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# Direct Current Conduction in Ammonium Perchlorate Single Crystals

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The dc electrical conductivity of pure and doped ammonium perchlorate (AP) has been studied in two different crystal orientations, with the electric field applied perpendicularly to either (001) or (210) planes. The conductivity along the direction of the *c* axis was found to be lower than that normal to (210) by a factor of 5 to 10. The dc electrical conductivity of AP is decreased by $Pb^{2+}$ ions but increased by $SO_4^{2-}$ and $CrO_4^{2-}$ ions. The conductivity of pure AP and of $Pb^{2+}$-doped AP displays two regions with activation energies for conduction of 0.56 and 0.87 eV, respectively. The conductivity of the anion-doped crystals has a single activation energy, 0.66 eV for $SO_4^{2-}$ and 0.72 eV for $CrO_4^{2-}$. Exposure to ammonia enhances the conductivity of pure AP. A proton conduction mechanism is proposed that takes due regard of the structure of AP. The effect of the various additives on the conductivity are attributed to their influences on the formation of charge-carrying protons.

## Introduction

The first conductivity experiment on ammonium perchlorate (AP) was carried out by Zirkind and Freeman (*1*) using pellet samples under vacuum and in oxygen and argon. Electronic and ionic conduction mechanisms were proposed. Wise (*2*) compared the conductivity of AP pellets in $N_2$ and $NH_3$ above 450°K and found that $NH_3$ increased the conductivity and lowered the activation energy from 1.4 to 0.90 eV. He interpreted his data in terms of a proton transfer mechanism. Jacobs and coworkers (*3, 4*) studied the ac conductivity of pure and doped AP crystals rather extensively, including the effect of thermal cycling, water vapor, $NH_3$, and the additives $Ba^{2+}$ and $SO_4^{2-}$. They suggested a mechanism which involved the formation of proton holes ($NH_3$ molecules at cation sites) followed by migration of these defects via a proton jump process.

Owen *et al.* (*5, 6*) measured the dc conductivity of pure and doped AP and pure rubidium perchlorate (RP). As unit cell dimensions and ion sizes are practically the same for RP and AP, the similarity in both the activation energy (1.1 and 1.2 eV) and the magnitude of the conductivity of the two compounds, led these authors to reject a proton transfer mechanism. Their observations that the conductivity of AP was increased by $SO_4^{2-}$ but not affected by $Ba^{2+}$ led to the proposal that interstitial $NH_4^+$ ions were the major charge carriers. From dielectric loss and dc conductivity measurements on AP doped with $HSO_4^-$, Khairetdinov and Boldyrev (*7*) obtained an activation energy of 0.76–0.81 eV for the migration of charge carriers and proposed a proton conduction mechanism involving the orientation of $HClO_4$ molecules. Recently Keenan and Ohanian (*8*) obtained

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values of 0.12 and 1.04 eV, respectively, for the activation energy of the low- and high-temperature conductivity of AP. Their dc conductivity readings were obtained 1 min after the application of the electric field. The low activation energy of 0.12 eV was accounted for by a proton conduction mechanism in which interstitial water molecules act as both proton donor and acceptor sites. At higher temperatures the migration of $NH_4^+$ via cation vacancies was thought to prevail over the proton conduction mechanism.

The inconsistencies between the conductivity results published by different authors are indeed very serious, amounting, for instance, to a factor of 100 in the conductivity of pure AP. While the earlier experiments were usually performed on pellet samples for which an irreproducible conductivity is perhaps understandable, the situation does not seem to have improved much with the use of single crystals in the more recent works. Poor reproducibility in the conductivity of AP is apparently due to several factors: (a) the crystals used were not of good quality; (b) the low thermal stability of AP was not taken into consideration; (c) improper annealing treatment of samples; and (d) polarization effects in dc measurements were not studied carefully. Above all, some conduction mechanisms have been proposed without paying proper attention to the crystal structure of AP, and isotropic conductivity for the orthorhombic AP crystals seems to have been universally assumed.

The present work was carried out in an attempt to clarify some of the existing discrepancies in the results obtained and in the models proposed by various authors.

