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# Thermal Depolarization in Ammonium Chloride Crystals, I

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The thermal depolarization of crystals of $NH_4Cl$ polarized above the phase transition temperature (242.5K) by an applied electric field was studied in 13 crystals prepared under a variety of conditions in order to examine the effects of doping with divalent anions or cations and of acid or alkaline conditions during crystal growth. All the features found in crystals grown from solution also occur in a crystal grown from the vapor. We may conclude, therefore, that the depolarization effects observed are properties of crystalline $NH_4Cl$ and are not due to water or urea occluded during crystal growth. Four main depolarizations were observed: one of these is ascribed to space charge and the other three are attributed to dipole relaxation processes. The activation energies for these are 0.58, 0.73, and 0.85 eV, respectively. The various doping experiments lead to the conclusion that one of these is favored by acid conditions and the presence of cation vacancies and the other two by alkaline conditions and the presence of anion vacancies. Specific models for the dipolar defects are formulated and discussed.

## 1. Introduction

Previous studies of thermal depolarization (TD), also called ionic thermoconductivity (ITC), in $NH_4Cl$ have been reported by only one group (*1–4*) and the results (see, e.g., Fig. 1 of Ref. (*4*)) seem to be sufficiently complicated to justify further detailed investigation. Kessler (*2*) first noticed that when a $NH_4Cl$ crystal which had not been previously polarized was allowed to warm up at a constant rate through the phase transition at 242.5K a current was recorded between electrodes attached to opposite faces of the crystal. This current was observed whether the electrodes were in electrical contact with the crystal or insulated from it and is indicative of spontaneous polarization in the low-temperature phase. Sometimes more than one peak was observed and thus was attributed to the existence of domains. Kessler (*2*) also observed a second spontaneous current peak between room temperature and ~350K and attributed this to a flow of cation vacancies into the crystal caused by adsorbed water. Experimentally, the current increased with water vapor pressure and its temperature dependence indicated an activated process with an activation energy $E$ of about 1 eV. In an accompanying paper (*3*) Kessler has recorded four TD peaks between 180 and 350K. Peaks 1 and 2 occur at $T_m$ = 180 and 220K, respectively, and their positions are unaltered by variations in the polarization temperature $T_p$. They were therefore ascribed to dipole orientation processes.

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Peaks 3 and 4 were found to shift linearly with $T_p$ and were considered to be due to charge release associated with macroscopic space charge.

In a brief comment in another paper Kessler (*1*) recorded the appearance of two linear sections in a plot of log($IT$) vs $T^{-1}$, where $I$ is the depolarization current measured on warming previously polarized $NH_4Cl$ crystals doped with $NiCl_2$. These linear sections correspond to first-order depolarization processes with activation energies of 0.39 and 1.15 eV and peak temperatures $T_m \sim 210$ and 320K, respectively. No explanation of the source of these depolarization currents was offered in this paper. In a more detailed paper on defect disorder in $NH_4Cl$, Berteit *et al.* (*4*) state that the peaks labeled 1 and 4 for pure $NH_4Cl$ are enhanced by doping with $NiCl_2$ and they therefore attributed peak 1 to a dipole orientation process associated with $Ni^{2+}$-cation vacancy complexes and peak 4 to the relaxation of space charge formed by the motion of cation vacancies in the applied field. The activation energies associated with the processes responsible for these TD peaks were found to be (1) 0.12, (2) 0.34, (4) 0.70, and (5) 0.83 eV. Peak 3 is associated with the phase transition.

In the above investigations Kessler *et al.* employed melt-grown crystals (*2, 4–6*) or solution-grown crystals either undoped or doped with $CuCl_2$ or $NiCl_2$ (*2*). In the case of solution-grown crystals the pH of the solutions, which is known to affect the electrical conductivity (*7*), is not stated. Because of the unsolved problems associated with the defect disorder and charge transport in $NH_4Cl$ we made detailed investigations of thermal depolarization in $NH_4Cl$ crystals grown from the vapor and from solutions at two different pH values. Crystals doped with $Ni^{2+}$ ions or $CrO_4^{2-}$ were used in an attempt to categorize the effects of cation and anion vacancies. The results of these investigations form the subject of this paper (I). In part II, the effects of exposure to $NH_3$ and HCl are described and the evidence which these experiments provide for the models developed in I is discussed. We confirmed the occurrences of spontaneous charge release at the phase transition but because of the prior discovery of this phenomenon (*2, 8*) the results we shall describe are limited to temperatures above the phase transition temperature, that is, to $NH_4Cl$ in the disordered CsCl structure.

