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INTERACTIONS OF POINT DEFECTS WITH DISLOCATIONS AND SURFACES IN SILVER HALIDE CRYSTALS (*)

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Résumé. — Deux aspects d'interactions de défauts sont discutés dans AgCl et AgBr. 1) L'établissement d'un équilibre entre les crans chargés (sur les surfaces et dislocations) et les défauts ponctuels produit des charges superficielles, régions de charge d'espace, et des variations locales dans le potentiel électrique et la concentration de défaut. La localisation et l'environnement des crans jouent un rôle important dans la détermination de la nature de la charge d'espace. Dans les halogénures d'argent, l'impact de ces effets sur les processus photographiques est discuté. Les informations actuelles sur les charges d'espace aux surfaces et dislocations sont décrites ; alors que la production d'un Ag⁺ interstitiel nécessite moins d'énergie qu'une lacune sur un cran, l'opposé peut être vrai sur une dislocation. 2) Des techniques de frottement interne ont été utilisées pour étudier la liaison entre des solutés et les dislocations. Dans AgCl, l'énergie de liaison est approximativement 0,2 eV. Après une légère perturbation de l'atmosphère de Maxwell autour d'une dislocation, la réorganisation suit une loi en $t^{1/3}$; un modèle simple donne cette dépendance ainsi que la valeur correcte de l'énergie d'activation. Des études semblables dans AgBr cependant ont montré un régime étrange où la constante de vitesse de réorganisation a une énergie d'activation négative. La grandeur de cet effet et le domaine de température dépendent de la concentration en dopant. Il n'existe pas d'explication simple à l'heure actuelle.

Abstract. — Two aspects of defect interactions in AgCl and AgBr are discussed. 1) The establishment of equilibrium between charged jogs (on surfaces and dislocations) and point defects produces surface charges, space charge regions, and local changes in electric potential and defect concentration. The locus and environment of the jogs play a large role in determining the nature of the space charge. For the silver halides, implications of these effects to the photographic process are discussed. The available information on the space charges at surfaces and dislocations in both AgBr and AgCl is surveyed ; it is seen that whereas it is energetically cheaper to produce an interstitial Ag⁺ than a vacancy at a surface jog, the opposite may be true at dislocations. 2) Internal friction techniques have been used to study the binding of solutes to dislocations. In AgCl, the binding energy is approximately 0.2 eV. After a small perturbation of the Maxwell atmosphere around the dislocation, the recovery follows a $t^{1/3}$ law ; a simple model yields this dependence, and also the correct activation energy. Similar studies in AgBr, however, have revealed a strange regime in which the rate constant for recovery has a negative activation energy, the magnitude and temperature range of the effect depending on concentration of dopant. No simple explanation is yet available.

1. Introduction. — The interactions of point defects with dislocations and surfaces are especially interesting in ionic crystals because these lattice imperfections and discontinuities are usually electrically charged. Thus, in addition to the interaction phenomena observed in metallic crystals, one finds for ionic systems such effects as space charges and electric fields near surfaces and dislocations [1], [2], additional ionic conductivity [3] and diffusion [4] in these space charge regions, the development of macroscopic electric potential differences upon inhomogeneous plastic deformation [5]-[8], a transient enhancement of ionic conductivity due to production of point defects by moving dislocations [9], sensitivity of surface hardness to composition of an adjacent ionic solution [10], [11], an effect of surface charge on sublimation [12], and

the influence of dislocation charges on a variety of other physical properties [13].

Of these many phenomena, the present paper discusses the current state of knowledge about only two such effects in crystalline silver chloride and silver bromide : *a*) the equilibrium between point defects and the jogs on dislocations and surfaces, with their accompanying space charges, and *b*) the pinning of dislocations by point defects, as studied by internal friction techniques.

2. Charged surfaces and dislocations. — Electrical charges on line and surface imperfections arise because their jogs can create or annihilate separately each component of the native thermal defect pair [1], [2]. These processes, and their compensating space charge region and local electric field, are discussed by Whitworth in another paper in these proceedings [14].

