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Thermal Depolarization in Ammonium Chloride Crystals. II. Effect of Hydrochloric Acid and Ammonia

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1. Introduction

In this paper we present the results of a study of the thermal depolarization of NH_4Cl crystals which had been exposed to dry NH_3 gas or dry HCl gas. These experiments complement those described in Part I (*1*) which dealt mainly with the effects of doping and of polarization temperature on the subsequent thermal depolarization (TD). There have, to our knowledge, been no previous published investigations of the effect of HCl on TD in NH_4Cl. Kessler and co-workers (*2, 3*) have observed four TD bands in the depolarization spectrum of NH_4Cl; these occur at (1) 185, (2) 215, (4) 290, and (5) 330K. The first three of these are also observed in thermally stimulated polarization (TSP) experiments. In the terminology adopted by Kessler's group, (3) refers to the spontaneous polarization associated with the phase transition at 242.5K. Our investigations of TD in NH_4Cl recorded in Part I were confined to the disordered CsCl phase at temperatures above the phase transition and we observed three TD bands in which the maximum depolarization currents occurred at a (mean) temperature T_m of (I) 278, (II) 292, and (III) 318K, respectively. Bands II and III we believe to be the same as those designated 4 and 5 by Kessler (*2, 3*). We also recorded a fourth depolarization band, IV, that peaked at 350K; this we ascribed to space charge rather than to dipole-related polarization. Kessler and Ebert (*3*) observed that their band 1 increased considerably, while bands 2 and 4 decreased or even disappeared under exposure to NH_3. These effects were reversed by thorough degassing of the crystal. Only band 5 was unaffected by NH_3. Since our observations of the effects of HCl and NH_3 were again confined to temperatures above the phase transition, the only overlap between our work and that of the Kessler group (*2, 3*) refers to the effect of NH_3 on bands 4 and 5. Moreover, their paper (*3*) described the effect of NH_3 only on undoped NH_4Cl, whereas the present work includes experiments on six different kinds of NH_4Cl crystals.

2. Experimental

The necessary experimental details on the preparation of the crystals and the depolarization experiments are given in Part I (*1*) or in references cited therein. See especially Table I of Ref. (*1*), which summarizes the preparation of the crystals and defines

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the nomenclature used to describe the crystals. Particular care was taken to ensure that the crystals were thoroughly dried by degassing and then heating in helium gas, as in a depolarization experiment, and that the gases introduced were dried by condensing them in a cold trap, such that the partial pressures of $NH_3(g)$ and HCl(g) were 26 and 57 Torr, respectively.

3. Results

3.1. *Effect of NH_3*

Figure 1 shows the effect of NH_3 on the TD of an NH_4Cl crystal (V) grown from the vapor. Prior to exposure to NH_3 the TD spectrum (□) shows the usual three bands, I, II, and III, with II the most prominent. After exposure to NH_3 for 15 hr, flushing out the NH_3, replacing it by He, and allowing the crystal to equilibrate in He for 3 hr, the TD spectrum (△) shows that I and II have increased considerably. What happens to III is not very clear-cut: probably it is not much changed, the apparent slight increase in depolarization current being due to an increased amount of space charge. The rather symmetrical appearance of this TD curve (△) and the flat region near 315–330K indicate the presence of other bands which we judge to be the band III initially present together with newly introduced space charge. Polarization at 250K followed by removal of most of the first two bands in a preliminary heating ("peak cleaning") reveals the presence of band III, still mixed with II, and the space charge band IV. (Compare Fig. 2 of Ref. (*1*).) Notice that the "divide by 10" against the third curve (+) means that the currents read from the