## 2. Experimental

The $NH_4Cl$ used was A.C.S. Certified grade from Fisher Scientific Co. The principal impurities are 20 ppm of $SO_4^{2-}$, 8 ppm of $Ca^{2+} + Mg^{2+}$, 4 ppm of iron and heavy metals, and 1 ppm $PO_4^{3-}$. It was used without further purification. The pH of a saturated solution at 30°C was 5.5. Crystals were grown from seeds suspended in this solution using the method described by Jacobs *et al.* (*9*). In some batches the pH was adjusted to 8 by bubbling $NH_3$ through the solution. These two types of crystals grown from solutions of pH 5.5 or 8 are referred to as "acid-grown" or "alkaline-grown," respectively. Doping was effected by addition of $CrO_4^{2-}$ or $Ni^{2+}$ to the solutions in amounts equal to 0.1 mole% of the $NH_4Cl$. For convenience of reference the various crystals used in this research are listed in Table I along with a summary of their preparation. Urea (10% by weight) was added to ensure the growth of large cubic crystals, from which plates 2 to 3 mm thick were cleaved for the polarization experiments. It has been confirmed from neutron diffraction experiments that there is no substantial incorporation of urea in $NH_4Cl$ grown from such solutions (*10*). The apparatus used for the TD measurements has been described previously (*11*). The applied field was usually $\sim 25$ V mm$^{-1}$ and the heating rate $\sim 0.066$ K sec$^{-1}$. The noise level in the measured current was $3 \times 10^{-15}$ A.

TABLE I

DESIGNATION AND PREPARATION OF CRYSTALS USED IN THERMAL DEPOLARIZATION EXPERIMENTS ON $NH_4Cl$

| Designation | Conditions of crystal growth | No. of such crystals measured |
|---|---|---|
| V | From the vapor | 1 |
| H | From a saturated solution of $NH_4Cl$ at pH 5.5 | 4 |
| A | From a solution of $NH_4Cl$ saturated with $NH_3$ gas (pH 8) | 2 |
| CH | From a solution of $NH_4Cl$ containing 0.1 mole% $CrO_4^{2-}$ at pH 5.5 | 2 |
| NH | From a solution of $NH_4Cl$ containing 0.1 mole% $Ni^{2+}$ at pH 5.5 | 2 |
| NA | From a solution of $NH_4Cl$ containing 0.1 mole% $Ni^{2+}$ and saturated with $NH_3$ gas (pH 8) | 2 |

## 3. Results

### 3.1. *Ammonium Chloride Crystals Grown from the Vapor*

A crystal of $NH_4Cl$ grown from the vapor was kindly given to us by Professor S. Radhakrishna. Figure 1 shows the thermal depolarization spectrum $I(T)$ for this crystal. Notice the very large peak currents, as high as $7.6 \times 10^{-12}$ A at $T_m = 292K$ for curve *a*. In this run the crystal was polarized at $T_p = 268K$. Curves *b, c, d* show the effect of increasing $T_p$ to 280, 291, and 303K, respectively. As $T_p$ increases the peak current increases and a new TD peak emerges at 324K on the high-temperature side of the first peak. This has the effect of an *apparent* shift in $T_m$ for the first peak. Curve *e* shows the result of a peak cleaning experiment. After polarization at 301K most of the low-temperature 292-K peak was removed by heating and the crystal was then recooled and reheated without further polarization. This clearly establishes the high-temperature 324-K peak: the dashed line shows the existence of further depolarization at still higher temperatures (which is also, in fact, evident in *d*).

Unfortunately, from the point of view of a quantitative analysis, neither of these 292- and 327-K peaks represents a single depolarization. Slight shifts in $T_m$ with $T_p$, and a depolarization current that decreases gradually on the high-temperature side, are sure signs of a complex spectrum due to more than one type of center. There are actually four peaks in these spectra as shown by the careful peak cleaning experiment depicted in Fig. 2. Curve *a* shows the depolarization of a crystal polarized at 249K. Curves *b, c, d, e* show four successive runs in which the crystal (repolarized each time at 249K) was depolarized along curve *a* up to the points

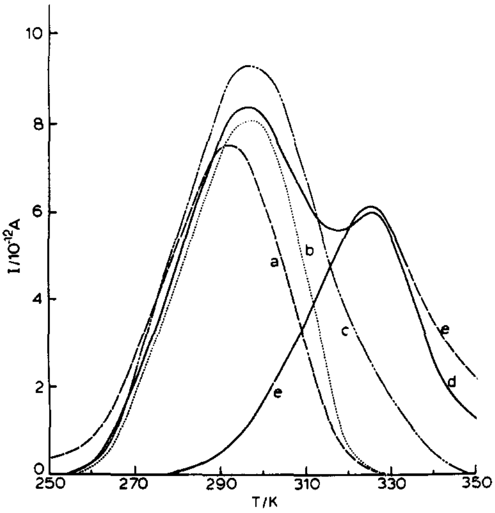

FIG. 1. Thermal depolarization of a crystal of $NH_4Cl$ grown from the vapor after polarization at temperatures $T_p$. (*a*) $T_p = 268K$; (*b*) $T_p = 280K$; (*c*) $T_p = 291K$; (*d*) $T_p = 303K$. Curve (*e*) shows the second depolarization of a crystal polarized at 301K, depolarized up to 298K (not illustrated), recooled to 250K, and reheated without further polarization.