In the silver halides, the native defect is the cation

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Frenkel pair. The halide lattice can be considered to be virtually immobile and perfect, so that the equilibrium of significance to us is that between the jogs and the defects in the cation lattice — silver vacancies, interstitial silver ions, and divalent cation impurities. For a pure crystal, the potential difference that is established between the surface and the deep interior is given by [15]

$$\varphi_x = \frac{1}{2e} (G'_v - G'_i).$$

Here, G'_v is the free energy required to create a vacancy from a jog, i. e., to remove a silver ion from an interior lattice site to a negatively charged jog, and is given by

$$G'_v = G_v + kT \ln M,$$

where G_v is the free energy required to create the vacancy exclusive of configurational contributions and M is the ratio of the number of positively charged jogs to that of negative jogs; the second term on the right-hand side is only important if the density of jogs is not large compared to the net charge density. Similarly, G'_i , the free energy required to create an interstitial by the removal of an Ag^+ from a positively charged jog to an interstitial site in the interior, is given by

$$G'_i = G_i - kT \ln 2 - kT \ln M.$$

The entropic contribution ($kT \ln 2$) arises because there are two interstitial sites per lattice point.

The importance of G'_v and G'_i is that their difference determines the signs and the magnitudes of the space charge distribution and of φ_x ; moreover, the fractional concentration of the j^{th} defect at a depth x is given by $\exp - \{ [G'_j - q_j \varphi(x)] / kT \}$, where q is the charge on the defect. Thus, if it is easier to create vacancies than interstitial silver ions from the jogs (i. e., $G'_v - G'_i < 0$), then the surface will be positively charged, and the compensating space charge will consist of an excess of vacancies. In such a case, if one adds divalent cation impurity to the crystal, thereby increasing the bulk vacancy concentration, ultimately the charge on the surface or dislocation must go through zero (this is called the isoelectric point) and become negative — the space charge now consists of impurity cations and interstitial Ag^+ . On the other hand, if $G'_v - G'_i > 0$, then the surface is negatively charged, regardless of cation impurity, and there is no isoelectric point; the space charge layer now will always contain an excess of interstitial silver ions.

3. Photographic implications. — It seems most likely that these surface potential phenomena are of great importance in the functioning of the photographic process [6]. It will be seen below that the surface is generally negative, relative to the bulk, by about

0.15 to 0.3 V, this potential difference being accomplished over a depth of the order of 0.1 μm . The average electric field in the space charge region is thus of the order of 2×10^4 V/cm. Since the thickness of a typical grain in a photographic emulsion is only perhaps a few tenths of a micron, it is clear that most of the volume of the grain is in a region of intense field.

This field will, for example, quickly extract from the interior of the grain the photohole produced by the primary photon absorption act, thereby decreasing the probability of recombination. In AgBr , the hole mobility at room temperature is $1 \text{ cm}^2/\text{V/s}$; in a field of 2×10^4 V/cm, the hole will drift across a distance of 0.1 μm in 5×10^{-10} s. By contrast, in the absence of a field, its diffusion time would be $l^2/(kT\mu/e) = 4 \times 10^{-9}$ s, or ten times longer.

This field will also, of course, influence the dynamics of the photoelectron. One reason for the high sensitivity of photographic emulsions is that the majority of surface sites are ineffective as electron traps, so that successive photoelectrons ultimately collect at just one or a few sites — the so-called « sensitivity specks » — thereby increasing the efficiency for production of the latent image. It is likely that it is the negative potential at the surface that prevents all but the deepest surface traps from serving as sites for the formation of atomic silver. In support of this notion, Fatuzzo and Coppo [16] have found that Ag metal and Ag_2S are both at a positive potential when in contact with AgBr ; thus the sulfide sensitivity center and the silver latent image precursor would both provide electrostatic « windows » in the otherwise repulsive surface layer.

Lastly, a negatively charged surface will guarantee an enhanced concentration of interstitial silver ions in the layer just underneath it. This is consistent with the large ionic conductivities found in small grains of AgBr by Brady and Hamilton [17], and is most surely an essential ingredient in the efficient formation of surface latent image from photoelectrons.