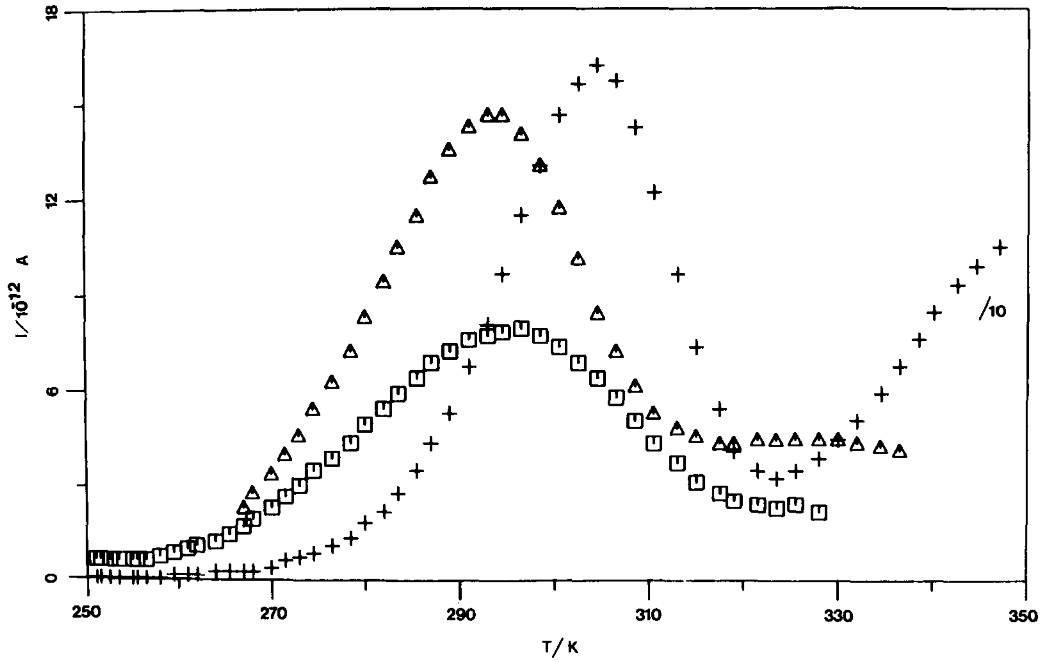

FIG. 1. Thermal depolarization of a crystal of NH_4Cl (V) grown from the vapor after polarization at T_p. $T_p = 292K$: □, before treatment with NH_3; △, after exposure to NH_3 for 15 hr and then equilibrating in He for 3 hr. $T_p = 250K$: +, after peak cleaning to remove bands I and II (/10 against this curve means that the currents read from the I scale are to be *divided* by 10).