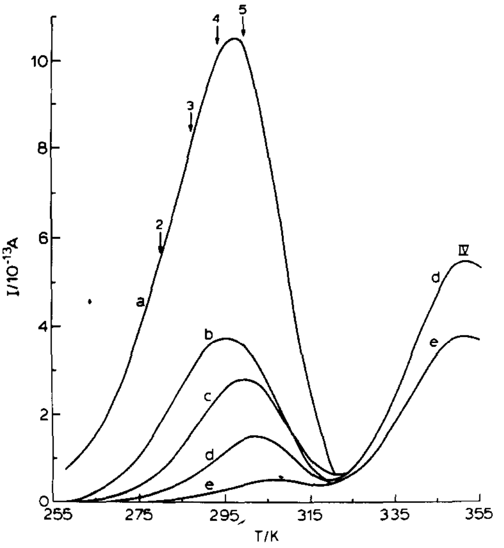

FIG. 2. Thermal depolarization of a crystal of $NH_4Cl$ grown from the vapor after polarization at 249K, curve *a*. Curves *b*, *c*, *d*, and *e* show the depolarization of the same crystal after polarization at 249K, warming along curve *a* to the points marked 2 (280K), 3 (287K), 4 (293K), and 5 (299K), respectively, recooling to 249K without an applied field, and then heating the crystal at the usual constant rate. (Curves *c* and *d* are indistinguishable between 324 and 336K, the upper limit for run *c*).

marked 2, 3, 4, 5, respectively. Removal of the low-temperature peak with $T_m$ at about 275K demonstrates the existence of a second peak with a $T_m$ near 290–295K (Curve *b*). Curves *d* and *e* demonstrate the existence of a weak third peak at around 306K and a fourth peak with $T_m$ near 351K. This is clearly the peak that is responsible for the slow decline of $I(T)$ on the high-temperature side of the third peak (see curve *e* in Fig. 1). It is remarkable that this peak at 351K (marked IV in Fig. 2) shows up at all in a crystal polarized at the low temperature of 249K. One should not expect to orient dipoles in a field at a temperature 100K below the temperature corresponding to their maximum rate of depolarization. We conclude, therefore, that this peak is not due to dipole relaxation but to the decay of space charge induced by the application of the electric field at 249K. By the same argument the third peak, which is only present to a small extent after polarization at 249K, is a dipole relaxation peak; the first and second peaks also exhibit the characteristics of depolarization due to the relaxation of dipoles.

The dipole relaxation parameters for a single peak can be determined by fitting the experimental $I(t)$ curve to the equation

$$I(t) = (Q_0/\tau_0)\exp(-E/kT)$$
$$\exp[(-1/b\tau_0)\int_{T_0}^{T}\exp(-E/kT')dT'], \quad (1)$$

where $Q_0$ is the total charge liberated during depolarization and $b$ is the (linear) heating rate $dT/dt$. The temperature dependence of the relaxation time $\tau$ for the depolarization process is expressed by the Arrhenius equation

$$\tau = \tau_0 \exp(E/kT), \quad (2)$$

where $E$ is the activation energy for the liberation of the stored charge. For a dipole orientation process one expects $\tau_0^{-1}$ to be of the order of magnitude of a lattice vibrational frequency. The fitting of experimental $I(t)$ data was accomplished using a nonlinear least-squares program that yielded the values of $Q_0$, $E$, and $\tau_0$ for each relaxation. A composite curve comprising several peaks can be analyzed using the expression

$$I(t) = \sum_j I_j(t) \quad (3)$$

with each $I_j(t)$ term given by Eq. (1). If the peaks are well separated the nonlinear least-squares fitting of $n$ relaxations works well with $3n$ unknown parameters (*11*), but if the peaks overlap considerably the relaxation parameters are best determined by a judicious combination of variations in $T_p$, peak cleaning, and computer fitting.

### 3.2. *Pure Ammonium Chloride Grown from Acid Solution (pH 5.5)*

Measurements were made on four such crystals and the results presented in Fig. 3 represent typical behavior. Curve *a* shows the depolarization of a crystal which had been polarized at 288.5K. The broad, more or less symmetrical peak suggests that two depolarization mechanisms are involved. This is confirmed by a combination of varying the polarization temperature $T_p$ and peak cleaning. Curve *b* shows the depolarization of a crystal polarized at 268K. The peak in the depolarization current shifts to 292K as a result of the big reduction in the high-temperature peak which is shown clearly in curve *c*. In this run the crystal was polarized at 292K; it was then warmed at the usual linear rate to 296K, recooled to 250K and the usual depolarization experiment then continued without further polarization. The first heating has virtually removed the 292-K peak and the depolarization with a peak current at 315K is clearly displayed. For ease of future reference the depolarization associated with the 292-K peak is designated II and that at 315K is marked III in Fig. 3. The results of several computer analyses of the spectra are given in Table II.

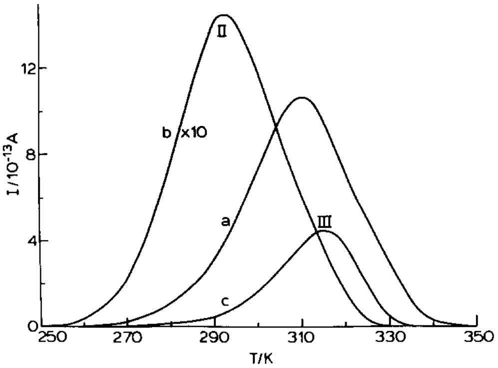

FIG. 3. Thermal depolarization of a crystal of $NH_4Cl$, grown from a solution of pH 5.5, after polarization at temperature $T_p$. (*a*) $T_p$ = 288.5K; (*b*) $T_p$ = 268.5K; (*c*) $T_p$ = 292K, after removal of most of the low-temperature peak by first warming the crystal to 296K. (For curve (*b*) I has been multiplied by 10 to display the 292-K peak adequately.)