4. Jog equilibria. — Although the sum of G'_v and G'_i is required to equal G_r , the free energy of formation of the Frenkel pair in the bulk, the details as to how this total energy is divided into the vacancy and the interstitial components depend on the properties of the jogs themselves, and their ambients. Call G_1 the free energy required to remove a lattice silver ion from the crystal to the vacuum, and G_2 the free energy required to remove an interstitial silver ion from the crystal; $G_1 - G_2 = G_r$. Also, call G_j the free energy required to remove an Ag^+ from a positively charged jog to the vacuum. Then, if we form point defects from such jogs, we must have that :

$$\begin{aligned} G_i &= G_j - G_2, \\ G_v &= G_1 - G_j, \end{aligned}$$

and

$$G_v - G_i = -2G_j + G_1 + G_2.$$

Now, whereas G_1 and G_2 are thermodynamic properties of the crystal, the quantity G_j may well depend on the locus and the surroundings of the jog. Its value for a surface jog is not likely to equal that for a jog on a dislocation. Thus, the quantity $G'_v - G'_i$, which plays the dominant role in determining the space charge properties, may be different — in sign as well as in magnitude — for dislocations and surfaces. Unfortunately, there is as yet no quantitative information about the relative magnitudes of $2G_j$ and $(G_1 + G_2)$.

In addition, G_j probably depends on the orientation of the dislocation or surface. This means that the electric potential difference between the interior and the surface of the crystal depends on the orientation of the surface, and that there must therefore be tangential electric fields wherever the surface abruptly changes orientation; such fields might well affect the chemical and catalytic reactivity of crystal edges.

One would also expect that G_j , and hence the space charge distribution, could be influenced by adsorption of ions or molecules from the surroundings of the crystal. Two other mechanisms whereby an ambient ionic solution can produce or affect a space charge within the crystal are well-known. First, Mott and Grimley [18] have shown that the requirement of uniform electrochemical potential of the silver ions within the system causes an exchange of Ag^+ between crystal and an adjacent solution of a silver salt, the magnitude and direction of the transfer depending on the concentration of silver ion in the aqueous solution. This effect has been studied by measuring the electrical characteristics of a thin silver halide membrane mounted between aqueous solutions of a silver salt [19-21]; there is, however, some disagreement among the several researchers as to the variation of electrical conductivity of the membrane with changing concentration of silver ion in the solution. A second mechanism for producing a space charge within the crystal is the formation of an electric double layer (not necessarily involving Ag^+) just outside the crystal surface: the resulting change in electrostatic potential within the crystal requires a transfer of Ag^+ between crystal and solution [22]. Our effect on G_j of adsorption, however, can take place even when neither of these other two processes are operative. For example, the adsorption from « vacuum » of neutral O_2 at surface jogs could perturb the potential difference between surface and interior by preferentially stabilizing the negatively charged jogs.

One further point of interest is that the steady state charge density on a moving dislocation is not necessarily the same as the equilibrium charge on the stationary dislocation [8]. As an example of

this, the sweeping up of cation vacancies by moving dislocations in NaCl has been convincingly demonstrated by Whitworth, Turner, and Huddart [23], [24].

5. Experimental results on silver bromide. — Although AgBr and AgCl are very much alike in many of their properties, we must here take care to distinguish between them, because the present experimental evidence — if taken literally — suggests a great difference in the two substances in the magnitude, and perhaps also in the sign, of the critical quantity ($G'_v - G'_i$). It will also be seen that there are some conflicts within the presently available data, indicating the need for careful evaluation of possible artifacts. Finally, there is some confusion in the literature between enthalpies (which are what emerge from Arrhenius plots of temperature dependences) and free energies: fortunately, this generally makes no qualitative difference, since for temperatures not far above room temperature the entropic contributions to the G 's are considerably smaller than are the enthalpies.

Of the two substances, AgBr has been studied more intensively, because of its greater photographic import. Most of these experiments have been done by the Kodak group. Some ten years ago, a sequence of ingenious experiments was performed on AgBr photographic grains by Brady and Hamilton [17], [25]. They studied the displacement of the latent image produced by pulsed flashes and synchronously pulsed electric fields. By delaying either the field pulse or the light flash, it was possible to measure the electron lifetime and the ionic relaxation time, respectively. They found that in microcrystals bounded by (111) planes the ionic conductivity is several hundred times greater than expected from bulk crystals of comparable purity. Moreover, this conductivity was decreased if the vacancy concentration was increased by doping with Cd^{++} . These results are thus consistent with a negatively charged surface, compensated by a space charge cloud that consists largely of interstitial silver ions. Comparable experiments on grains bounded by (100) surfaces gave ionic conductivities lower than those for (111) grains by a factor of 4: this is presumably a reflection of the dependence of $G'_v - G'_i$ on surface orientation, and indicates a greater potential difference φ_x for (111) than for (100) in AgBr. (In such thin grains, the potential in the interior actually never does reach φ_x : this situation has recently been analyzed by Tan and Høyen [26]).