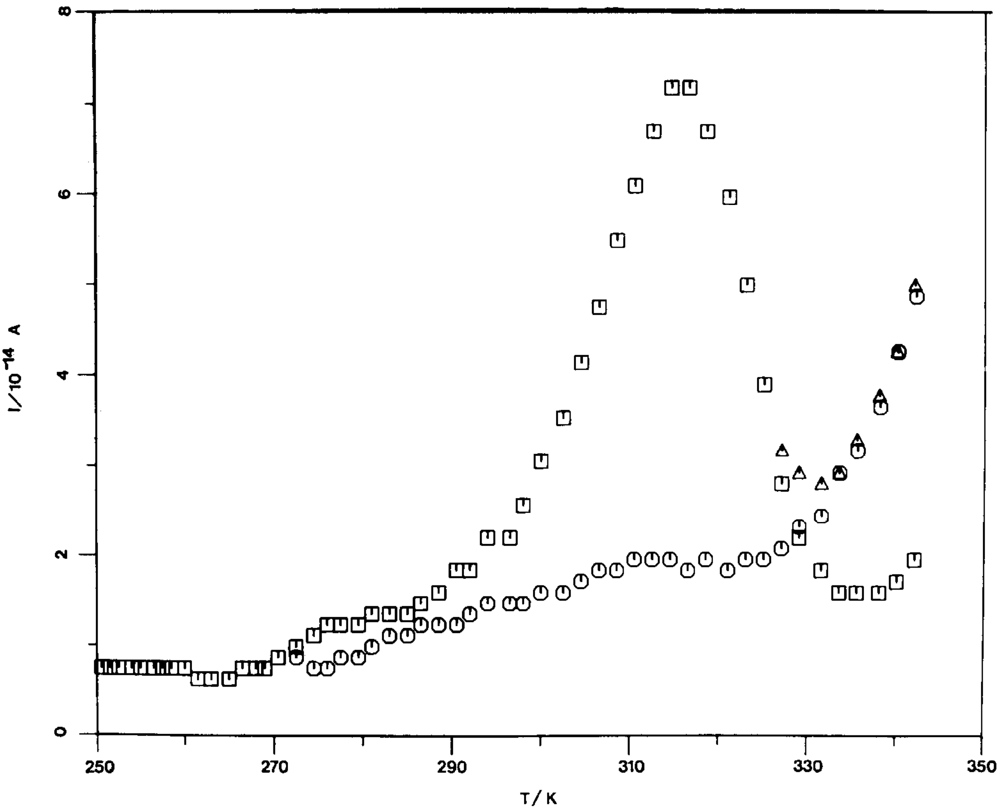

FIG. 2. Thermal depolarization of a crystal of NH$_4$Cl (H) grown from acid solution (pH 5.5). T_p = 292K. □, after 15 min exposure to NH$_3$ (essentially the same as an untreated crystal); ○, after 5½ hr exposure to NH$_3$); △, after 4½ hr in He. (Below 325K the curve marked by △ is the same as that marked by □.)

ordinate for this curve are to be *divided by 10*. The conclusions to be drawn from the data presented in Fig. 1 are (a) that NH$_3$ treatment of an NH$_4$Cl(V) crystal increases the number of centers responsible for the 278-K band I and also the number of centers responsible for band II; and (b) that even after NH$_3$ treatment there exists a small band III, although it is not clear-cut as to whether this has been affected by the NH$_3$.

Figure 2 shows the effect of NH$_3$ on a crystal of pure NH$_4$Cl grown from slightly acid solution. After 15 min exposure to NH$_3$ the TD curve (□), after polarization at 292K, shows one peak, as in the untreated crystal (compare curve *a* of Fig. 3 in Ref. (*1*)). We know that this curve, peaking at 310K, contains mainly band III along with some II, while there is also some space charge polarization, band IV. Exposure to NH$_3$ for a further 5½ hr (○) results in a considerable reduction in III along with an increase in space charge, IV. After removal of the NH$_3$ and 4½ hr in He, band III has recovered completely but the space charge IV introduced by the NH$_3$ remains. (This curve is marked by △ where it differs noticeably from that marked by □; below 325K the curves superimpose.) The conclusions to be drawn from this experiment are that in NH$_4$Cl H crystals the centers responsible for band III are removed rather slowly in NH$_3$ and reform in about the same

