

## ELECTRICAL CONDUCTIVITY AND THERMALLY STIMULATED CURRENT IN THE PARAELECTRIC PHASE OF $(\text{NH}_4)_2\text{SO}_4$

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Anomalous variations of d.c. electrical conductivity with temperature are observed in ammonium sulphate single crystals, suggesting a possible phase transition at  $150^\circ\text{C}$ . Measurements of thermally stimulated current also support these results. The mechanism of electrical conduction is explained on the basis of studies made on doped and quenched crystals.

### 1. INTRODUCTION

AMMONIUM SULPHATE (AS) is known to undergo a first order ferroelectric phase transition at  $-50^\circ\text{C}$ . The symmetry of the crystal changes from  $D_{2h}^{16}-Pnam$  in the paraelectric phase to  $C_{2v}^9-Pna2_1$  in the ferroelectric phase ( $T < -50^\circ\text{C}$ ). The nature of this transition is rather unique and it has features which are different from those of usual ferroelectrics. The peculiarity of this transition has been the subject of a large number of investigations which include structural [1], mechanical [2], dielectric [3–14], magnetic resonance [15–23] as well as infrared and Raman spectral studies [24–28]. On the other hand the paraelectric phase of this material is less well investigated. In this paper we present the results of our studies on the d.c. electrical conductivity along the three crystallographic axes in the paraelectric phase of pure, doped and quenched samples of  $(\text{NH}_4)_2\text{SO}_4$  single crystals. Thermally stimulated current (TSC) for the poled and unpoled samples also are investigated. No detailed investigations on the electrical conduction mechanism of this crystal with particular reference to the crystallographic axes and to the effects of doping and quenching in the paraelectric region have been carried out so far. The only conductivity measurement reported in the literature is that due to Hugo Schmidt [29] who apparently obtained a linear conductivity plot throughout the paraelectric region with an activation energy value of 0.76 eV.

### 2. EXPERIMENTAL

Single crystals of AS were grown from aqueous solution by slow evaporation method. Thin plate specimens having typical size of  $5 \times 5 \times 1 \text{ mm}^3$  were cut perpendicular to the  $a$ -,  $b$ - and  $c$ -axes. The broad faces of the samples were coated with quick drying silver conducting paint. The sample holder and the chamber for temperature variation studies used here have been

described previously [30]. The specimens were left for 24 hr in vacuum ( $10^{-3}$  torr) and all measurements were carried out in the same condition to avoid surface conduction. The rate of the temperature variation was  $2^\circ\text{C hr}^{-1}$  in the region  $140\text{--}160^\circ\text{C}$  and  $10^\circ\text{C hr}^{-1}$  in other regions for conductivity measurements. Different rates varying from  $10^\circ\text{C hr}^{-1}$  to  $2^\circ\text{C min}^{-1}$  were used for TSC measurements. Temperature measurements were carried out by two copper–constantan thermocouples arranged just above and below the specimen. A potential difference of 10–20 V was applied across the crystal for conductivity measurements. The measurements of both conductivity and TSC were done by a vibrating condenser electrometer (Electronic Corporation of India Ltd. Model EA 815) and each reading was checked by means of a d.c. Microvoltmeter (Marconi Model TF 2655).

### 3. RESULTS

The results of the electrical conductivity measurements on pure AS single crystals along the three crystallographic axes are shown in Fig. 1 in the conventional  $\log \sigma$  vs.  $10^3/T$  plot. It can be seen that contrary to the previous result [29], the present plot has two distinct straight line regions characteristic of ionic crystals. The magnitude of conductivity along the  $c$ -axis ( $\sigma_{33}$ ) is higher than that along  $a$  and  $b$  ( $\sigma_{11}$  and  $\sigma_{22}$ ) by a factor of about two. A significant aspect of the present result is that in between the straight line regions (in the vicinity of  $150^\circ\text{C}$ ) the curves exhibit a definite anomalous behaviour. In this portion the conductivity goes to a maximum and then decreases by a small amount forming a peak and remains constant afterwards corresponding to an increase in temperature of about  $15^\circ\text{C}$ . For the second run of the measurement on the same crystal sample, after a very slow cooling (at a rate of  $5^\circ\text{C hr}^{-1}$ ) this anomalous effect becomes more pronounced with a subsequent rise in conductivity of

