

## Thermal Depolarization in Ammonium Perchlorate Crystals Doped with Sulfate and Chromate Ions

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Thermal depolarization has been measured in single crystals of pure ammonium perchlorate and of  $\text{NH}_4\text{ClO}_4$  doped with  $\text{SO}_4^{2-}$  and  $\text{CrO}_4^{2-}$  ions. In the pure crystals faint depolarization peaks were observed at the same two temperatures as for the doped crystals, but the former were too weak for quantitative analysis. The relaxation parameters determined for the anion doped crystals are: for the low-temperature peak,  $\tau_0 = 10^{-3}$  sec,  $E = 0.25$  eV; and for the high-temperature peak,  $\tau_0 = 10^{-6}$  sec,  $E = 0.50$  eV. These extremely long preexponential factors are interpreted in terms of a charge separation process involving protons, rather than the usual dipole orientation process.

### Introduction

Ammonium perchlorate (AP) is a technologically important material primarily because of its use as the oxidizer in solid fuel composite rocket propellants. Consequently there have been several studies of its thermal decomposition and a mechanism (1, 2) based on proton transfer has gained general acceptance. There have been a number of investigations of charge transport in both compressed pellets and single crystals of AP and divergent views as to the nature of the conducting species have been expressed. Zirkind and Freeman (3) suggested electronic and ionic conduction mechanisms whereas Wise (4) favored proton transport because of the enhancement of conductivity by  $\text{NH}_3$  above  $450^\circ\text{K}$ . Maycock *et al.* (5, 6) interpreted dc measurements on single crystal AP in terms of surface conduction and bulk Frenkel defects. Jacobs and co-workers (7, 8) studied the effects

of water vapor,  $\text{NH}_3$ , and doping with  $\text{Ba}^{2+}$  and  $\text{SO}_4^{2-}$  ions on the ac conductivity of AP and concluded that their results were consistent with proton transfer conduction in the cation sublattice. However, because of the similarity of the dc conductivities of AP and rubidium perchlorate and the enhancement of the conductivity of AP by  $\text{SO}_4^{2-}$ , Owen *et al.* (9, 10) proposed that interstitial  $\text{NH}_4^+$  ions were the majority carriers in AP. For  $\text{NH}_3$ -treated AP, however, proton conduction was favored (11).

Khairtdinov and Boldyrev (12) investigated dielectric loss and dc conductivity of AP doped with  $\text{HSO}_4^-$  ions and proposed a proton conduction mechanism involving reorientation of  $\text{HClO}_4$  molecules. Keenan and Ohanian (13) measured the dc conductivity of pure AP up to  $450^\circ\text{K}$  and interpreted the low- and high-temperature regions in terms of proton conduction, in which interstitial water molecules functioned as both donors and acceptors, and cation vacancy conduction involving a novel "turnstile" mechanism (14). Most recently, Hor and Jacobs (15) have interpreted their results on dc conduction in pure AP and AP

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doped with  $\text{SO}_4^{2-}$ ,  $\text{CrO}_4^{2-}$ , and  $\text{Pb}^{2+}$  ions in terms of proton transfer in both the cation and anion sublattices.

There has been no previous published work on thermal depolarization (TD) in AP crystals. Such an investigation was thought to be of potential value in the complex task of resolving the conflicting views that have been expressed on charge transport in AP because of its capacity to reveal the existence of dipoles in the crystal. For example, if charge transport in AP proceeds via cation or anion vacancies, then the dipoles formed by association of these vacancies with divalent impurity ions should be detected. Moreover, the jump frequency associated with the relaxation of these dipoles would be expected to be of the order of magnitude of  $10^{13} \text{ sec}^{-1}$ . The preexponential factor in the dipole relaxation time is not, in general, simply related to one of these jump frequencies but for vacancy complexes it is generally within a couple of orders of magnitude of  $10^{-14} \text{ sec}^{-1}$  (16). Thus the detection of dipoles with relaxation parameters of the appropriate magnitude would support a vacancy charge transport mechanism.