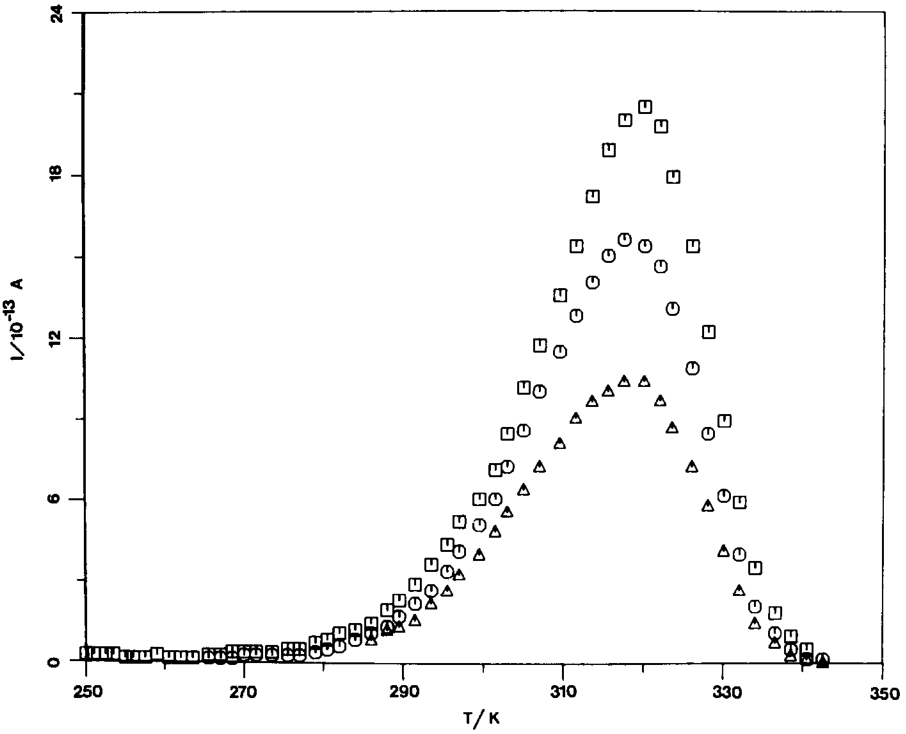

FIG. 3. Thermal depolarization of a crystal of NH_4CL (NH) grown from an acid solution (pH 5.5) containing $NiCl_2$. T_p = 292K. □, before exposure to NH_3; ○, after 3½ hr in NH_3; △, after 6½ hr in He.

time period when the NH_3 atmosphere is replaced by He.

The TD spectrum of NH_4Cl grown from a slightly acid solution containing $NiCl_2$ (crystals NH) shows only band III (□ in Fig. 3). After 3½ hr exposure to NH_3 the band is reduced by 25% (○). The NH_3 was then replaced by He. The next spectrum (△) after 6½ hr shows that the NH_3 already in the crystal continues to diffuse and to remove the centers responsible for III. This experiment yields the same result as NH_3 treatment of H crystals, namely, that NH_3 attacks the III centers, but there seems to be a difference in the response of the two crystals to He gas following NH_3 treatment. Whereas the H crystal recovered its former state, in the Ni^{2+}-doped crystal III centers continued to be removed. This difference may be due to the Ni^{2+} doping or it may be connected in some way with the larger number of III centers present in Ni^{2+}-doped crystal.

Figure 4 shows the TD of a crystal (CH) grown from a slightly acid solution containing CrO_4^{2-} ions. After polarization at 292K such crystals display the three bands, I, II, and III. (Compare the curve marked by □, which refers to the untreated crystal, with Fig. 5a of Ref. (*1*), for example.) Exposure to NH_3 for 3½ hr removes III (see the curve marked by (○) in Fig. 4) and increases the space charge release (IV). After 7 hr in He (△) IV has returned to its original amount and I and II are lower. After 12 hr pumping (+) I and II have recovered completely and III is 60% recovered. This behavior is again slightly different from that of H and NH crystals. In all three types of crystals showing band III, this band is removed by NH_3; in an H crystal it recovered on standing in He, in the CH crystal it recovered only on pumping off the NH_3, while in the NH crystal it continued to decrease on standing in He. These variations may be connected with the type of doping, and hence with the cation and anion vacancy concentrations, or they may be related to the number of III centers present in the three crystals (which also depends on the type of doping).

3.2. *Effect of HCl*

The effect of HCl(g) on the TD of NH_4Cl grown from an alkaline solution containing excess NH_3 (A crystals) is shown in Fig. 5. In such crystals bands I and II are the most prominent. Compare the curve marked by □ in Fig. 5 with Fig. 4a of Ref. (*1*). After 5 hr exposure to HCl (○) bands I and II are reduced and III appears unaltered. After 48 hr in He (△) bands I and II have recovered. (The *apparent* difference between the results of the first and the third experiments can be traced to an approximately constant difference along the low-temperature side of the curves. This could perhaps be traced to a slight increase, of the order of 10%, in the number of I centers but is more likely due to the slowly decaying polarization current that frequently persisted during the cooling of the crystals and was sometimes present even after removing the field.)

Crystals of NH_4Cl grown from alkaline solution containing Ni^{2+} ions also display prominent bands I and II (see □ in Fig. 6). It is a little problematical to decide whether the flat region near 320K is due to a contribution from band III or to the small current referred to above, which is not connected

