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## Ionic space charge and dissolution of AgCl (\*)

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**Résumé.** — Si l'on dissout, dans un solvant très faible (10 % aqueux NaCl), un cristal recuit d'AgCl, dopé avec plusieurs parties par million d'un cation divalent ( $\text{Cd}^{2+}$  ou  $\text{Mn}^{2+}$ ) et gardé dans une lumière jaune de sûreté, on trouve que pendant la première minute, environ 150 à 250 Å est enlevé. Des dissolutions subséquentes en solutions fraîches, cependant, n'enlèvent que des quantités beaucoup plus petites (souvent par un facteur de 4). Le vieillissement du cristal à la température ambiante du jour au lendemain, soit en air soit en azote sec, restitue le comportement original. Encore une fois, une quantité de 200 Å est dissoute rapidement ; après cela la vitesse décroît considérablement. On propose que la région qui se dissout rapidement est la même que celle de la charge ionique d'espace, qui compense la charge négative de la surface. En accord avec ce modèle sont ces faits : (a) le vieillissement à la température de l'azote liquide ne restitue pas la dissolution rapide initiale ; (b) l'effet est plus petit pour les cristaux non dopés (contenant  $\sim 1$  ppm de cation divalent) ; et (c) la portée de diffusion de l'impureté pendant une période de l'ordre de 20 h à la température ambiante, est du même ordre de grandeur que l'épaisseur de la région de la charge d'espace. En plus, la lumière actinique, qui produit des photoélectrons libres, rehausse la vitesse de dissolution dans un solvant faible.

**Abstract.** — If an annealed crystal of AgCl, doped with a few parts per million of divalent cation ( $\text{Cd}^{2+}$  or  $\text{Mn}^{2+}$ ) and kept under yellow safelight, is dissolved in a very weak solvent (10 % aqueous NaCl), it is found that during the first minute some 150 to 250 Å is removed. Subsequent etchings in fresh solutions, however, remove only much smaller (often by a factor of 4) amounts. Ageing the crystal overnight at room temperature, in either air or dry nitrogen, restores the original behaviour : once again, the first 200 Å is rapidly dissolved, after which the rate drops considerably. It is proposed that the rapidly dissolving region is that of the ionic space charge, which compensates the negative surface charge. Consistent with this model are the facts that : (a) ageing at liquid nitrogen temperature does not restore the rapid initial dissolution ; (b) the effect is much smaller for undoped crystals (containing  $\sim 1$  ppm divalent cation) ; (c) the diffusion range of the divalent solute during a period of the order of 20 hrs. at room temperature is of the same magnitude as the thickness of the space charge region. Also of interest is the observation that actinic light, which produces free photoelectrons, enhances the rate of dissolution in a weak solvent.

**1. Introduction.** — In ionic crystals, the native point defects always occur in pairs ; e.g., the Frenkel defect pair which is predominant in the silver halides. In general, the free energies required to create individually the two components of such a pair, from a source such as jogs on the crystal surface, are not equal to one another. This results in the accumulation of a net ionic charge on the surface, compensated by a space charge distributed over a depth beneath the surface of the order of several hundreds of angströms. This space charge is comprised of an excess of point defects and impurity ions of a particular electrical sign. At equilibrium, the magnitude of the resulting potential difference between the interior of the crystal and the surface equals  $(1/2 e)$  times the difference between the formation free energies of the two component point defects.

It is known that in the case of AgCl and AgBr, the surface ordinarily carries a negative charge, and the potential difference between it and the interior is about 0.1 to 0.3 V [1-4]. Depending on the purity of the crystal, the space charge consists of excess interstitial silver ions and uncompensated divalent solute ions. In experiments preliminary to a mapping of this space charge region, we have observed a new effect — a substantial variation with depth in the rate of dissolution of an aged crystal which is immersed in a very weak solvent. It is suggested that this effect is an additional manifestation of the formation of the ionic space charge.

**2. Experimental.** — Etching studies have been made on six crystals of AgCl : two nominally pure (with about 1 ppm divalent cation), two doped with  $\text{Cd}^{2+}$  (8 and 35 ppm), and two doped with  $\text{Mn}^{2+}$  (7 and 10 ppm). All crystals were grown by Mr. Charles B. Childs, in this laboratory. They were sawn into the form of rectangular parallelepipeds, with edge dimen-

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sions ranging from 0.5 to 2 cm. They were then polished, etched, and annealed to remove residual strains.