### 3.3. *Pure Ammonium Chloride from Ammonia-Saturated Solution of pH 8*

Figure 4 shows the thermal depolarization of an $NH_4Cl$ crystal grown from an aqueous solution that had been saturated with $NH_3$ (pH 8). Comparison of curve *a* ($T_p$ = 291K) with curve *a* of Fig. 3 shows immediately that there is much more depo-

TABLE II

TOTAL CHARGE $Q_0$ AND ACTIVATION PARAMETERS $\tau_0$, $E$ (in Eq. (2)) FOR THE DIELECTRIC RELAXATION PEAKS OBSERVED IN THE THERMAL DEPOLARIZATION OF $NH_4Cl$

| Crystal | Run | $Q_0$ (C) | $\tau_0$ (sec) | $E$ (eV) | $T_m$ (K) |
|---|---|---|---|---|---|
| V | 1-36 | $4.5 \times 10^{-11}$ | $1.1 \times 10^{-8}$ | 0.565 | 278 |
| | | $4.2 \times 10^{-10}$ | $6.3 \times 10^{-11}$ | 0.730 | 295 |
| | 1-36 | $1.4 \times 10^{-10}$ | $6.1 \times 10^{-11}$ | 0.728 | 295 |
| | | $1.1 \times 10^{-10}$ | $1.9 \times 10^{-12}$ | 0.846 | 307 |
| H | 1-7 | $1.5 \times 10^{-11}$ | $9.5 \times 10^{-11}$ | 0.722 | 295 |
| | 2-4 | $6.4 \times 10^{-11}$ | $5.1 \times 10^{-11}$ | 0.722 | 290 |
| | 2-7 | $\left\{ 1.1 \times 10^{-11} \right.$ | $2.5 \times 10^{-11}$ | 0.722 | 285 |
| | | $\left\{ 7.2 \times 10^{-10} \right.$ | $6.9 \times 10^{-13}$ | 0.900 | 316 |
| | 3-2 | $1.5 \times 10^{-10}$ | $1.6 \times 10^{-13}$ | 0.936 | 316 |
| | 4-1 | $8.1 \times 10^{-11}$ | $1.2 \times 10^{-11}$ | 0.751 | 289 |
| A | 2-2 | $\left\{ 1.3 \times 10^{-9} \right.$ | $3.5 \times 10^{-9}$ | 0.592 | 278 |
| | | $\left\{ 5.0 \times 10^{-10} \right.$ | $2.3 \times 10^{-11\,a}$ | 0.755[a] | 296 |
| | 2-5 | $2.4 \times 10^{-10}$ | $2.3 \times 10^{-11}$ | 0.755 | 295 |
| CH | 2-2 | $6.1 \times 10^{-11}$ | $8.9 \times 10^{-12}$ | 0.840 | 320 |
| | 2-1 | $2.0 \times 10^{-10}$ | $2.9 \times 10^{-9}$ | 0.614 | 285[b] |
| NH | 1-18 | $7.9 \times 10^{-10}$ | $4.0 \times 10^{-12}$ | 0.860 | 319 |
| | 1-19 | $6.2 \times 10^{-10}$ | $5.6 \times 10^{-12}$ | 0.848 | 318 |
| | 1-21 | $4.4 \times 10^{-10}$ | $4.3 \times 10^{-11}$ | 0.795 | 319 |
| | 1-11 | $4.2 \times 10^{-10}$ | $2.9 \times 10^{-11}$ | 0.808 | 320 |
| NA | 2-2 | $2.1 \times 10^{-10}$ | $8.9 \times 10^{-9}$ | 0.577 | 279 |
| | 2-5 | $8.1 \times 10^{-11}$ | $9.9 \times 10^{-11}$ | 0.803 | 330 |
| | 1-4 | $1.6 \times 10^{-10}$ | $7.0 \times 10^{-12}$ | 0.815 | 308 |

*Note*. Results bracketed together were obtained from a least-squares analysis assuming the presence of more than one depolarization (Eq. (3)). For the other results, the depolarization was isolated sufficiently by varying $T_p$ and only peak cleaning so that a single relaxation could be assumed to dominate over the temperature range employed.

[a] Parameter fixed during minimization.

[b] Not included in averaging because $T_m$ indicates the presence of a significant amount of peak II.