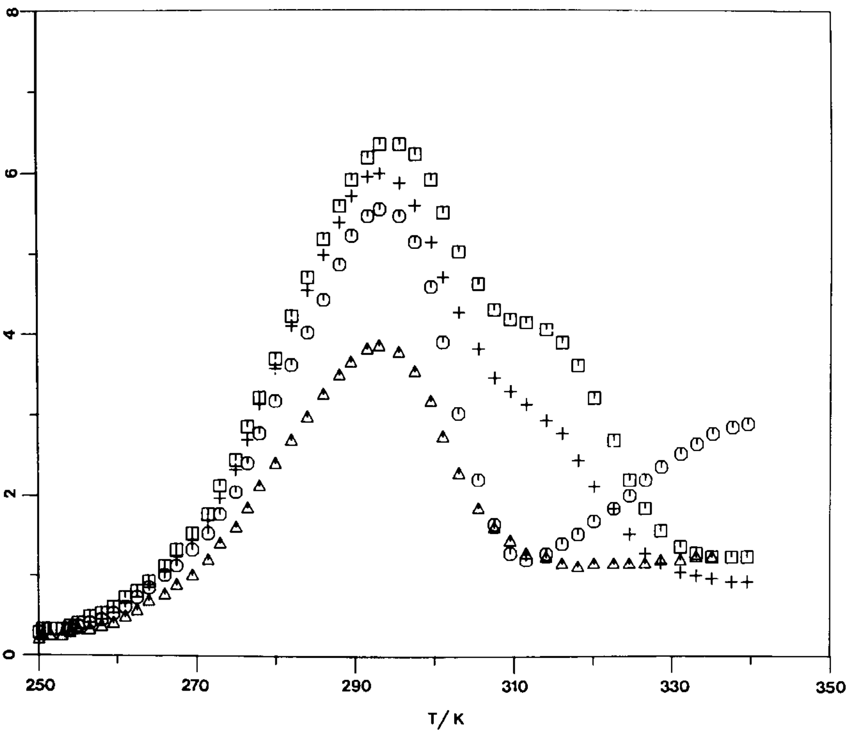

FIG. 4. Thermal depolarization of a crystal of NH_4Cl (CH) grown from acid solution (pH 5.5) containing CrO_4^{2-} ions. T_p = 292K. □, untreated crystal, showing the presence of three bands I (T_m = 278K), II (T_m = 292K), and III (T_m = 318K). ○, after exposure to NH_3 for 3½ hr; △, after 7 hr in He; after 12 hr in vacuum.

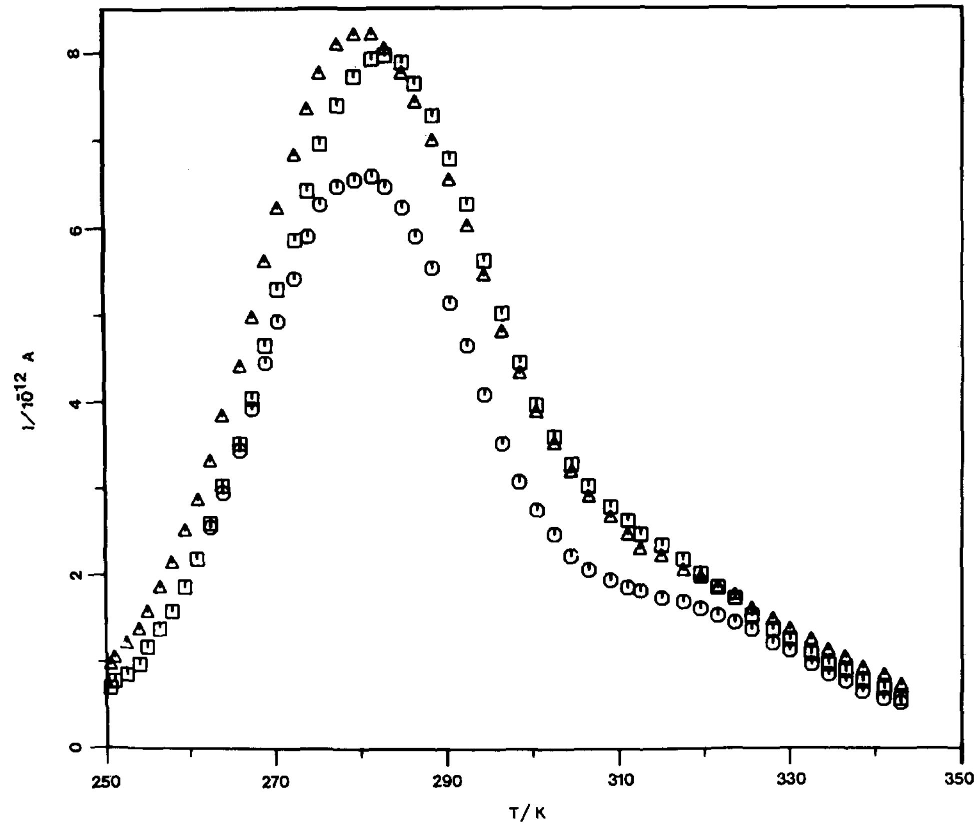

FIG. 5. Thermal depolarization of a crystal of NH_4Cl (A) grown from an alkaline solution (pH 8). T_p = 292K. □, untreated crystal; ○, after exposure to HCl for 5 hr; △, after 48 hr in He.