## Experimental

Ammonium perchlorate of 99.99% purity was purchased from the Fisher Scientific Company. Both pellets and single crystals were used in this work and they were prepared according to the method described by Jacobs and Ng (*3*). Doped crystals were grown from solutions containing 1 mole% $Ba(ClO_4)_2$, 5 mole% $Pb(ClO_4)_2$, 0.1 mole% $(NH_4)_2SO_4$, 0.1 and 1 mole% $(NH_4)_2CrO_4$, respectively. For the sake of brevity, the designation *x*% AP : *Y* refers to the doped crystal 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 but the successful solution of the added impurities was evident from their effect on the conductivity.

The AP single crystals cleaved readily along the (001) and (210) planes. Samples used were ~2 mm thick and had an area of ~1 cm². Initially the Pt foil electrodes were applied directly to the cleaved crystal. However, preliminary measurements showed that the results obtained in this manner were irreproducible and that electrical contact between the crystals and the electrodes was satisfactory if the crystal surface was coated first with a thin film of vacuum-deposited Pd or with Ag paint. Measurements using Pt foil alone would yield results showing large variations in conductivity by a factor of as much as five. A three-terminal electrode arrangement was generally employed in preference to the simpler two-electrode system because any spurious surface currents would be removed by the guard ring.

The sample was mounted in a conductivity cell similar to that used by Allnatt and Jacobs (*9*); measurements could be performed under vacuum or in different gaseous atmospheres. The conductivity measurements were purposely restricted to temperatures below 430°K in order to avoid the possibility of thermal decomposition of AP which would cause complications in subsequent runs (*3, 4*). It was also found that annealing of samples under vacuum at ~380°K was necessary in order to ensure reproducible conductivity results.

A dc electric field of 40 V/mm was applied across the sample and the resulting current was measured using a Cary 401 electrometer, the output of which was connected to a strip-chart recorder. The current flowing through the sample was found to decrease from an initial value to a final steady-state value. The time taken to reach the final value decreased as the temperature increased. This time varied from 30 min at room temperature (RT) to less than 1 min at 420°K.

The initial conductivity $\sigma_0$ was calculated from the highest point on the recorded current curve; this occurred at about 3 sec after the applied electric field was switched on. While $\sigma_0$ is not an accurate measure of the conductivity at $t = 0$, it has some interesting properties. The steady-state conductivity $\sigma_\infty$ was determined from the final steady-state current. The conductivity of single crystals was usually studied in two different crystal orientations with the electric field normal to either the (001) or (210) planes. Convenient notations like $\sigma_0(001)$, $\sigma_\infty(210)$, etc., are used in the text to follow; $\sigma_0(001)$ referring to the initial conductivity obtained with an electric field normal to (001) planes, and so on.

## Results

### *Pellets of AP in Nitrogen and Ammonia*

Some preliminary experiments were performed on the pellets of AP in dry nitrogen, and the results are shown in Fig. 1. The sample had been thoroughly annealed at 383°K under a vacuum of $10^{-5}$ Torr for 2 days, and a reproducible conductivity plot was obtained in several repeated runs between room temperature and 430°K. An activation energy $E$ of 1.08 eV was found between 390 and 423°K, while below 390°K $E$ was 0.90 eV. The conductivity plot could be further extended linearly when the sample was first heated to about 450°K. However, subsequent measurements after this run would usually produce a higher conductivity and a greater scatter of the conductivity data than those obtained in the lower-temperature runs. It is widely recognized that pellet samples may yield only qualitative results because of the possibility of significant surface conduction occurring on the extensive internal surfaces of the pellet. Despite this disadvantage reproducible data were obtained below 430°K but the behavior of the conductivity of an AP pellet after being heated above 430°K confirmed our belief that the thermal decomposition of AP above this temperature was sufficient to cause observable variations in conductivity. Since pellets decompose more readily than single crystals (*10*) we feel confident that our results using both compressed pellets and crystals are unaffected by thermal decomposition (except as referred to above) and that 430°K is a safe maximum temperature in our conductivity experiments (compare Ref. (*11*)).