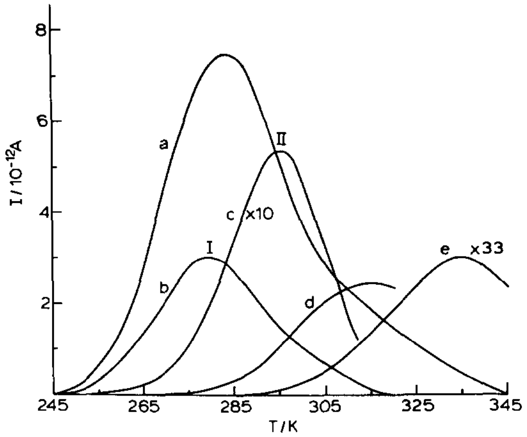

FIG. 4. Thermal depolarization of a crystal of $NH_4Cl$, grown from a solution of pH 8, after polarization at temperature $T_p$. (*a*) $T_p$ = 291K; (*b*) $T_p$ = 249K; (*c*) $T_p$ = 249K, after removal of the low-temperature peak by first warming the crystal to 295K; (*d*) $T_p$ = 291K, after first warming from 250 to 290K, which removes the low-temperature peak (curve *b*); (*e*) the same run as (*d*), after heating to 320.5K and recooling to 250K.

larization at lower temperatures in $NH_4Cl$ crystals grown from a slightly alkaline solution than for the crystals grown from acidic solution (pH 5.5). Two such crystals behaved similarly. Polarization at 249K reduces the high-temperature components relative to the low-temperature one. Curve *b* shows that the maximum depolarization current occurs at ~295K but the long tail on the high-temperature side indicates the presence of small high-temperature components. Notice that the scale of Fig. 4 is ten times larger than that of Fig. 3, so that the peak current for Fig. 4(*a*) is much larger than that for Fig. 3(*b*), for example, and comparable with that for Fig. 1(*c*).

The high-temperature components can be emphasized, but not isolated, by peak cleaning. Polarization at 249K followed by preheating to 295K removes most of the low-temperature peak and shows a depolarization with a clear maximum at 295K. The slow decline in *I* on the high-temperature side shows, however, the presence also of the depolarization previously labeled III. Polarizing at 291K, cooling to 250K with the field on, and then heating to 290K without the field results in a large depolarization (not illustrated) with $I_{max} = 9 \times 10^{-12}$ A at 282K (i.e., similar to curve *a*). Cooling and reheating this crystal yielded curve *d*, which is mainly III, with some residual II. This run was interrupted at 320.5K, and the crystal was recooled and then reheated. The shift in the peak to 335K shows the presence of depolarization at still higher temperatures, which is possibly the same as IV observed in the vapor-grown crystal (see Fig. 2(*d,e*)).

### *3.4. Ammonium Chloride Doped with Chromate Ion Grown from Acid Solution (pH 5.5)*

The thermal depolarization of a $NH_4Cl$; $CrO_4^{2-}$ crystal is shown in Fig. 5. These crystals were a pale golden color showing that $CrO_4^{2-}$ ions had been incorporated into the crystal. Curve *a*, for a crystal polarized at 292K, is double-humped, indicating at least two polarization events. Lowering $T_p$ to 268K (curve *b*) reduces, but does not eliminate, the high-temperature polarization. It is, however, very much reduced (curve *c*) by polarizing at 255.5K. Consideration of these depolarization curves and comparison with those of Fig. 4 leads to the qualitative conclusion that there are three main processes here: the labels I, II, and III on the curves indicate where each dominates, though none of them has been separated clearly in these runs. In addition, space charge release occurs above ~330K (curves *a* and *b*).

Peak cleaning to 303K left a small high-temperature peak (III) with $T_m$ = 319.5K and activation parameters shown in Table II. Curve *c* and a similar run from a second $CrO_4^{2-}$-doped crystal were analyzed as single peaks, but they are not sufficiently pure to yield accurate parameters for peak I,

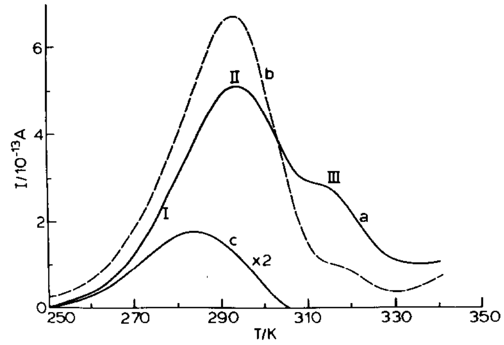

FIG. 5. Thermal depolarization of a crystal of $NH_4Cl$, grown from a solution containing 0.1 mole% of $CrO_4^{2-}$ at pH 5.5, after polarization at temperature $T_p$. (*a*) $T_p$ = 292K; (*b*) $T_p$ = 268K; (*c*) $T_p$ = 255.5K. (For curve (*c*) I has been multiplied by 2 for greater clarity.)

while the contributions from peak II are too weak to support a computer resolution. Nevertheless, the activation parameters are reasonably characteristic of peak I. For the $CrO_4^{2-}$-doped crystals we did not succeed in isolating peak II by a computer resolution of curve *b*, which, however, clearly demonstrates its presence.