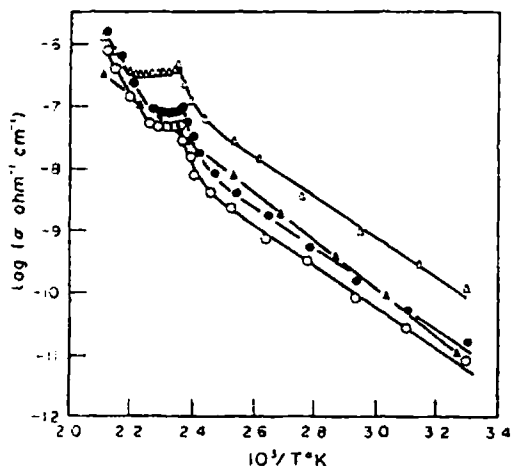


Fig. 1. Conductivity plots for pure  $(\text{NH}_4)_2\text{SO}_4$  single crystals. —●—●— along the  $c$ -axis; —○—○— along the  $a$ - or  $b$ -axis; —▲—▲— result reported previously in [29]; —△—△— result for a second run of the measurement after a very slow cooling at a rate of  $5^\circ\text{C hr}^{-1}$  (along the  $c$ -axis).

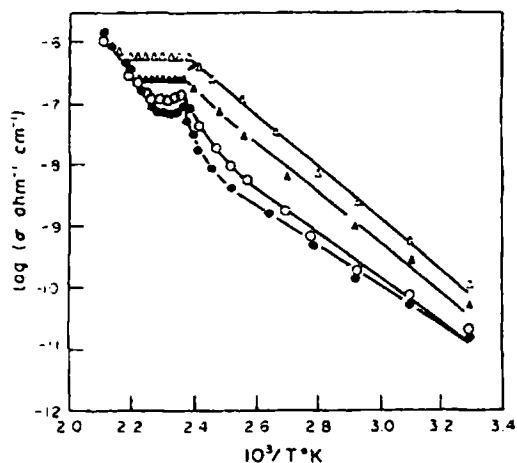


Fig. 2. Conductivity plots for doped  $(\text{NH}_4)_2\text{SO}_4$  single crystals along the  $c$ -axis. —●—●— undoped; —○—○— sample doped with  $\text{Mn}^{2+}$ ; —▲—▲— doped with  $\text{Cu}^{2+}$ ; —△—△— doped with  $\text{Zn}^{2+}$ .

about one order of magnitude in the lower straight line region (Fig. 1). The third run shows no appreciable change from the second one. The linear regions of the curve corresponding to the pure crystal along the  $c$ -axis can be described by the following equations:

$$\sigma_e = 1.05 \times \exp(-7627/T), \quad (1)$$

$$\sigma_i = 8.01 \times 10^9 \exp(-17219/T), \quad (2)$$

so that the conductivity of the pure crystal along the  $c$ -axis throughout the whole region except in the vicinity of the anomalous part can be represented by

$$\sigma_{33} = \sigma_e + \sigma_i. \quad (3)$$

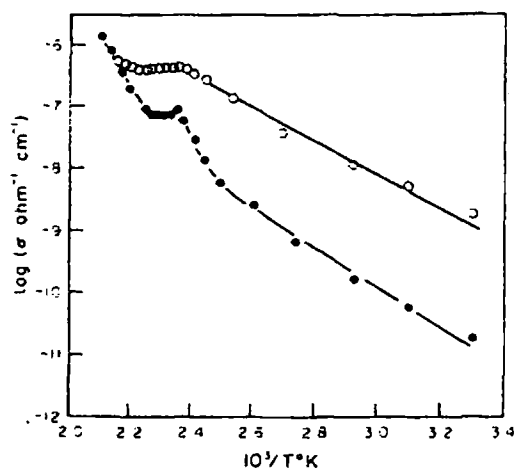


Fig. 3. Conductivity plots along  $c$ -axis for a pure sample (—●—●—) and for a sample quenched from  $150^\circ\text{C}$  (—○—○—).

The activation energies corresponding to the lower and higher regions are given by 0.67 and 1.50 eV respectively. These activation energy values are found to be independent of the axes of the crystal.