The TD technique was introduced by Bucci *et al.* (17), who termed it *ionic thermoconductivity* (ITC). Since the method has also been used to investigate electronic defects in solids, as well as dielectric relaxation in polymers and liquids, the more general term *thermal depolarization* is to be preferred. In a TD experiment the crystal is subjected to an electric field, usually of a few thousand volts per centimeter, at a temperature at which any dipoles present are sufficiently mobile to become oriented in the field. Preferably the polarization temperature is sufficiently low for the steady-state dc conductivity to be negligibly small. The crystal is then cooled to a low temperature at which the motion of the dipoles is frozen, the field is removed, and the crystal is warmed at a constant rate of a few degrees kelvin per minute. The current through the crystal is monitored during heating and at temperatures at which the dipoles become

mobile they adopt random orientations once again and the corresponding depolarization current is measured using an electrometer. Clearly polarization in a crystalline medium can result from charge separation as well as from dipole orientation and so the thermal depolarization technique may be used to detect such charge separation as well as the presence of dipoles.

The depolarization current  $J$  obeys the equation

$$J(T) = (Q_0/\tau_0) \exp(-E/kT) \times \exp \left[ (-1/b\tau_0) \int_{\tau_0}^T \exp(-E/kT') dT' \right], \quad (1)$$

where  $Q_0$  is the total charge liberated during depolarization and  $b$  is the heating rate. The 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 charge. For a simple dipole orientation process one expects  $\tau_0^{-1}$  to be of the order of magnitude of a lattice vibrational frequency (although it should be emphasized that for reasons of orientational degeneracy and symmetry  $\tau^{-1}$  is not generally simply related to a single lattice jump (16)). Experimental  $J(T)$  curves can be computer fitted (18) to Eq. (1) to yield numerical values of  $Q_0$ ,  $E$ , and  $\tau_0$ . The TD experiment thus reveals information about the activation parameters involved in the removal of polarization and these should be consistent with any model proposed for the polarization process.

## Experimental

Single ammonium perchlorate crystals were grown from solutions according to the method described by Jacobs and Ng (7).  $(\text{NH}_4)_2\text{CrO}_4$  and  $(\text{NH}_4)_2\text{SO}_4$  were used for introducing di-

valent anion dopants into the AP. For brevity, the designation  $x\%$  AP:Y refers to the doped crystals grown from an AP solution containing  $x$  mole% of dopant Y. The actual amounts of the various dopants incorporated in the crystals were not determined. However, proof of incorporation of the dopants is available from the changes they cause in dc conductivity [Hor and Jacobs (15)] and, in the case of chromate ion, from Raman scattering and optical absorption experiments [Hor *et al.* (19)]. The AP crystals were cleaved along the (001) and (210) planes into prisms of the desired size. Samples used were  $\sim 2$  mm thick and had an area of  $\sim 1$  cm<sup>2</sup>. Good electrical contact between the crystals and the electrodes was achieved by coating the crystal surface with a thin film of Ag paint.

The apparatus used for studying TD consisted of two stainless-steel chambers. The sample chamber was heated by an Inconel-shielded Thermocoax heater without undesirable electrical interference from the heater circuit. Inside this chamber the sample was positioned on a Pt electrode which was insulated from the supporting platform by a sapphire insulator. The upper electrode, which was connected to the input terminal of a Cary 401 vibrating reed electrometer, has a spring-loaded tip in contact with the sample. The sample chamber was enclosed by a larger outer chamber and the whole assembly could be evacuated to a vacuum of  $10^{-5}$  mm Hg. Helium gas was admitted into the apparatus to act as a heat-exchanging medium. The noise level of the apparatus was about  $5 \times 10^{-15}$  A.

In a typical TD run, the sample was polarized by an electric field of strength 2000 V/cm at a chosen temperature. The apparatus was then cooled by a liquid nitrogen bath. When the sample had been cooled to the required temperature, the electric field was removed and the sample was warmed at a constant heating rate of 4°K/min. The TD current and thermocouple readings were continuously monitored by a two-pen chart recorder.

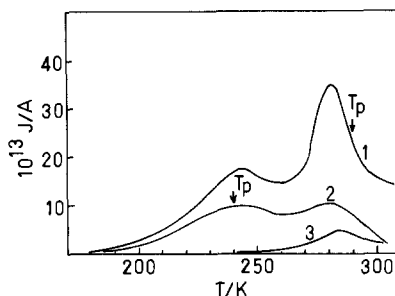


FIG. 1. Thermal depolarization current in 0.1%  $\text{NH}_4\text{ClO}_4:\text{SO}_4^{2-}$ . Curve 1, polarization temperature  $T_p = 300^\circ\text{K}$ ; curve 2,  $T_p = 240^\circ\text{K}$ ; curve 3, after depolarization up to  $260^\circ\text{K}$  and recooling.