### *3.5. Ammonium Chloride Doped with Nickel Cations, Grown from Acid Solution (pH 5.5)*

These crystals were a yellowish green color proving the incorporation of $Ni^{2+}$ ions. Figure 6 shows that $NH_4Cl:Ni^{2+}$ polarized at 268K (curve *a*) shows two depolarization peaks which correspond in position to peaks II and III. Particularly on fresh crystals there is a significant depolarization current above about 340K: in some crystals this had the opposite sign to the current associated with relaxation phenomena (e.g., curve *a*). Peak II is rather small (contrast curve *a* in Fig. 6 with curve *b* in Fig. 5 for $NH_4Cl:CrO_4^{2-}$) and hence we did not persist with systematic polarization experiments at lower temperatures. It is possible, therefore, that peak I could also occur in $NH_4Cl:Ni^{2+}$ but, if so, it is unlikely to be a strong peak. Polarization at higher temperatures ($T_p$ = 291K for curve *b*) accentuates peak III. This was the 19th depolarization run on this particular crystal and it showed zero high-temperature space-charge release. The results of computer analysis of several depolarization spectra for crystals polarized at 291K are given in Table II.

### *3.6. Ammonium Chloride Doped with Nickel Cations, Grown from Alkaline Solution (pH 8)*

The solution was dark blue and the crystals were a pale pink color. This shows that $Ni^{2+}$ ions are incorporated in $NH_4Cl$ under these conditions and that their coordination is different from that in crystals grown from acid solution. The thermally induced depolarization of a pink $NH_4Cl:Ni^{2+}$ grown from alkaline solution is shown in Fig. 7. Curves *a*, *b*, and *c* show the results when the crystal is polarized at 249, 268, and 318K, respectively. Clearly, there are three depolarization events. The first (I) occurs with a peak current at about 278K, but appears to be prolonged because some peak II is present. This is the dominant peak at higher $T_p$, as shown by curve *b*. In *c* there is less of II, because the higher polarization temperature favors III at the expense of II,

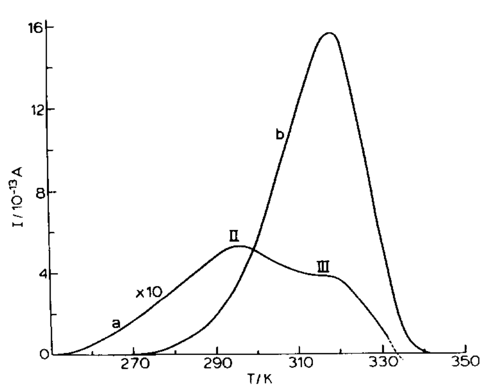

FIG. 6. Thermal depolarization of crystals of $NH_4Cl$, grown from a solution containing 0.1 mole% of $Ni^{2+}$ ions at pH 5.5, after polarization at a temperature $T_p$. (*a*) $T_p$ = 268K; (*b*) $T_p$ = 291K.

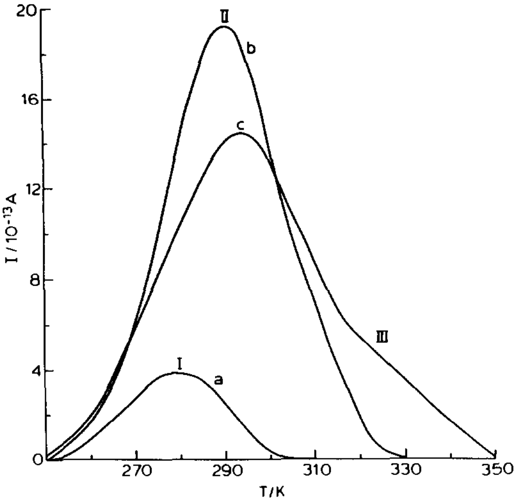

FIG. 7. Thermal depolarization of crystals of $NH_4Cl$, grown from a solution containing 0.1 mole% of $Ni^{2+}$ at a pH of 8, after polarization at a temperature $T_p$. (*a*) $T_p = 249K$; (*b*) $T_p = 268K$; (*c*) $T_p = 318K$.

but nevertheless peak II is still much larger than III. The relative strengths of I, II, and III do not favor their separation by the usual peak-cleaning technique. Figure 8 shows clearly the existence of the three depolarizations but also that we have not been able to separate them completely. The crystal was polarized at 291.5K and then depolarized in three stages, without further polarization. First it was heated to 286.5K and this emphasizes I (curve *a*). Next it was heated to 318K and this shows the main depolarization peak II, although a considerable fraction of the polarization had already been lost in the first heating (curve *b*). The last curve *c* shows the final depolarization, and is probably a fairly pure representation of the third source of polarization, III, possibly mixed with a small amount of space charge. The leading edge of curve *a* in Fig. 7 as well as curve *c* in Fig. 8 and another like it were analyzed and the results are included in Table II.

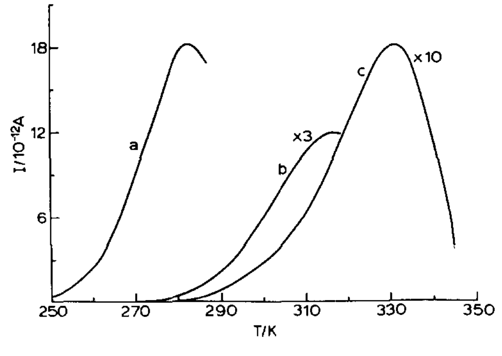

FIG. 8. Thermal depolarization of a crystal of $NH_4Cl$, grown from a solution containing $Ni^{2+}$ at a pH of 8, after polarization at 291.5K and depolarized (*a*) up to 286.5K, (*b*) after cooling (without repolarization), up to 318K, and (*c*) again after cooling without repolarization. Note that the depolarization currents have been multiplied by 3 and 10, respectively, before plotting, so that $I_{max}$ for curve *c* is $\sim 1.8 \times 10^{-13}$ A and for curve *b* $\sim 4 \times 10^{-13}$ A.