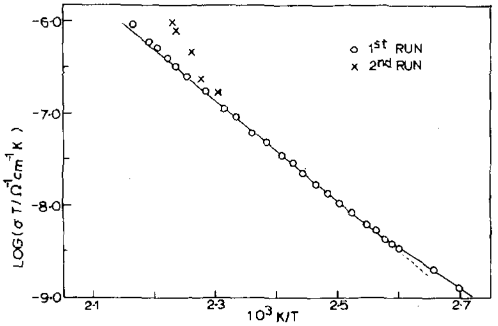


FIG. 1. Conductivity of a compressed pellet of AP in dry nitrogen.

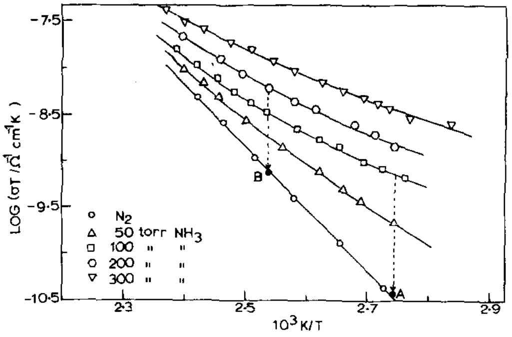


FIG. 2. Conductivity of an AP pellet under various pressures of $NH_3$. Points A and B show the conductivity measured after pumping off the $NH_3$ after runs 3 and 5, respectively.

The effect of dry ammonia gas on the conductivity of an AP pellet is shown in Fig. 2. The conductivity increased with the pressure of ammonia as indicated in experiments done at four different pressures, namely, 50, 100, 200, and 300 Torr. The enhancement of conductivity by ammonia was most pronounced in the low-temperature region, thus producing a set of curves with varying but increasing slopes.

Ammonia was found to be reversibly adsorbed on the AP because the conductivity returned to its original value in nitrogen after the system had been evacuated for 24 hr. Points A and B were obtained after complete removal of ammonia at the ends of the third and fifth runs, respectively.

### *Pure AP Crystals in Nitrogen and Ammonia*

The complete annealing of AP crystals took about 10 hr, much shorter than the time required for pellets, presumably because more moisture and adsorbed gaseous impurities were present in the powder from which the pellets were made. In Fig. 3 plots are shown for measurements in which the polarizing field was applied normal to the (001) planes of an AP crystal. The $\sigma_{\infty}(001)$ plot consists of two distinct linear regions from which the values of the activation energy were calculated to be 0.87 ± 0.05 eV, from 393 to 423°K, and 0.56 ± 0.05 eV below 393°K. In contrast with the steady-state conductivity, the initial conductivity $\sigma_0(001)$ only increased slightly over most of the temperature range under investigation, corresponding to the rather low activation energy of 0.06 eV.

The effect of ammonia on the conductivity of an AP crystal was examined in two different ways. Dry ammonia gas was admitted into the conductivity cell and the crystal was allowed to equilibrate with the ammonia for 24 hr at 353°K. The conductivity was then measured in $NH_3$ on the usual time scale, i.e., the temperature range 345–415°K was covered in about 10 hr. The effect of the $NH_3$ (not illustrated) was to raise the conductivity in both temperature ranges without changing the activation energies. However, if the conductivity was measured on a time scale that allowed longer times for equilibration of the crystal with the $NH_3$ gas at each temperature (Fig. 4) the enhancement of conductivity was accompanied by a decrease in activation energy to $\leqslant$0.25 eV. This suggests that a slow process, which probably involves bulk diffusion into the crystal, is occurring. At least part of the ammonia was absorbed irreversibly.

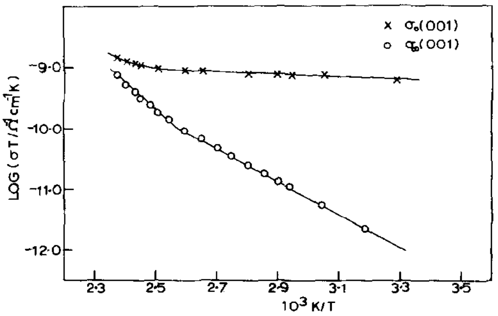


FIG. 3. Conductivity of an undoped AP crystal. ×: initial conductivity; O: steady-state conductivity.