with the randomization of dipoles, so that the base line for this curve should really be around 0.8×10^{-12} A. The depolarization current would then change sign about 320K; negative space charge currents are, however, not uncommon in these crystals. Exposure to HCl for 5 hr effects a big reduction in bands I and II as shown by the curve marked by (○) (Fig. 6). There is now a small positive space charge current.

4. Discussion

The results obtained in the experiments described in Section 3 may be summarized as follows. (i) Bands I and II increase on exposure to NH_3 (V crystals) and decrease on exposure to HCl (A and NA crystals). On standing in He they recover (A crystals). (ii) Band III decreases on exposure to NH_3 (H, CH, and NH crystals). On pumping it recovers (CH crystals), but the behavior on standing in He after treatment with NH_3 shows some variation: in NH crystals III continued to decrease, whereas in H crystals it recovered.

These results are in keeping with the behavior of the untreated crystals which is reported in Ref. (*1*). There we recorded that bands I are favored in vapor-grown crystals (V) and by alkaline conditions during crystal growth (A, NA). They also occur under acid conditions when CrO_4^{2-} ions are also present. The latter introduce anion vacancies which are good traps for the proton holes—that is, NH_3 molecules replacing

NH_4^+ ions on normal cation sites and therefore designated by $[NH_3]_c$—that are introduced by the presence of NH_3 during crystal growth. Thus we believe that the centers reponsible for the depolarization band II are proton holes trapped at anion vacancies,

$$[NH_3]_c \square_a. \qquad (1)$$

This center is clearly a dipole which can orient either by anion vacancy jumps in the anion sublattice or by proton-hole jumps in the cation sublattice. In the vapor-grown crystals (V) we expect that adsorption of NH_3 and its subsequent diffusion into the crystal will enhance band II, as is indeed observed.

The behavior of band I is hard to characterize. It is smaller than II and is overlapped by II to a considerable extent. Indeed it is only seen clearly after polarization at low temperatures (~250K)—see, for example, Figs. 4 and 5 on Ref. (*1*). Nevertheless, Fig. 1 shows band I increasing on exposure to NH_3. Thus I may be due to the same kind of centers as II but situated near the surface or near dislocations. The lower activation energy for the randomization of I centers and its appearance always along with II are in accord with this hypothesis.

The behavior of bands I and II on exposure to HCl are also just what we expected from the models, for HCl will react with a trapped proton hole to form the normal basis, NH_4^+ and Cl^- ions:

$$[NH_3]_c \square_a + HCl = NH_4^+ \, Cl^-. \qquad (2)$$

The recovery of these centers on pumping off the HCl from the crystal shows that reaction (2) is reversible. The mechanism is undoubtedly similar to that proposed long ago by Herrington and Staveley (*4*) to account for the conductivity of NH_4Cl. Pro-