## 4. Discussion

### 4.1. *Dipole Relaxation or Space Charge Release?*

The parameters $\tau_0$ and $E$, as well as $T_m$, given in Table II, display quite a variation. The reason for this is the close proximity of the three TD bands and the consequent difficulty in resolving the components effectively. However, there is no doubt that the three bands do exist (see Figs. 6, 7, and 8, for example). The mean values of these parameters (arithmetic mean for $E$ and $T_m$, geometric mean for $\tau_0$) are given in Table III. As pointed out in Section 1, our investigations were confined to the TD of crystals polarized at $T_p \geq 249K$, i.e., to the disordered phase of $NH_4Cl$. Kessler and Ebert

TABLE III

MEAN VALUES OF THE PARAMETERS FOR THE THREE PRINCIPLE RELAXATION PEAKS OBSERVED IN $NH_4Cl$ ABOVE 250K

| Peak | $\tau_0$ (sec) | $E_0$ (eV) | $T_m$ (K) |
|---|---|---|---|
| I | $7.0 \times 10^{-9}$ | 0.58 | 278 |
| II | $3.9 \times 10^{-11}$ | 0.73 | 292 |
| III | $5.6 \times 10^{-12}$ | 0.85 | 318 |

(*5*) have reported on a thermally stimulated polarization (TSP) investigation of $NH_4Cl$ and found bands at 185, 215, 290 and 330K. The first two bands are found in the ordered phase below the phase transition which occurs at 242.5K. The third band is probably the same as our band II, for although no relaxation parameters for their 290-K band are given by Kessler and Ebert (*5*), in earlier work (*4*) $E$ for the TD bands is given as 0.70 eV, in quite acceptable agreement with our value for II. The 330-K band is probably the same as our band III ($T_m$ = 307–330K), possibly along with some space charge release (Müller (*12*); see also Fig. 2 above). Again no activation parameters are given, but in the earlier work (*5*) $E$ for a TD band in the same $T$ range is given as 0.83 eV, in quite good agreement with our value of $E$ for band III. Kessler and Ebert (*5*) attribute both their 290- and 330-K bands to space charge rather than to dipole relaxation. However, the relaxation parameters for bands II and III in Table II appear to be quite consistent with a defect dipolar relaxation. Since $\tau_0^{-1}$ is $2.6 \times 10^{10}$ and $1.8 \times 10^{11}$ $sec^{-1}$, respectively, for II and III, these values of $\tau_0^{-1}$ correspond to activation entropies of 4.6 and 2.8 k if an attempt frequency of $3 \times 10^{22}$ $sec^{-1}$ is assumed. Such entropy values are perhaps a little on the high side for vacancy jumps but not at all inconsistent with proton transfer mechanisms. Thus we believe bands II and III are associated with dipolar relaxation processes. Space charge release can occur at any temperature above 249K (the lower limit studied) but is generally most significant above 320K.

The mechanism of space charge release is the following. During polarization at $T_p$ a dc current flows. This current decreases with time in an approximately exponential fashion and arises from (i) a displacement current associated with the orientation of dipoles and (ii) the flow of charge carriers in the field (Müller (*12*), Kessler (*13*)). In $NH_4Cl$ the polarizing current usually approached a steady, or slowly decreasing, value of about $10^{-14}$ A after a polarization time $t_p$ of 30 min in a field of ~250 V $cm^{-1}$. Charge carriers migrating in the dc field may become trapped within or at the surface of the crystal and on raising the temperature in a TD experiment the release of this space charge occurs along with any dipole depolarization processes. It may be difficult to distinguish experimentally between dipole relaxation peaks and space charge peaks, but generally, in $NH_4Cl$ at least, the space charge current seems to be far less reproducible in successive runs on the same sample, and this was one of our reasons for assigning the 350-K peak (IV) to space charge release. The other, and principal argument, is its appearance, in the V crystal, for example, at a temperature 100K above $T_p$. The temperature of space charge release depends on the trap depth and in $NH_4Cl$ this is much greater than the activation energy for carrier mobility at low temperatures. Thus free carriers migrate easily to the deep traps at 250K but are not released until the temperature reaches about 325K (Fig. 2(*d,e*)).