## Results

For pure AP the TD current obtained was very weak ( $\sim 2 \times 10^{-14}$  A) and barely appeared as two tiny peaks at about 240 and  $290^\circ\text{K}$ . Poor signal-to-noise ratios ruled out any reasonably accurate analysis of these peaks. However, divalent anion doped crystals showed fairly intense TD and were suitable for a systematic investigation.

Figure 1 shows the results of three TD experiments performed on a 0.1%  $\text{NH}_4\text{ClO}_4:\text{SO}_4^{2-}$  crystal. Curve 1 was obtained after the sample had been polarized at  $300^\circ\text{K}$ . The high-temperature peak ( $283^\circ\text{K}$ ) was almost twice as high as the low-temperature peak ( $241^\circ\text{K}$ ). By decreasing the polarization temperature to  $240^\circ\text{K}$ , curve 2 was produced in which two peaks of about equal heights occurred at the same temperatures as the peaks in the curve 1. A rough comparison revealed that the high-temperature peak diminished to about one-third of its previous size whereas the low-temperature peak still retained about 60% of its original size. Application of peak-cleaning techniques could remove the low-temperature peak and result in a smaller high-temperature peak, as represented by curve 3; the sample had been allowed to depolarize up to  $260^\circ\text{K}$  and then re-cooled without further application of the polarizing field. The results of an analysis of

TABLE I

THERMAL DEPolarIZATION PARAMETERS FOR 0.1%  
 $\text{NH}_4\text{ClO}_4:\text{SO}_4^{2-a}$

Curve	1	2	3
$T_p$ (°K)	300	240	240
$Q_{01}$ (C)	$0.145 \times 10^{-8}$	$0.497 \times 10^{-9}$	$0.180 \times 10^{-9}$
$\tau_{01}$ (sec)	$0.308 \times 10^{-8}$	$0.366 \times 10^{-7}$	$0.300 \times 10^{-8}$
$E_1$ (eV)	0.60	0.54	0.65
$T_{m1}$ (°K)	283	283	285
$Q_{02}$ (C)	$0.995 \times 10^{-9}$	$0.650 \times 10^{-9}$	—
$\tau_{02}$ (sec)	$0.224 \times 10^{-3}$	$0.134 \times 10^{-2}$	—
$E_2$ (eV)	0.29	0.26	—
$T_{m2}$ (°K)	241	241	—

<sup>a</sup>  $T_p$  is the polarization temperature;  $Q_0$  is the charge liberated during depolarization;  $\tau_0$ ,  $E$  are the relaxation time activation parameters; and  $T_m$  is the temperature of the peak maximum. Subscripts 1 and 2 refer to high- and low-temperature peaks, respectively.

the TD curves by computer fitting are listed in Table I and the  $\log J$  vs  $T^{-1}$  plots presented in Fig 2 show both the experimental and fitted results. The high-temperature peak occurred at  $\sim 284^\circ\text{K}$  with  $E = 0.54\text{--}0.65$  eV and the low-temperature peak at  $241^\circ\text{K}$  with  $E = 0.26\text{--}0.29$  eV. Both peaks were found to have unusually high  $\tau_0$  values.

The 0.1%  $\text{NH}_4\text{ClO}_4:\text{CrO}_4^{2-}$  behaved similarly to 0.1%  $\text{NH}_4\text{ClO}_4:\text{SO}_4^{2-}$  in displaying two peaks in its TD curves. Figure 3 shows the TD spectra observed at three

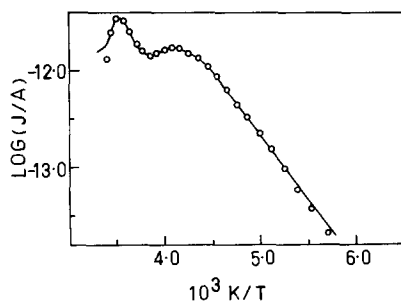


FIG. 2. Thermal depolarization current for 0.1%  $\text{NH}_4\text{ClO}_4:\text{SO}_4^{2-}$  polarized at  $300^\circ\text{K}$ . The continuous curve shows the experimental data; the points were calculated from Eq. (1) with the parameters given in Table I.