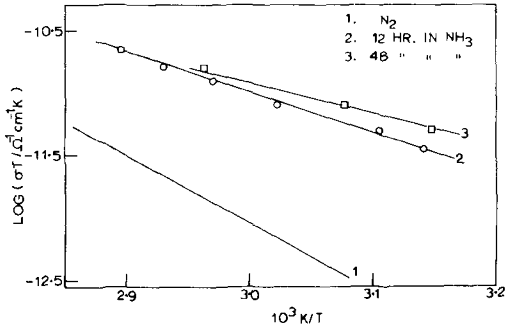


FIG. 4. Low-temperature conductivity of an AP crystal showing the effect of varying exposure to $NH_3$.

### *AP Doped with Divalent Cations*

The 1% AP:$Ba^{2+}$ crystal did not show any significant difference in conductivity from the pure crystal (Fig. 3); this is in agreement with results obtained by Thomas *et al.* (*6*). No further work was done on 1% AP:$Ba^{2+}$ because it seemed that $Ba^{2+}$ was not incorporated into the AP lattice to any significant extent.

In contrast the 5% AP:$Pb^{2+}$ crystal had a substantially lower conductivity than the pure crystal. Figure 5 shows the results of two measurements performed on the same piece of

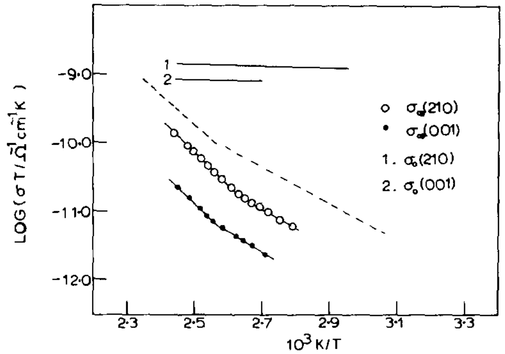


FIG. 5. Initial and steady-state conductivity of an AP crystal grown from solution containing 5 mole% of $Pb(ClO_4)_2$. The dashed line shows the steady-state conductivity of a pure AP crystal.

crystal. $\sigma_\infty(210)$ is about five times larger than $\sigma_0(001)$. The conductivity plots resemble that for a pure crystal in shape, being made up of two linear regions. The high-temperature segment yielded an activation energy of 0.88 ± 0.03 eV and the low-temperature segment gave 0.56 ± 0.05 eV. The initial conductivity of $Pb^{2+}$-doped AP showed hardly any temperature dependence.

### *AP Doped with Divalent Anions*

The presence of divalent anions in AP greatly enhanced its conductivity implying that the incorporation of divalent tetrahedral anions into the AP lattice took place more readily than that of divalent cations. Optical absorption and Raman scattering measurements of 0.1% AP:$CrO_4^{2-}$ have proved that $CrO_4^{2-}$ ions enter the AP crystal substitutionally (*12*). Both 0.1% AP:$SO_4^{2-}$ and 0.1% AP:$CrO_4^{2-}$ were characterized by conductivity plots with a single activation energy.

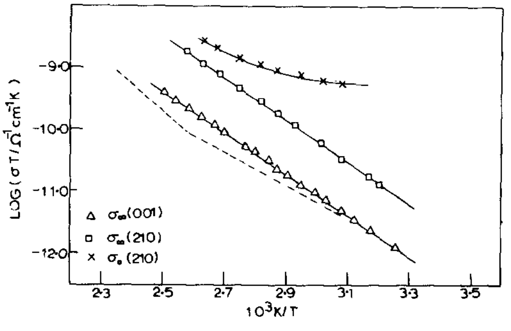


FIG. 6. Initial and steady-state conductivity of an AP crystal grown from solution containing 0.1 mole% of $(NH_4)_2SO_4$. The dashed line shows the steady-state conductivity of a pure AP crystal.