### *4.2. Effect of Preparation of $NH_4Cl$ Crystals*

Certain conclusions regarding the nature of the defect centers responsible for peaks I, II, and III may be drawn from the doping experiments (see Table I for crystal designations). A comparison of the TD spectra for crystals H and NH shows that in neither crystal was I detected, while there is relatively more III than II in NH. Similarly comparing the TD of crystals H and CH, we find III reduced in CH but I and II increased. We may conclude that III requires cation vacancies (cv) and acid conditions but that II and I require alkaline conditions, in crystal growth from solution, and also anion vacancies. However, the dominant peak in the vapor-grown $NH_4Cl$ is II; I is present to a small extent, while III is also seen in crystals polarized at 291K (Fig. 1(*c*)) and distinctly evident when $T_p = 303$K (Fig. 1(*d*)). During sublimation of $NH_4Cl$ both free $NH_3$ and free HCl are present, since the mechanism of sublimation is

$$NH_4^+Cl^- = NH_3(g) + HCl(g) = NH_4^+Cl^-. \quad (4)$$

We conclude, therefore, that peak III requires HCl for its formation and that peak II requires $NH_3$.

In growth from the vapor, HCl(g) is adsorbed on the growing surface and incorporated into the crystal as $H^+$ and $Cl^-$,

$$HCl(g) = \square_c[HCl]_a = [H^+]_c[Cl^{-1}]_a, \quad (5)$$

where subscripts c and a denote cation and anion sites, respectively, and □ denotes a vacant site. These centers may be visualized as protons trapped in the anion sublattice, because of the equilibrium

$$\square_c[HCl]_a = [H^+]_c[Cl^{-1}]_a. \quad (6)$$

We propose that the existence of the equilibrium (6) accounts for peak III. The vacant cation site carries an effective negative charge and the anion site occupied by HCl a positive charge. On nearest-neighbor sites the two together constitute a dipole which can orient either by cv jumps in the cation sublattice or by proton jumps in the anion sublattice,

$$[HCl]_aCl_a^- = Cl_a^-[HCl]_a. \quad (7)$$

We believe that proton jumps are the more facile and account for the dipole orientation observed as depolarization peak III. (It is not completely clear whether or not there might be two peaks in the neighborhood of 320K. The spread of the values found for $E$ and for $T_m$ might seem to indicate this; or they could simply be due to the difficulty in isolating III, as we are inclined to assume here.)

In solution $NH_4Cl$, being a salt formed from a weak base and a strong acid, hydrolyzes to produce protons so that the resulting solution used for crystal growth is slightly acid (pH 5.5).

$$NH_4^+ + H_2O = NH_4OH + H^+. \quad (8)$$

The $NH_4OH$ molecules are in equilibrium with $NH_3 + H_2O$, and this dissociation would result in loss of $NH_3$ from solutions allowing free evaporation of water. Our crystal growth apparatus was a sealed one with growth achieved by a gradual lowering of temperature. Thus the amount of hydrolysis is modest and the pH is constant during growth. The acid solutions, however, supply the protons that are incorporated in the crystal substitutionally on cation sites. Thus acid solutions and gaseous HCl behave similarly in producing the trapped proton centers responsible for III (see Eqs. (5)–(7)).

In solutions in which $NH_3$ was added until the pH was 8, $NH_3$ molecules are present in equilibrium with $NH_4OH$. Thus either during sublimation or in growth from alkaline solution, $NH_3$ will be adsorbed on cation sites and incorporated into the crystal as $NH_3$ molecules on cation sites, $[NH_3]_c$, along with the anion vacancies necessary to preserve the structure. The $[NH_3]_c$ sites carry on effective negative charge and the anion vacancies an effective positive charge so that the two together on nearest-neighbor sites constitute a dipole. The $[NH_3]_c$ sites we regard as *proton holes* and these dipoles,

$$[NH_3]_c\square_a, \quad (9)$$

can orient either by vacancy jumps in the anion sublattice or by proton-hole jumps in the cation sublattice,

$$[NH_3]_c[NH_4^+]_c = [NH_4^+]_c[NH_3]_c. \quad (10)$$

The experimental results are consistent with the $[NH_3]_c\square_a$ dipole being responsible for peak II.

These models are consistent with the experimental results recorded in this paper. For example, comparing H crystals with A, II is 10× larger in A than in H. I is also much larger in A, showing that I is also favored by alkaline conditions. A possible mechanism is the incorporation of $OH^-$ on anion sites, leading to the formation of $[NH_3]_c[H_2O]_a$ dipoles via the equilibrium

$$[NH_4^+]_c[OH^-]_a = [NH_3]_c[H_2O]_a \quad (11)$$

(III is still found to a small extent, indicating that $H^+$, which still exist in the alkaline solution though at a much lower concentration, are incorporated very readily in $NH_4Cl$). If I were not found in the vapor-grown crystals then this would be the favored model for I; it may still be correct if a small amount of water vapor is present during sublimation. Unfortunately, it is not possible to say whether or not this is likely to be so. Comparing A and NA we see that the relative amounts of I, II, and III are not very different, although the currents are 5× larger in A, showing that cation vacancies incorporated along with $Ni^{2+}$ reduce II by reducing the anion vacancy concentration. Finally, comparing NH with NA we note that for $T_p = 291K$, the maximum depolarization current is approximately the same in the two crystals but is due to III in NH and to II in NA, as expected from our above models for these centers.

In the following paper, our investigations of the effect of HCl(g) and $NH_3$(g) on thermal depolarization in $NH_4Cl$ will be described.

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