A related experiment on sheet crystals of AgBr with approximately (100) surfaces was reported in 1968 by Saunders, Tyler and West [27]. Synchronous light and field pulses were used to drive the photoelectrons toward the rear surface, and the resulting distribution in depth of latent image specks was taken to reflect the ranges of the photoelectrons. For fields less than about 21 kV/cm, most of the

photoelectrons did not reach the rear surface, but were stopped at a distance from it which decreased for greater applied fields.

These results were analyzed by Trautweiler [28] in terms of the effect of the space charge distribution at the rear surface, and on the assumption that the AgBr was sufficiently pure to be intrinsic at room temperature (this assumption is not trivial, since it is not obvious that one can melt down a drop of AgBr into a sheet only 100 μm thick, between two Vycor glass plates, and still maintain an impurity content of only 10^{-7}). Trautweiler's analysis, for this predominantly (100) surface, gave $G_i = 0.32$ eV and $G_v = 0.60$ eV; hence it is easier to make interstitials from the surface jogs than to make vacancies, and the negative surface charge is compensated by a space charge consisting of interstitial silver ions. This, of course, agrees with the results of the experiments on microcrystals by Brady and Hamilton, although the magnitude of the conductivity predicted for microcrystals was somewhat less than observed. Trautweiler also deduced that for the sheet crystals, the Debye thickness of the space charge layer was 0.14 μm , the potential difference between surface and interior was 0.14 V, the maximum field (just under the surface) was about 3×10^4 V/cm, and the charge density on the surface was 2×10^{11} e/cm². One still unexplained feature of the experiment is that the adsorption of various types of dye on the surface — which would be expected to affect the value of G_j — produced no observable effect on the space charge field.

The Kodak group have recently measured the ionic conductivity of thin, epitaxial evaporated films [3], [29], with thicknesses in the range 0.2 μm to 2 μm . For (111) films, the conductance *versus* thickness yields a straight line, but with a positive, non-zero intercept when extrapolated to zero thickness. The value of this intercept is interpreted as the conductance due to the space charge layer, while the slope gives the « bulk » conductivity. This « bulk » conductivity is much larger than the conductivity of a large crystal, presumably because of the very high density, $10^{10}/\text{cm}^2$, of dislocations in the films. The temperature dependences of both conductances are analyzed on the assumption that the material is intrinsic, a premise which is corroborated by the fact that addition of Cd^{++} lowers both contributions. The authors conclude that $G_i' = 0.21$ eV and $G_v' = 0.85$ eV; hence $\varphi_\infty = 0.32$ eV and the space charge layer consists of extra interstitial silver ions. This is consistent with a model of the (111) surface previously proposed by Hamilton and Brady [30].

Also, the conductivities due to the space charge layer agree with data on self-diffusion of Ag^+ in (111) films of AgBr [4]. Although this agreement validates the data from both experiments, it does not necessarily confirm the interpretation.

With (100) films, however, no space charge contri-

bution is observed, although the « bulk » conductivity is here also much greater than for large crystals, and — as in the case of (111) films — has an activation energy only about half that for large crystals. The non-observance of a space charge effect for the (100) films is reconciled with the experiments on (100) sheet crystals, described above [27], by contrasting the relatively perfect surfaces of the evaporated films with the only approximately crystallographic surfaces of the sheet crystals.

There are some uncertainties, however, in the interpretation of the numbers obtained from such an experiment. First, the temperature dependences give only enthalpies, not the G' values which are needed to calculate φ_∞ . Second, in the expression for the concentration of interstitials there is also, as we have seen above, a factor $\exp e\varphi(x)/kT$, where φ itself is a complicated function of temperature; thus, the Arrhenius plot of interstitial concentration versus $1/T$ does not simply yield the enthalpy of formation. It would appear, then, that while these beautiful pioneering experiments are very valuable, a somewhat more detailed analysis may be required in order to extract quantitative information.