A total of several dozen series of etches were performed on these specimens. In a particular series, an annealed crystal was etched successively for one minute in each of five to eight identical fresh baths of a very weak solvent, all at room temperature. We have found that, depending on the value of room temperature, 10 to 13% (by weight) NaCl serves as a suitable weak solvent. For comparison with the case of a larger free energy of dissolution, several series of etches were also made in 30% NaCl, a somewhat stronger solvent for AgCl.

The thickness of the layer removed by each individual etch was determined from the loss in weight of the specimen. After each etch of the series, the crystal was rinsed in pure water (but saturated with AgCl and also containing a small amount of detergent), dried by draining onto a soft absorbent tissue and then exposing to a stream of warm air, allowed to come to room temperature, and weighed on a semi-micro balance. Gloves were used to prevent contamination of the surface with grease and care was taken to minimize deformation of the surfaces of the crystals during handling. All etchings were performed under yellow safelight, except when it was desired to explore the effect of ionizing light (blue to the near UV, in the case of AgCl). After a series of etches was completed, the crystal was aged at room temperature (in the dark) for about 20 hrs, or more. A new series was then carried out.

**3. Results.** — Our most recent data are shown in figure 1. These consist of the results of twenty series of etches, five series on each of four crystals of various purities. The scatter in the results (i.e., the range of data points for a particular etch number in a set of five series) is entirely accounted for in terms of

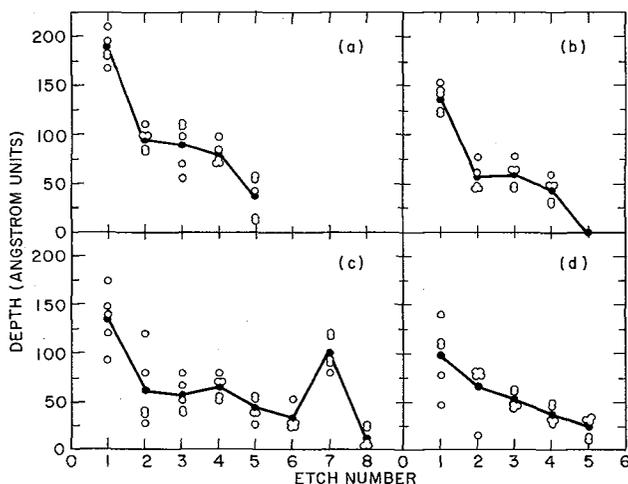


Fig. 1. — Thickness removed in successive etches, five series on each crystal. The average value for each etch number is shown by the filled circle and the solid line. For (a) the etchant was 13% NaCl; for (b)-(c) it was 10% NaCl. Dopant: (a) 10 ppm Mn<sup>2+</sup>; (b) 7 ppm Mn<sup>2+</sup>; (c) 35 ppm Cd<sup>2+</sup>; (d) undoped, 1.5 ppm.

random weighing errors: an error of 0.02 mg gives a 25 Å error in the calculated thickness. Hence, for each etch number for a given crystal, it is reasonable to take the average of the five recorded values; the solid lines in the figure are drawn through these averages.

For the doped crystals, it is apparent that the depth removed by the first one-minute etch, some 150-200 Å, is much larger than that dissolved during the following etches, often by a factor of 3 to 4. This behaviour was almost invariably observed in all of the many series of etches which were performed. (It is not clear what significance is to be attached to the peak in etch rate which occurs at etch no. 7 for the most heavily doped specimen (35 ppm Cd); this is discussed further below.) The most striking aspect of these results is that the 20-hr ageing at room temperature, that took place between the end of the final etch in one series and the beginning of the next series, invariably restored the crystal surface region to its original state, in which the first 200 Å is somehow different from the remainder.

Experiments were also made on the possible role of the ambient atmosphere during the ageing, by substituting dry nitrogen for room air. The same effect was found for either atmosphere, implying that the ageing does not involve a chemical reaction (dry nitrogen should be inert to AgCl). A preliminary test of the effect of the temperature was made by ageing the crystal near liquid nitrogen temperature instead of room temperature. In this case, no restoration of the effect occurred, indicating that the process is thermally activated.

In contrast to the behaviour of doped crystals, the effect is much weaker in the case of the nominally pure specimen of figure 1d. Experiments on another undoped crystal showed even smaller differences between the dissolution rate of the surface region and the interior. The effect thus appears to be related to the presence in the crystal of divalent impurity ion.

Several series of etches were also performed with a somewhat stronger solvent, 30% NaCl solution. In these runs, the dissolution rates were not only considerably greater, but also there was no obvious difference between the initial and subsequent etch rates; apparently, the surface effect is only observable when the free energy of dissolution is quite small.

