the fundamental band or with longer wavelengths. Radiation lying in the center of the fundamental band is so strongly absorbed that only a very low surface density of *F*-centers is formed (*ca.* 10¹³ per cm²). Although this represents a volume density near 10¹⁹ centers per cc, it is insufficient to detect by direct means; however, their observations fit in so well with other known facts that the over-all implications of their work appear to be unmistakable. It seems likely that

²⁰ F. Seitz, *Trans. Faraday Soc.* **35**, 74 (1939); see also A. von Hippel, *Zeits. f. Physik* **101**, 680 (1936).

²¹ Casler, Pringsheim and Yuster, *Argonne Quarterly Reports* (1949); *J. Chem. Phys.* **18**, 887 (1950). The writer is deeply indebted to these investigators for extensive discussions of their work. They have proposed that the *V*-band observed in the near ultraviolet in KCl when crystals are irradiated at liquid air temperature be termed the *V*₁-band and that the bands which are observed farther in the ultraviolet be termed *V*₂ and *V*₃. *V*₁, which is shown in Fig. 3 of the paper by these investigators, and which bleaches when the crystal is warmed above liquid air temperatures, is presumably formed by combination of an isolated positive-ion vacancy and a hole.

²² L. Apker and E. Taft, *Phys. Rev.* (to be published). I am deeply indebted to these investigators for advance copies of their paper and a detailed discussion of their work.

¹⁸ H. Harten, *Zeits. f. Physik* **126**, 619 (1949).

¹⁹ I. Estermann and O. Stern, *Reports under Contract OEMsr-900*, Division 14, NDRC.

clusters of vacancies or dislocations provide the agency for forming F -centers in these cases, as well as in those in which grosser darkening is obtained. There is a chance that the excitons produced in these cases decompose into trapped electrons plus free holes or into trapped holes plus free electrons, in the vicinity of the cluster, for sufficient energy is available; however, the effect of irradiation in the long wave-length part of the fundamental band shows that this assumption is not necessary.

It should be added that Alexander and Schneider²³ have suggested that a free hole possesses a very low mobility and will not contribute an observable component to conductivity. If this assumption is correct, it is possible to conclude that free holes (and bound electrons) may be produced by irradiation in the fundamental band either directly or by disintegration of excitons. This assumption does not appear to be essential for providing an explanation of the darkening of crystals by light absorbed in the fundamental band if it is assumed that a trapped exciton is metastable.

Plastic flow should have an influence on the speed with which the alkali halides can be darkened by the addition of a stoichiometric excess of the alkali metal from the vapor, in the manner employed by Pohl²⁴ and his co-workers (additive coloring). This process depends on the migration of electrons from the surface of the crystal to the interior where they join negative-ion vacancies, and, presumably the migration of positive-ion vacancies to the surface to compensate for the electronic charge. Pick²⁵ has found that the addition of divalent impurities greatly increases the rate of darkening, presumably because the density of mobile positive-ion vacancies is increased. Since plastic flow increases the density of both types of vacancies, we might expect it to have a similar if not even more pronounced effect in the case of very pure crystals.

III. BLEACHING EFFECT

Smekal¹⁵ and Schroeder²⁶ have found that crystals of the alkali halides which have been darkened by x-rays

²³ J. Alexander and E. E. Schneider, *Nature* **164**, 653 (1949).

²⁴ R. W. Pohl, *Physik. Zeits.* **39**, 36 (1938).

²⁵ H. Pick, *Ann. d. Physik* **35**, 73 (1939); G. Heiland and H. Kelting, *Zeits. f. Physik* **126**, 689 (1949).

²⁶ H. J. Schroeder, *Zeits. f. Physik* **76**, 608 (1932).

in such a manner as to produce F - and V -centers undergo appreciable bleaching in the F -band when the crystals are deformed plastically. The influence of plastic flow on the V -band has not been examined. In the case of the F -band, Schroeder quotes cases in which the darkening was reduced by about 20 percent as a result of the application of uniaxial stresses of $4 \cdot 10^6$ dynes/cm² which is near the yield point, although stresses about ten times larger are usually needed. The amount of bleaching is critically dependent upon the history and purity of the specimen, being greatest for pure synthetic crystals.

The simplest explanation to offer of the bleaching effect of cold work is to assume that the region about the vacancies associated with the color centers become heated when a dislocation passes very close and that the electrons or holes evaporate and have an opportunity to recombine. The vacancies involved probably lie very close to dislocations, since the clusters from which they were formed were undoubtedly energetically more stable there. Thus the color centers produced in this way should be in an ideal position to experience the thermal effects which accompany the motion of dislocations. It is also possible that the color centers are induced to migrate without losing their electrons or holes and that recombination occurs in the bound state. It has also been suggested by Dr. F. C. Frank that the density of vacancies becomes sufficiently high in the vicinity of the dislocations immediately after plastic flow that the electron holes are able to wander about by tunnelling from vacancy to vacancy until they come sufficiently close to combine.

It is a pleasure to acknowledge the stimulation derived from discussion of this subject at the Pittsburgh Symposium on Plastic Deformation of Crystalline Solids (May 19 and 20, 1950) and to thank the participants for critical comments.

Note added in proof: Professor R. W. Pohl and Dr. H. Pick have kindly informed the writer that the specimens of natural crystal employed in the work of Gyulai and Hartly may have been very pure, containing only of the order of one part in ten million of divalent impurity. In this event, the rise of 100 or more in ionic conductivity during cold-work near room temperature, may imply the generation of 10^{17} mobile vacancies per cc and not the value 10^{18} estimated in part I. This lower value seems more consistent with the energy expended in cold work.