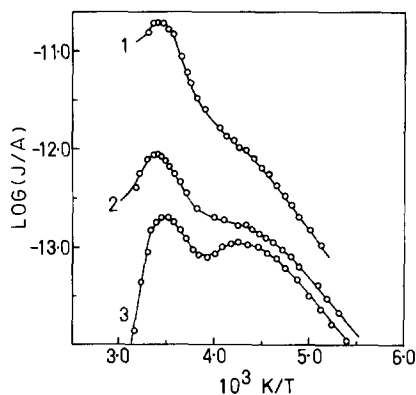


FIG. 3. Thermal depolarization currents in 0.1%  $\text{NH}_4\text{ClO}_4:\text{CrO}_4^{2-}$ . Curve 1,  $T_p = 300^\circ\text{K}$ ; curve 2,  $T_p = 220^\circ\text{K}$ ; curve 3,  $T_p = 200^\circ\text{K}$ . Continuous curves show the experimental data; points were calculated from Eq. (1) with the parameters given in Table II.

polarization temperatures 200, 220 and  $300^\circ\text{K}$ . The intensity of TD peaks increased with increasing polarization temperature, the high-temperature peak ( $292^\circ\text{K}$ ) being found to increase at a much faster rate than the low-temperature one. Of the three runs, only in that at the lowest polarization temperature did the TD current decay rapidly to zero on the high-temperature side of the peak, as expected for a normal dipolar TD. Table II summarizes the computer-fitted parameters for the TD of 0.1%  $\text{NH}_4\text{ClO}_4:\text{CrO}_4^{2-}$ , the high-temperature peak at  $292^\circ\text{K}$  and the low-temperature peak at  $236^\circ\text{K}$  have activation energies of 0.50 and

TABLE II

THERMAL DEPolarIZATION OF 0.1%  $\text{NH}_4\text{ClO}_4:\text{CrO}_4^{2-a}$

Curve	1	2	3
$T_p$ (°K)	300	220	200
$Q_{01}$ (C)	$0.108 \times 10^{-7}$	$0.547 \times 10^{-9}$	$0.118 \times 10^{-9}$
$\tau_{01}$ (sec)	$0.572 \times 10^{-7}$	$0.534 \times 10^{-5}$	$0.131 \times 10^{-5}$
$E_1$ (eV)	0.56	0.45	0.47
$T_{m1}$ (°K)	294	295	288
$Q_{02}$ (C)	$0.624 \times 10^{-9}$	$0.111 \times 10^{-9}$	$0.709 \times 10^{-10}$
$\tau_{02}$ (sec)	$0.321 \times 10^{-3}$	$0.545 \times 10^{-2}$	$0.107 \times 10^{-2}$
$E_2$ (eV)	0.28	0.22	0.25
$T_{m2}$ (°K)	238	237	233

<sup>a</sup> Symbols are defined in Table I.

0.25 eV, respectively. It is worthwhile mentioning that the fitting of curve 3 was considered very good, with a standard deviation of  $0.6 \times 10^{-14}$  A, but for curves 1 and 2 the slowly decaying currents at high temperatures rendered a good fit to the data impossible.

### Discussion

The TD curves for 0.1%  $\text{NH}_4\text{ClO}_4:\text{SO}_4^{2-}$  and 0.1%  $\text{NH}_4\text{ClO}_4:\text{CrO}_4^{2-}$  display two peaks whose positions are only slightly shifted by a large change in the polarization temperature. This implies that the relaxation processes giving rise to these peaks are essentially dipolar in nature, with increasing interference from other types of mechanisms when the polarization temperature is raised. Most surprisingly,  $\tau_0$ , the preexponential factor in the relaxation times corresponding to the observed peaks, is unusually large, being several orders of magnitude greater than the reciprocal of a typical lattice vibration frequency.

Traditionally, the dielectric relaxation processes in ionic solids are associated with the reorientation of impurity-defect complexes, e.g., divalent cation impurity-cation vacancy pairs in alkali halides and trivalent cation impurity-interstitial anion pairs in  $\text{CaF}_2$ . The defect possesses an effective charge equal in magnitude but opposite in sign to that of the impurity ion. They are held together to form an electric dipole by Coulombic attraction. The electric dipole alters its orientation when the defect jumps around the rather immobile impurity ion. Consequently, the preexponential factor  $\tau_0$  in the relaxation time for the reorientation of the dipole is expected to be comparable with the inverse of the lattice vibration frequency.