There is also some information on defect energetics at AgBr surfaces from electrical studies of the equilibrium between crystals and aqueous solutions of silver salts. Matejec, Meissner and Moisar [22] give an energy level diagram which indicates that the energy of an Ag^+ at a jog on a (100) surface is 0.44 eV above that of a regular lattice site and 0.64 eV below that of an interstitial site. This scheme then says that the formation enthalpy of a vacancy from a (100) surface jog is less than that for an interstitial by 0.2 eV. If, at room temperature, the difference between the entropic terms in G_v' and G_i' is less than 0.2 eV, then these results give $G_v' - G_i' < 0$. This is in conflict with the Kodak work on sheet crystals and films, and would suggest that the negative surface charge on the Kodak specimens arose because the specimens were not intrinsic. On the other hand, the effect of Cd^{++} doping is strong evidence for the Kodak interpretation, and implies either an error in the conclusions of Matejec *et al.* or else a very large entropy contribution.

The effect of the nature of the interface on sub-surface space charge has been illustrated by Fatuzzo and Coppo [16] in a complex series of measurements on triangular-prism-shaped crystals on which a third, biasing electrode was mounted. They concluded that the space charge is positive when the crystal is in contact with an electrolyte such as KBr, but is negative if the surface is coated with a layer of evaporated silver.

Turning now to dislocations, Sonoike [5] studied the voltage peaks produced by longitudinal plastic stress applied to truncated cone-shaped crystals. From the sign of the signal, he concluded that, for pure AgBr, the moving dislocations were positively

charged. By adding Cd^{++} or by decreasing the temperature — either of which makes the material extrinsic — the sign could be reversed. If one can neglect vacancy sweep-up effects for the pure crystals, then these results require that, for dislocations, $G'_v - G'_i < 0$, in contrast to the Kodak results on surfaces. On the other hand, recent measurements of voltage pulses produced by indentation, by Hediger, Junod, and Wullschleger [7], gave negatively charged dislocations. This, of course, could be reconciled with Sonoike's data if their specimens were extrinsic at room temperature (not unlikely, since at room temperature an impurity content of only 10^{-7} is required to shift the specimen into the extrinsic region). If this interpretation is correct, then the specimens of Hediger *et al.* should show an isoelectric point somewhat above room temperature. Unfortunately, the only results reported above room temperature are with nominally uniform plastic compression, for which one cannot correlate the sign of the electrical signal with that of the dislocations.

6. Experimental results on silver chloride. — Baetzold [31] has performed measurements of ionic conductivity on thin films of AgCl, analogous to the work on AgBr described above. The results are qualitatively similar to those obtained for AgCl: the (111) surface is negative, compensated by a space charge of interstitial Ag^+ (deduced from suppression of surface conductance by Cd^{++}), whereas no surface component is seen for (100). Baetzold deduces $G'_i = 0.56$ eV and $G'_v = 0.69$ eV, but the same reservations should apply to these numbers as discussed for AgBr. Also, it was found that in cadmium-doped films, the dopant is distributed uniformly throughout the depth, whereas one might expect [32], [33] a segregation toward the surface by a factor $\exp(e\phi_s/kT) = 16$ at room temperature, using Baetzold's value of $\phi_s = 0.07$ V. One cannot explain this discrepancy in terms of the association of Cd^{++} with vacancies, since for low doping levels the space charge layer should have very few vacancies if it is enriched in interstitials; perhaps this discrepancy simply reflects a lack of resolution in the Auger analysis and sputter etching.

With regard to dislocations in AgCl, Sonoike's [5] data on inhomogeneous deformation of AgCl are similar to those from AgBr: positively charged dislocations in intrinsic material and negatively charged in extrinsic. McGowan [6], [34] obtained similar results, but also determined the dependence of the isoelectric temperature on concentration of divalent cation, c . Since in this case, the vacancy appears to be the dominant defect in the space charge for intrinsic material, the relation between c and the isoelectric temperature is: $c = \exp(-G'_i/kT_{iso})$. The plot of $\ln c$ versus $1/T_{iso}$ gave the formation enthalpy of the vacancy to be 0.63 ± 0.1 eV and the formation entropy to be approximately $8 k$.