Conductivity measurements were extended to samples doped with divalent cationic impurities,  $\text{Zn}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Mn}^{2+}$  (Fig. 2) with a view to explain the mechanism of electrical conduction in the crystal. It is found that these impurities have in general the effect of increasing the conductivity and activation energy in the lower linear part. The effect is more pronounced in the case of  $\text{Zn}^{2+}$  doped samples which show an increase in conductivity of about one order of magnitude. The activation energy in this case increases by 0.2 eV. The doped samples also exhibit conductivity anomaly with a difference that the constant conductivity region increases in these cases.

To understand the mechanism of electrical conduction in the anomalous and in the upper straight line regions, measurements were carried out on crystals quenched from higher temperatures to room temperature (Fig. 3). Three types of quenched samples were used: (1) crystals quenched from  $150^\circ\text{C}$  corresponding to the anomalous region, (2) those quenched from  $190^\circ\text{C}$  and (3) samples quenched from  $140^\circ\text{C}$ . The quenching was done by keeping the sample in vacuum at the appropriate quenching temperature for 10 hr and then suddenly exposing it to a dry air jet at room temperature. Measurements reveal that the conductivity of first type of samples increases by more than two orders of magnitude with a lowering of activation energy by an amount of 0.11 eV (Fig. 3), while the second type of samples show a still higher conductivity with a decrease in activation energy by 0.3 eV. The third type of samples show only a slight increase in conductivity with a decrease in activation energy by 0.04 eV.

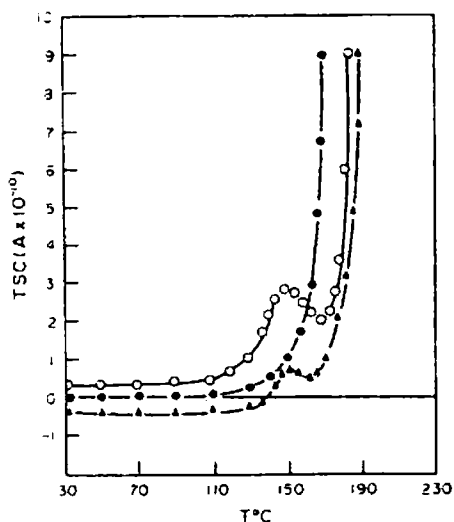


Fig. 4. TSC vs. temperature plot for pure  $(\text{NH}_4)_2\text{SO}_4$  single crystals along the  $c$ -axis. The rate of variation of temperature is  $1^\circ\text{C min}^{-1}$ . —●—●— for poled samples (poled at  $2\text{KV cm}^{-1}$ ); —○—○— and —▲—▲— for unpoled samples.

Measurement of TSC in AS in the short circuited condition also show anomalous variations in the vicinity of  $150^\circ\text{C}$  (Fig. 4). Poled and unpoled samples were used with different heating rates. For both samples TSC is found to be dependent on the time variation of temperature. For unpoled samples the direction of TSC reverses in certain cases (Fig. 4). In the vicinity of  $150^\circ\text{C}$ , the TSC corresponding to the unpoled samples has a peak followed by a sudden increase. For poled samples TSC starts nearly from zero and goes up abruptly around  $150^\circ\text{C}$ . No appreciable changes in the shape of the curve is observed during the second and third cycle of heating.

All the above results for conductivity and TSC were confirmed by repeating the measurements on ten samples or more in each case. The values given here are an average over these measurements.

#### 4. DISCUSSION

Anomalous effects in conductivity were reported [30–33] in various ammonium containing ionic crystals viz.  $\text{NH}_4\text{Cl}$ ,  $\text{NH}_4\text{Br}$  and  $\text{LiNH}_4\text{SO}_4$  at their high temperature phase transition point. In AS no such high temperature phase transition has been reported previously. Now the observed conductivity anomaly at  $150^\circ\text{C}$  may indicate in all possibility a phase transition taking place in AS. Being an improper ferroelectric AS may not exhibit a detectable dielectric anomaly at this temperature. This could be the reason that Hoshino *et al.* did not detect any anomalous change in dielectric constant even though they made measurements from  $-130$  to  $+170^\circ\text{C}$  [3]. Our previous work in  $\text{LiNH}_4\text{SO}_4$  [30, 31]

in this line reported that conductivity study is a very effective method for the detection of a phase transition in crystals which come under the class of improper ferroelectrics. Apparently this anomalous phenomenon on the d.c. conductivity of AS went unnoticed in the measurement reported previously [29]. We believe that this may be due to a higher heating rate that might have been employed in that experiment.