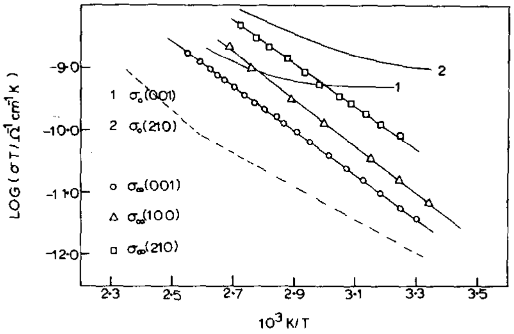


FIG. 7. Initial and steady-state conductivity of an AP crystal grown from solution containing 0.1 mole% of $(NH_4)_2CrO_4$. The dashed line shows the steady-state conductivity of a pure AP crystal.

The conductivity plot of a 0.1% AP:$SO_4^{2-}$ crystal is shown in Fig. 6. $\sigma_\infty(210)$ was found to be seven times that of $\sigma_\infty(001)$ but the conductivity curves have the same activation energy: 0.68 ± 0.04 eV. The temperature dependence of $\sigma_0$ was larger than that of both pure AP and AP : $Pb^{2+}$.

Figure 7 shows the conductivity plot of a 0.1% AP:$CrO_4^{2-}$ crystal. $\sigma_\infty(210)$ was ten times larger than $\sigma_\infty(001)$ and an activation energy of 0.72 ± 0.02 eV was obtained for both orientations. The initial conductivity appear as though they would intersect their respective $\sigma_\infty$ curves had measurements been possible at higher temperatures.

## Discussion

Significant conclusions regarding possible conduction mechanisms in AP may be drawn from the results of our doping experiments. $Pb^{2+}$ ions reduce the steady-state conductivity in both temperature regions but with no change in activation energy. $SO_4^{2-}$ or $CrO_4^{2-}$ increase the conductivity and replace the two segment plot (Fig. 3) by a single line (Figs. 6 and 7). Now the incorporation of $Pb^{2+}$ would increase the concentration of cation vacancies or decrease the concentration of cation interstitials or anion vacancies. Electrical conduction in AP cannot therefore be due to the motion of cation vacancies, as proposed by Keenan and Ohanian (*8*) for $T > 373°K$. Although an increase in $\sigma$ by divalent anions and a decrease by divalent cations might at first be construed as consistent with a charge transport mechanism that involves the migration of either anion vacancies or cation interstitials, we are compelled to reject these possibilities because of the change in activation energy that accompanies divalent anion doping, but not $Pb^{2+}$ doping. Modification, by doping, of defect concentrations, when these defects are the charge carriers, shifts the extrinsic conductivity up or down without changing the activation energy, since the jump of the unassociated defect is unaffected by the impurity. (Some curvature of the extrinsic region may be induced by a temperature-dependent association of impurities and defects). The intrinsic region (upper segment of a two-segment plot for conventional ionic conductors) is unaffected in position and slope, although it may be shortened by the increase in conductivity at lower temperatures. In AP the activation energy changes from 0.56 to 0.68–0.72 eV on anion doping. The proposal by Owen *et al.* that charge transport in AP is due to interstitial $NH_4^+$ ions is not, therefore, valid. Nor can anion vacancies be the mobile species; we must look for other mechanisms in which anion vacancies or cation interstitials play a role in the generation of the charge carriers without being the mobile species. We can, however, see no convincing arguments for a mechanism that would depend on cation interstitials and we henceforth limit the discussion to models that involve anion vacancies.

The enhancement of the conductivity of AP by ammonia (Figs. 2 and 4) and by $HSO_4^-$ (*7*) strongly implies that protons are the mobile species. In the presence of such additives proton transfer mechanisms can be conceived that depend on the migration either of proton holes in the cation sublattice or of protons in the anion sublattice (*3, 7*). In the absence of proton donors or acceptors the proton defects must be formed by the transfer of a proton from an $NH_4^+$ cation to a $ClO_4^-$ anion (*3*). The formation of such a molecular defect is believed to be an essential step in the sublimation of $NH_4Cl$ and of AP (*13*) and has been proposed by Herrington and Staveley (*14*) as the initial step in the charge transport in $NH_4Cl$. One should be clear, however, that the complete three-stage Herrington–Staveley mechanism is one for the motion of anion or cation vacancies and thus corresponds to ionic transport. Harris and Vella (*15*) have shown that in ADP there is surface decomposition to $NH_3$ and $H_3PO_4$ down to at least 313°K and have proposed that the formation of molecular defects is the initial step in proton conduction in pure ADP.