Our conductivity investigations (15) have indicated that a vacancy jump mechanism is not likely in AP. The fact that AP shows a lower conductivity when divalent cation  $\text{Pb}^{2+}$  is present practically rules out the existence of mobile cation vacancies. On the other hand,

the increase in the conductivity of AP doped with divalent anions cannot be explained in terms of anion vacancy jump mechanism because of the low mobility of the perchlorate anion due to its large size. From this and other experimental evidence, and from structural considerations, we have concluded that proton conduction prevails in AP and we have proposed the following model. Proton conduction is initiated by the formation of molecular defects:  $\text{NH}_3$  (proton hole) and  $\text{HClO}_4$  (protonated  $\text{ClO}_4^-$ ), which are formed preferentially at anion vacancies. The proton hole has an effective negative charge because it is created from an  $\text{NH}_4^+$  ion by loss of a proton. The proton transfer can proceed simultaneously in the  $\text{NH}_4^+$  and  $\text{ClO}_4^-$  sublattices. A proton switch from an  $\text{NH}_4^+$  to a proton hole would produce an apparent motion of the hole in an opposite direction to the proton jump.

Under the action of an externally applied field, the proton jumps in the  $\text{ClO}_4^-$  sublattice correspond to a motion of positive charges toward the cathode whereas in the  $\text{NH}_4^+$  sublattice, migrations of negative charges (proton holes) toward the anode correspond to proton jumps in the cation sublattice. The TD experiments are generally performed at low temperatures where the steady-state ionic conductivity is practically negligible. We may therefore conclude that the proton migration ceases when the polarization caused by the separation of oppositely charged  $\text{NH}_3$  and  $\text{HClO}_4$  becomes sufficient to counterbalance the effect of the applied field. The sample is then fully polarized with the molecular defects having moved several lattice sites away from their original formation sites. The crystal now contains large dipoles each with its positive end consisting of  $\text{HClO}_4$  and its negative end  $\text{NH}_3$ . When the electric field is removed and the sample is heated, the proton jumps proceed in the reverse sequence to that occurring during polarization and the sample will be restored to its initial unpolarized state when the molecular defects finally return to

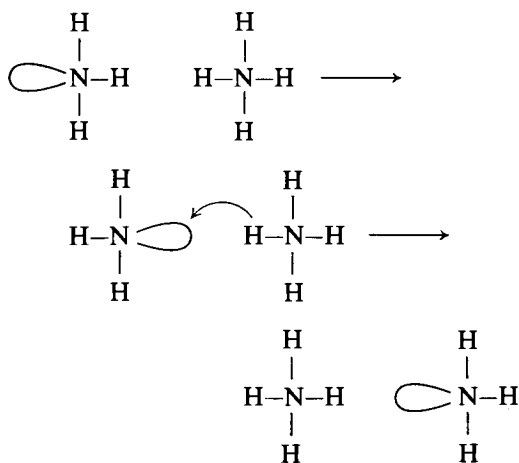
their nearest-neighbor positions at the anion vacancies.

Some important features of the TD observed for AP can be explained on the basis of this proposed charge separation model. First, there is a direct connection between the conductivity and the TD because they involve identical proton jumps. The conductivity results have revealed that the rate-determining step for the electrical conduction is the migration of protons within the  $\text{ClO}_4^-$  sublattice, requiring an activation energy of 0.50 eV. The high-temperature peak of TD has an activation energy of  $\sim 0.55$  eV and hence most likely arises from the same process. The other relaxation process which causes the low-temperature peak in the TD would be the proton jump in the  $\text{NH}_4^+$  sublattice. This mechanism is thus assigned an activation energy of 0.25 eV. Divalent anions enhance both the conductivity and the TD of AP presumably through the effects of the anion vacancies they introduce which promote the formation of molecular defects.

The large values of  $\tau_0$  observed for the TD peaks we ascribe to: (i) the multiple jumps made by protons in removing the polarization and (ii) the cooperative motions between 2 neighboring  $\text{ClO}_4^-$  groups, and between  $\text{NH}_3$  and  $\text{NH}_4^+$ , as they participate in proton transfer. If the distance over which the proton can move is reasonably uniform throughout the sample, a single macroscopic relaxation time is associated with each type of proton transfer. The proton transfer in the  $\text{ClO}_4^-$  sublattice is made up of intra- and inter- $\text{ClO}_4^-$  jumps. during an inter- $\text{ClO}_4^-$  jump the participating  $\text{ClO}_4^-$ 's must rotate slightly in order to minimize the jump distance traversed by the proton. As free rotation of  $\text{ClO}_4^-$  does not occur below the phase-transition temperature of 513°K of AP, the chance of achieving favorable orientation for an inter- $\text{ClO}_4^-$  jump is reduced, and thus results in a long  $\tau_0$ .