Several mechanisms have been suggested by various authors for the electrical conduction in ionic crystals containing ammonium groups [30–38]. The conductivity data for the pure AS crystals in the paraelectric region fall into two straight line regions with activation energies 0.67 and 1.50 eV showing that more than one defect mechanism is involved in the conduction process. Unlike typical ionic crystals, AS has two ions of larger size (for ammonium ion, ionic radius is 1.43 Å; the sulphur–oxygen bond length in sulphate ion is 1.44 Å with oxygen having an ionic radius of 1.40 Å). On account of the large size of these ions, the probabilities of occurrence [39] of interstitial ammonium and sulphate ions, and the mobility of their vacancies are very low. Hence ammonium and sulphate ions and their vacancies cannot contribute to the conduction process in any significant manner. Even though the starting material is recrystallised five times using triply distilled water, it is known to contain cationic and anionic impurities of the order of  $10^{-5}$  molar fraction. Our experimentally well confirmed result is that addition of divalent cationic impurities into the crystal enhances the conductivity. Hence we can readily conclude that the conduction process in AS in the structure sensitive region is dominated by the inherent cations.

The anomalous part of the conductivity plot can be explained as follows. As in the case of  $\text{NH}_4\text{Cl}$  [33], normally, the ammonium ions in AS are assumed to be in a state of torsional oscillation, from which it changes to a state of free rotation in the vicinity of  $150^\circ\text{C}$ . This free rotation might cause the generation of a large number of protonic defects giving rise to an increase in conductivity. Part of the generated protonic defects can be suddenly reabsorbed by the surrounding lattice and when the temperature corresponding to the constant conductivity part is reached the concentration of the generated and reabsorbed defects become almost equal. The quenching of the crystal from the anomalous region ( $150^\circ\text{C}$ ) leads to freeze the excess carriers produced at the transition point and these frozen-in defects [40] can be responsible for the increase in conductivity of the quenched sample. Hence the decrease in activation energy of 0.11 eV should evidently correspond to the migration of these frozen-in defects. Miller *et al.* [41] found that the activation energy of  $(\text{NH}_4)^+$  rotation in AS is 0.1 eV. Assuming that the activation energy of

protons in AS is not widely different from this value, one can conclude that protonic conduction is responsible for the conductivity anomaly noted here. Above  $170^\circ\text{C}$  the plots for all the type of samples coincide and hence the region above this temperature can be considered as the intrinsic region. The conductivity at this region can be attributed to one of a mixed nature due to the following defects: (1) protonic defects, (2) inherent cationic defects and (3) ions dissociated from impurity–vacancy complexes.

It is well known that TSC in general has four components, viz., (1) thermoelectric, (2) pyroelectric, (3) piezoelectric (second order pyroelectric) and (4) electrochemical. In the present case since there is no thermal gradient existing between the electrodes, and since both electrodes are of the same material, the contributions due to the first and the last components can be neglected. This is also evident from the experimental result that the observed TSC is dependent on the time variation of temperature. Hence TSC plotted in Fig. 4 may have originated from first and second order pyroelectric effects. The peak at  $150^\circ\text{C}$  may be due to a sudden change in polarization at the onset of free rotation of ammonium group in the crystal. As the poled crystals can have single domain structure TSC from them will increase suddenly in the anomalous region.

### 5. CONCLUSIONS

The migration of inherent cationic impurities is suggested to be the dominant mechanism of electrical transport in single crystals of AS in the extrinsic region. This mechanism is the same along the different crystallographic axes of the crystal, since the activation energy values are independent of directions. The anomalies observed in the conductivity as well as TSC plot can be due to a hitherto unreported phase transition occurring in the crystal in the vicinity of  $150^\circ\text{C}$ . The former one is explained as due to release of protons from the ammonium group while the latter is attributed to a change in polarization. The intrinsic region starts from  $170^\circ\text{C}$  and in this region the dominant carriers are protonic defects, inherent cationic defects and ions dissociated from impurity–vacancy complexes.

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