We propose, therefore, that in AP below 390°K the initial step in charge transport is the formation of molecular defects, corresponding to protons in the anion sublattice and proton holes in the cation sublattice, by the proton transfer process

$$NH_4^+ + ClO_4^- = NH_3 + HClO_4 \qquad (1)$$

The doping experiments indicate that (1) is occurring at anion vacancies. The current seen after our rather slow instrument response time of 3 sec is largely the displacement current associated with (1)—although some other slower processes have also begun. The activation energy associated with step (1) is expected to be small by analogy with the value of 0.15 eV for the energy needed to transfer a proton from $NH_4^+$ to $Cl^-$ in $NH_4Cl$ (*16*). The small activation energy for $\sigma_0$ of 0.06 eV in pure AP and zero in $Pb^{2+}$-doped AP confirms this expectation. The initial current flow then is associated with the formation of trapped protons and holes; charge migration requires the activated motion of these species.

Electrical conductivity in single-crystal AP has been shown for the first time in this work

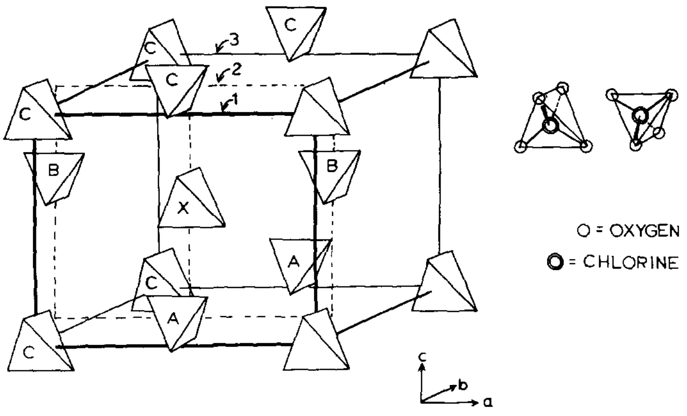
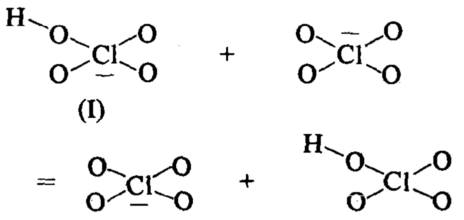


FIG. 8. Unit cell of AP showing the anion positions.

to be anisotropic. Figure 8 shows the $ClO_4^-$ anions in one unit cell of AP. Each central $ClO_4^-$ (x) is surrounded by 10 nearest $ClO_4^-$ neighbors, 2 (A) at a distance 4 Å, 2 (B) located at 4.7 Å in the mirror plane, and 6 (C) at 5.6 Å. Since the $ClO_4^-$ anions are not freely rotating below the orthohombic–cubic transition temperature of 513°K, the continuation of proton jumps in the anion sublattice would depend on the ability of the $HClO_4$ molecule (≡ a localized proton) to rotate sufficiently to bring the proton into a favorable position for the next jump. It seems that jump distance, although an important consideration, is not the only factor controlling proton mobility. By taking an indirect path a proton can proceed 10.5 Å in the direction ⊥(210) by taking jumps between anions whose centers are 4.7, 4.0, 4.0, and 4.7 Å apart. Although the most direct path ⊥(001) would involve two jumps between centers separated by 4.0 and 5.6 Å, an alterative path involves jumps between anions separated by 4.7, 4.0, 4.7, and 4.0 Å, i.e., the same jumps as the path ⊥(210) but in a different order. The net distance traversed is 7.2 Å. If jump distance were the only criterion an anisotropy factor of about 1.35, instead of around 7, would be expected. However, two of the jumps along [001] are almost perpendicular to the field so that the rotation of the $HClO_4$ dipole receives much less assistance from the very small component of the field (~0.17 ε along the jump direction) then it does for the other jumps along [001] or for any of the four jumps ⊥(210). Thus along the *c* direction the proton is faced either with excessively long jumps or with "normal" length jumps, some of which receive very little assistance from the field.