The proton transfer in the  $\text{NH}_4^+$  sublattice involves a strongly cooperative mechanism in which the lone-pair electrons of  $\text{NH}_3$  have to

be exactly positioned toward the H of a donating  $\text{NH}_4^+$ :



The proton hole  $\text{NH}_3$ , which results from an  $\text{NH}_4^+$  losing a  $\text{H}^+$  has to turn around to be ready to accept a  $\text{H}^+$  from its  $\text{NH}_4^+$  neighbor. The distance between a pair of nearest  $\text{NH}_4^+$  is 4.6 Å and the N–H bond lengths range from 1.03 to 1.06 Å. Even with the most favorable orientation existing the proton has to traverse the rather long distance of 2.5 Å in order to jump from an  $\text{NH}_4^+$  ion to an  $\text{NH}_3$ . The situation would be somewhat improved if the acceptor and the donor can vibrate closer to each other to form the transition state. This motion of the  $\text{NH}_3$  and  $\text{NH}_4^+$ , together with their attainment of the correct configuration, would account partly for the large  $\tau_0$ .

Generally speaking, the lower the polarization temperature, the better the fitting of the TD by a dipolar relaxation model. When the polarization temperature is raised the high-temperature peak does not return quickly enough to zero to permit a good fit. At a low polarization temperature, the average distance the protons have covered would be short and the dipoles created by the charge separation process would not interact with one another, as implied in our model. At high temperatures, more dipoles are formed as more defect-forming sites are activated, and also the length of dipole becomes longer due to the increasing

mobility of  $H^+$  with temperature. A strong dipole-dipole interaction may then occur which could lead to the failure of the simple model. Also, significant numbers of protons and holes may become trapped at grain boundaries requiring additional activation energy before recombination can occur. Macroscopic space charge polarization due to the pile up of charge carriers near the electrodes will also occur at high polarization temperatures.

The only comparable TD measurements on an  $NH_4^+$  salt are those of Kessler (20, 21) on  $NH_4Cl$ . He found four TD peaks and from the shift of the two highest-temperature peaks with polarization temperature  $T_p$  concluded that these were associated with the release of space charge. The two low-temperature peaks were associated with first-order processes. The activation energies for these two processes (22) are 0.12 and 0.34 eV. Assuming a heating rate of 4 K/min (as in our work) we may estimate preexponential factors of  $10^{-1}$  and  $3 \times 10^{-6}$  sec for the two relaxations which peak at 180 and 220°K, respectively. These extremely long  $\tau_0$  values are comparable with the values for AP and imply that a charge separation mechanism is also operative in  $NH_4Cl$ . ( $\tau_0(E, T_m)$  is inversely proportional to the heating rate  $b$  but our estimate of  $\tau_0$  is not likely to be affected by more than a factor of 10 or so by our arbitrary choice of  $b$ . The point is that  $\tau_0$  is very different to a lattice vibrational frequency.)

All the data discussed above were obtained with the electric field  $\mathcal{E}$  applied perpendicular to the (210) cleavage face of AP. Similar experiments were attempted with  $\mathcal{E} \perp (001)$  but only a very small depolarization current was measured. As this finite current occurred in the same temperature range as the depolarization peaks observed when  $\mathcal{E} \perp (210)$  we conclude that it is due to the same charge-displacement dipoles as are responsible for the TD peaks and that this charge displacement occurs preferentially in planes that are normal to [001]. This conclusion is in har-

mony with that drawn from dc conductivity measurements which showed that the conductivity in planes  $\perp [001]$  was much greater than that in the [001] direction.

Finally we suggest that it might prove interesting to attempt thermal depolarization measurements at low temperatures in view of evidence from neutron diffraction (23) and magnetic resonance (24) experiments that the  $NH_4^+$  ion in AP undergoes hindered rotation at very low temperatures. Such measurements were not feasible in our apparatus, which was designed specifically for measurements in the 100–300°K temperature range.

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