It was also observed that if crystals were etched in ordinary room light (which contains some blue and near ultraviolet, and hence can produce photoelectrons in the AgCl), the etch rates were greater than under the safelight. Although this was not investigated further, it seems reasonable that a sluggish dissolution process could indeed be accelerated by the excitation and ionization that results from absorption of short-wavelength light.

**4. Discussion.** — The main characteristics of the effect discussed in this paper seem to be: (a) for doped

AgCl crystals at equilibrium there exists a layer, extending about 200 Å below the surface, which dissolves more rapidly than does the bulk; (b) this differentiation is only visible if the solvent is very weak; (c) after dissolution, the 200 Å layer is restored upon ageing at room temperature for about 20 hours; (d) the restoration process is thermally activated and does not involve a chemical reaction of the crystal with the atmosphere; (e) the effect depends on the presence of charged impurity ions.

It seems reasonable to attribute the rapidly dissolving near-surface layer to the presence of the excess of uncompensated divalent cation in the space charge region. The depth of this space charge region is known to be of the order of hundreds of angström units, consistent with the thickness of the layer. Within this region, the equilibrium concentration of dopant is expected to be enhanced because of the negative potential created by the surface charge. For example, at a typical surface potential of  $-0.2$  V, the equilibrium concentration of  $\text{Cd}^{2+}$  or  $\text{Mn}^{2+}$  would be enhanced by a factor of  $\exp(0.2 e/kT)$ , or  $\sim 2500$  at room temperature. The rapid dissolution may well result from the establishment of a potential difference between the crystal and solvent, once the charged surface has been removed. In undoped crystals, on the other hand, the space charge consists almost entirely of interstitial silver ions, which are so mobile that they can follow the dissolution, preventing formation of a crystal-solvent potential difference.

One test of this model would be to compare the

kinetics of the restoration of the surface effect with the diffusivity of the dopant. We do not have detailed kinetics data, and the solute diffusivity is expected to depend on distance and time in a complicated manner, because the vacancy concentration is suppressed non-uniformly in the space charge region. Nevertheless, we can make a rough estimate of the consistency of the model. Extrapolating to room temperature Batra's determinations of the diffusivity of the  $\text{M}^{2+}$ -vacancy complex [5], one finds  $D$ 's of the order of  $10^{-14}$  to  $10^{-15}$   $\text{cm}^2/\text{s}$ . In the space charge region, however, the suppression of the concentration of cation vacancies will greatly lower the diffusivity, by dissociation of the complex. If we take this suppression factor to be about 100, then after 20 hrs.,  $(Dt)^{1/2}$  is found to be about 100 to 300 Å, in agreement with the observed layer thickness.

As for the peak at etch no. 7 in the case of the most heavily doped crystal, figure 1c, this may be a result of a depletion of dopant from the region just underneath the space charge layer. When the dissolution front reaches this depth, once again a potential difference (although of opposite sign) is established between crystal and solvent; this could conceivably also stimulate the dissolution. Clearly, more investigation would be required to be more definitive.

**Acknowledgment.** — The authors are grateful to Mr. Charles Childs for preparing the crystals used in this work.

## DISCUSSION

*Question.* — P. W. M. JACOBS.

It seems that curve (c) for  $\text{Cd}^{2+}$ -doped AgCl falls off more steeply than curve (a) for  $\text{Mn}^{2+}$ -doped AgCl. Could you please comment on the apparent dependence of the shape of these curves on the nature and concentration of the impurity?

*Reply.* — L. SLIFKIN.

We have not sorted out the detailed effects of variations in dopant concentration, the nature of the dopant (e.g. Mn versus Cd), variations in room temperature, small variations in strength of solvent, etc. The next step, in order to answer the sort of question you pose, will be to use a more sensitive measurement technique for depth removed (e.g., with radioactive  $\text{Ag}^+$  or  $\text{Na}^+$ ).

*Question.* — M. GEORGIEV.

It seems likely that at least one of the dissolution curves shown may reveal some periodic arrangement of the defects beneath the surface. In any event dissolution techniques can undoubtedly be used to study the defect distribution profiles.

*Reply.* — L. SLIFKIN.

The periodicity you refer to, I presume, is the peak shown in figure 1c for etch no. 7. This peak appears to be reproducible. I am sorry that we did not investigate the other crystals to greater etch depths (only the crystal in figure 1c was studied beyond 5 etches per series).

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