In the cation sublattice the $NH_4^+$ ions are free-rotating and an equivalent anisotropy of migration paths does not exist. We conclude that proton migration in the anion sublattice is rate-determining and is expected to be anisotropic with the *c* axis the least favored direction. Besides the detailed measurements ⊥(210) a few runs were made with the field oriented along [100] or [010] and the conductivity was found to be higher than along [001] (e.g., Fig. 7) as expected from the above analysis.

In pure AP, the energy to form a proton defect being 0.06 eV the migration activation energy for the process



(2)

is 0.50 eV. We consider this a reasonable value since (2) requires partial rotation of the $ClO_4^-$

ion I which temporarily has a proton attached. This is a very similar magnitude to the activation energy for proton conduction in the anion sublattices of ADP (0.47 eV) and KDP (0.52 eV) (*15*).

If only the protons migrated and the holes remained trapped a space charge would develop within the AP and the steady-state current would fall to zero. A finite steady-state current requires that the electrode processes at anode and cathode proceed at the same rate equal to the rate of arrival of charged species at the electrode. If the arrival rate exceeds the discharge rate then electrode polarization results. It was conceivable that the dc electrical conductivity might have told us nothing about charge migration processes except that they were faster than the one or other of the electrode processes, had the latter been rate determining. In that case, however, the activation energy of $\sigma_\infty$ would not have been altered by small changes in concentration of mobile species. Although the rates of electrode reactions could conceivably display some anisotropy it seems more likely that the observed factor of ~10 in $\sigma_\infty$ indicates a bulk effect rather than an electrode effect. We conclude then that the rate of proton transfer in the anion sublattice is rate determining and that once the protons arrive at the cathode they discharge

$$\begin{aligned} H^+ + e^- &= H, \\ H + H &= H_2, \end{aligned} \tag{3}$$

at a rate faster than the migration rate. Meanwhile proton holes are migrating to the anode; there they discharge, presumably by the process

$$NH_3 + ClO_4^- = e^- + NH_3 + Cl + 2O_2 \tag{4}$$

and in the steady state the rate at which process (4) takes place equals that of the $H_2$ evolution at the cathode. Since the rate of proton hole migration exceeds that of protons in the anion sublattice there develops a space charge in front of the anode until the magnitude of this is sufficient to slow the arrival rate of holes to that of protons at the cathode.

We summarize our model for the low-temperature (LT) dc conduction in undoped AP crystals <423°K. (i) On applying the field protons jump from $NH_4^+$ to $ClO_4^-$ next to anion vacancies. This is a fast process requiring an activation energy of only 0.06 eV. (ii) The proton defects in the anion sublattice require an activation energy of 0.50 eV to migrate and this process is rate determining. (iii) The migration of proton holes to the anode in the cation sublattice is more facile than of protons in the anion sublattice.

We now examine the consistency of the model with respect to the remaining experimental facts.

### *Pure AP Crystals above 423°K and $Pb^{2+}$-Doped Crystals*

The conduction process is marked by an increase in activation energy from 0.56 to 0.87 eV. This change in slope is not the usual change from extrinsic to intrinsic conduction in ionic crystals because the high-temperature (HT) $\sigma_\infty$ is also depressed by $Pb^{2+}$. "Pure" AP contains $SO_4^{2-}$ ion impurity and therefore the crystals grown from this material contain anion vacancies, $SO_4^{2-}$ and, inevitably, complexes (associated divalent anion–anion vacancy pairs) formed during crystal growth. Incorporation of $Pb^{2+}$ ions leads to a pairing up of $Pb^{2+}$ and $SO_4^{2-}$ on adjacent sites, as occurs in alkali halides, for example, and a reduction in the concentration of free anion vacancies, of divalent anion–anion vacancy complexes, and of free divalent anions. We propose, therefore, that the dc conductivity of "pure" AP consists of the processes outlined above that the formation of protons and proton holes occurs both at free anion vacancies with $E = 0.06$ eV, and at divalent anion–anion vacancy complexes with a more substantial activation energy, the latter process resulting in a proton which is trapped in the local field of the divalent anion. The energy needed to free the protons is just the difference between the two activation energies or 0.87 − 0.56 = 0.31 eV. Both processes leading to mobile protons go on simultaneously but at LT the one with the lower formation energy (0.06 eV) dominates and at HT that with the higher formation energy (0.06 + 0.31) eV.