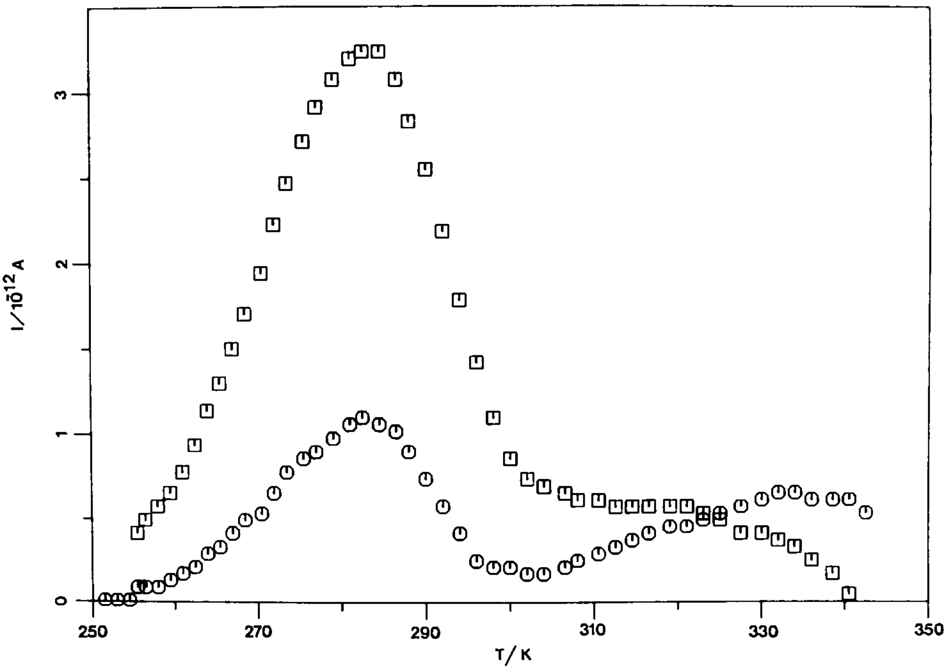

FIG. 6. Thermal depolarization of a crystal of NH_4Cl (NA) grown from an alkaline solution (pH 8) containing Ni^{2+}. T_p = 292 K. □, untreated crystal; ○, after exposure to HCl for 5 hr.

ton transfer from $[NH_4^+]_c$ to $[Cl^-]_a$ forms the molecular defect $[NH_3]_c[HCl]_a$. The $[HCl]_a$ is then mobile in the anion sublattice because of the mobility of the trapped protons,

$$[HCl]_a[Cl^-]_a = [Cl^-]_a[HCl]_a. \qquad (3)$$

At the surface HCl molecules escape, leaving behind anion vacancies, which diffuse into the crystal and eventually trap the mobile proton holes. We know that anion vacancies are mobile in NH_4Cl from the diffusion experiments of Heneisen and Laskar (*5*). Since both the reduction in band II on exposure to HCl and its recovery on pumping are quite slow processes at room temperature, this is a feasible mechanism. Moreover, both processes occur on about the same time scale, suggesting that HCl(g) diffuses down grain boundaries and dislocations as HCl molecules, and then into the crystal as protons in the anion sublattice. Once the protons annihilate the proton holes,

$$[HCl]_a[NH_3]_c\square_a = [Cl^-]_a[NH_4^+]_c\square_a, \qquad (4)$$

the anion vacancies liberated diffuse to dislocations and annihilate the cation vacancies produced when the HCl enters the lattice,

$$HCl(g) = \square_c[HCl]_a. \qquad (5)$$

Equations (4) and (5) thus supply the detailed mechanism of process (2).

The other main experimental result concerns band III. Its decrease on exposure to NH_3 is also consistent with the model proposed in the previous paper (*1*). The presence of band III is favored by acid conditions during crystal growth and by the presence of cation vacancies (from Ni^{2+} impurity, for example). We therefore proposed that the centers responsible for band III consist of protons trapped in the anion sublattice at cation vacancies,

$$\square_c[HCl]_a. \qquad (6)$$

Thus the annihilation of III centers by NH_3 is just the conjugate process to the removal of II centers by HCl. NH_3(g) enters the crystal by diffusing down boundaries and dislocations and is then incorporated in the lattice as proton holes and anion vacancies, $[NH_3]_c$ and $\square_a$. The proton holes diffuse rapidly into the crystal and annihilate III centers by

$$\square_c[HCl]_a[NH_3]_c = \square_c[Cl^-]_a[NH_4^+]_c.$$

The cation vacancies released diffuse away and are annihilated at dislocations by the diffusing anion vacancies that are formed when NH_3 enters the lattice, thus preserving the Schottky equilibrium.

Thus it appears that the models proposed for the three centers responsible for the TD of NH_4Cl above the transition temperature are consistent with the observations recorded in this paper on the effect of NH_3 and HCl on TD in NH_4Cl.

Acknowledgments

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