In a companion experiment, Kim and Fukai [6], [34] studied the dependence on solute concentration of a peak in internal friction versus temperature. This peak occurs near McGowan's isoelectric temperature (it is actually at a somewhat higher temperature, presumably because of elastic interaction between the dislocation and solute), and is believed to arise because of a decreased hysteresis experienced by the oscillating dislocation when there is no space charge cloud. When appropriate corrections were made for solute-vacancy association, the plot of $\ln c$ versus $1/T_{iso}$ gave a vacancy formation energy of 0.55 ± 0.1 eV. The difference between this value and that obtained by McGowan may reflect a difference between moving and virtually stationary dislocations, but both values agree within their experimental errors. Taking an average, we obtain a vacancy formation enthalpy of 0.59 eV. Also, subtracting this from the Frenkel formation energy of 1.47 eV [35], one obtains the formation energy of the interstitial from a dislocation jog to be 0.88 eV.

If one compares these various results, it would appear that, in intrinsic material, the sign of the space charge surrounding a dislocation is opposite that of the positive space charge under a (111) surface (on the other hand, in cation-doped extrinsic AgCl, both dislocation and surface would, of course, be negative, with a positive space charge). In conflict with this, however, the Kodak interpretation of the excess « bulk » conductivity in the films presumes that the dislocation space charge consists of interstitials. This question is not yet resolved.

7. Dislocation pinning. — The binding of dislocations by point defects in AgCl has been studied by internal friction techniques at 35 kHz by Kim and Fukai [36]. Using the Granato-Lücke theory [37] to analyze the dependence of damping on strain amplitude, an estimate of the density of pinning points was obtained; from the temperature dependence of this density, a point defect-dislocation binding energy of 0.2 eV was calculated. Further, the temperature dependence of the low-amplitude decrement (for which the damping varies as the fourth power of the loop length, L) gave a binding energy of 0.15 eV. These pins are probably either solute ions or solute-vacancy complexes. They are thus bound to the dislocations with an energy of approximately 0.2 eV.

More detailed experiments were performed on the decay of the low-amplitude decrement after prolonged oscillation at high strain amplitudes of very pure AgCl (better than 10^{-6}). At high amplitudes, the dislocations are torn from their pins, which are then free to redistribute themselves: at low amplitudes, however, the stress is too small to tear dislocations free, and the decrement gradually decays as the pins return. The Granato-Lücke L^4 law was found to be valid, and the arrival of pins to the dislocation was found to follow a $t^{1.3}$ law.

A simple, first-order model was proposed in which the pins are in equilibrium with a Maxwell atmosphere about the dislocation. Oscillation at high strain amplitudes converts the dislocation from a line source of elastic distortion to an effective strip source, and the $-1/r$ potential is assumed to be replaced by one of the form $(1+x)(-1/r)$, where x is assumed to be small compared to unity (and does indeed turn out to be small). Under this slightly perturbed potential, the solute concentration in the atmosphere, $n(r)$ changes to $n(r) + \Delta n(r)$. After turning off the perturbing high-amplitude oscillation, the subsequent decay of the damping is associated with the flow of this $\Delta n(r)$. Following the Cottrell-Bilby philosophy [38], and calculating only the drift component of the flux, one obtains the experimentally observed $t^{1/3}$ law. Moreover, the rate constant for the decay is found to vary as D/T^4 , where D is the diffusivity of the solute ion pin. Inserting experimental values for the rate constant at various temperatures, one obtains an activation energy for D of 0.42 eV. This

value agrees with activation energies of typical divalent solutes in extrinsic AgCl, and also with the activation energy previously reported by Kabler and Miller [39] for the strain aging of AgCl crystals.

These experiments have recently been extended to AgBr by Huff [40], who also studied the decay in doped as well as pure crystals. Huff finds the same $t^{1/3}$ law to hold in AgBr, but in doped crystals the temperature dependence of the rate constant is very strange: it shows a region of negative effective activation energy. This anomalous effect is more pronounced, and sets in at a lower temperature, the greater the concentration of dopant (cadmium). Since the extrinsic-intrinsic transition temperature, as well as any possible dislocation isoelectric temperature, must both increase with increasing concentration of dopant, there does not seem to be an obvious explanation for these observations. It could possibly involve an activated precipitation of dopant at special sites on the dislocation [41], but this suggestion is only speculation at present.

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