### *Crystals Doped with $SO_4^{2-}$ and $CrO_4^{2-}$ Ions*

Doping with divalent anions $A^{2-}$ increases the concentrations of anion vacancies, complexes, and free $A^{2-}$. The increase in $E$ by 0.12 eV in 0.1% AP:$SO_4^{2-}$ and 0.16 eV in 0.1% AP:$CrO_4^{2-}$ we attribute to an average increase in the formation energy of the mobile protons and proton holes due to the proximity of $A^{2-}$ ions to the formation site. A significant fraction of the anion vacancies is within a few lattice sites of a divalent anion. The local Coulomb field due to the $A^{2-}$ ions make it harder for protons to escape from the proton hole and so the formation energy is increased. Even order of magnitude calculations is impossible due to uncertain polarization effects. However, if the explanation of the high-temperature conductivity is correct and 0.37 eV is the trap depth for a proton trapped at an $A^{2-}$-anion vacancy complex, then effects of this magnitude (0.06 to 0.10 eV) do not seem unreasonable. (For consistency, it is necessary to quote $E$ values to the second decimal place but the accuracy of these small numbers may be ascertained from the statistical limits quoted in Table I. For example, the apparent difference in $E$ for $SO_4^{2-}$- and $CrO_4^{2-}$-doped AP may or may not be real, although it appears to be from the graphs.)

### *Crystals Treated with $NH_3$*

Crystals and pellets treated with $NH_3$ both show an enhanced conductivity. The effect is more pronounced for pellets and is easily reversed by pumping. The trend of the curves in Fig. 2 shows that $NH_3$, which presumably

TABLE I

VALUES OF ACTIVATION ENERGY FOR dc CONDUCTION IN PURE AND DOPED AP

| Sample | Activation energy (eV) | | Remark |
|---|---|---|---|
| (A) AP pellet | 1.08 | (HT)[a] | Reference line |
| | 0.90 | (LT)[b] | |
| AP pellet in $NH_3$ | 0.45–0.70 | | $\sigma$ increased |
| (B) AP crystal | 0.87 ± 0.05 | (HT) | Reference line |
| | 0.56 ± 0.05 | (LT) | |
| AP crystal in $NH_3$ | 0.87 ± 0.05 | (HT) | $\sigma$ increased |
| | 0.56 ± 0.05 | (LT) | |
| | Lower values if measurement time lengthened | | |
| AP:$Ba^{2+}$ | 0.80 ± 0.03 | (HT) | $\sigma$ unaffected |
| | 0.56 ± 0.02 | (LT) | |
| AP:$Pb^{2+}$ | 0.88 ± 0.03 | (HT) | $\sigma$ decreased |
| | 0.56 ± 0.05 | (LT) | |
| AP:$SO_4^{2-}$ | 0.68 ± 0.04 | | $\sigma$ increased |
| AP:$CrO_4^{2-}$ | 0.72 ± 0.02 | | $\sigma$ increased |

[a] HT means high-temperature region.

[b] LT means low-temperature region.

diffuses rapidly down the interstices between the particles so that the internal surfaces became covered, introduces an additional conductivity at low temperatures and that this has a low $E$. Figure 4 shows that $E \leqslant 0.25$ eV. Adsorption of $NH_3$ leads to the creation of additional proton holes which migrate through the crystal in the cation sublattice. Because the charge carriers are introduced by doping, rather than by dissociation of the crystal as in Eq. (1), there is no necessity for an equivalent transport of protons in the anion sublattice. The conductivity increases because of the larger number of carriers and $E$ is lowered because proton hole transport is more facile than that of protons, as was already deduced. From a purely structural point of view this may seem strange as the actual jump distance is quite large, about 2.5 Å, but presumably the freely rotating cations lead to many favorable jump opportunities.

## Acknowledgment

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