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## LETTER TO THE EDITOR

# DC electrical conductivity and phase transitions in $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$

U Syamaprasad and C P G Vallabhan

Department of Physics, Cochin University, Cochin 682022, India

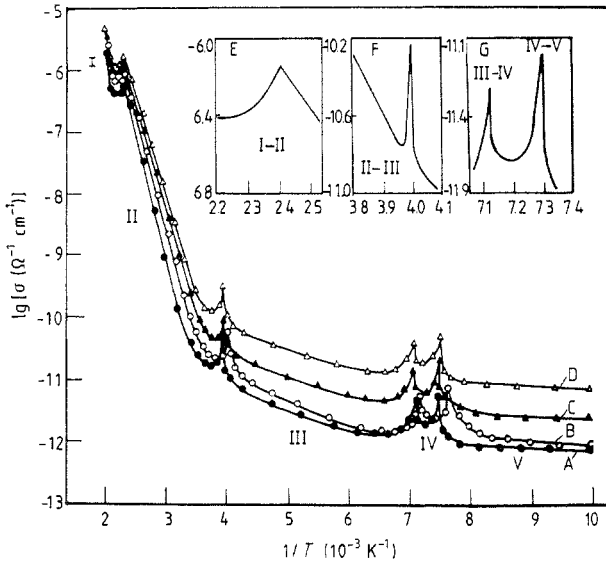
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**Abstract.** Four distinct peaks are observed at 140,  $-26$ ,  $-132$  and  $-140^\circ\text{C}$  in the  $\sigma_c$  against  $T^{-1}$  plot between 200 and  $-196^\circ\text{C}$  for  $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$ , corresponding to four different phase transitions of which the one at  $-26^\circ\text{C}$  is reported here for the first time. Data on doped samples reveal the charge transport mechanism in the crystal.

Triammonium hydrogen disulphate (TAHDS) is an extremely interesting crystal which at atmospheric pressure is reported to exhibit as many as five phase transitions at temperatures 140,  $-8$ ,  $-132$ ,  $-140$  and  $-210^\circ\text{C}$  (Gesi 1976a, 1980). The transition at  $140^\circ\text{C}$  is a ferroelastic one in which the crystal changes from trigonal ( $T > 140^\circ\text{C}$ ) to monoclinic (Suzuki 1979), while that occurring at  $-210^\circ\text{C}$  is a ferroelectric transition, the crystal remaining ferroelectric below this temperature (Gesi 1980). Besides the dielectric anomalies associated with the above phase transitions, this material also shows a broad peak in the dielectric plot around  $-28^\circ\text{C}$  (Gesi 1976a) which was believed to be too broad to be due to a phase transition. However, it was later found that this broad peak becomes more prominent and is sharpened by the application of external pressure. When the pressure increases above 4.9 kbar it splits into two well defined peaks between which a ferroelectric phase appears (Gesi 1976b). Even though some structural (Suzuki and Makita 1978), dielectric (Pepinsky *et al* 1958, Gesi 1976a, b, 1980), calorimetric (Suzuki *et al* 1979) and dilatometric (Suzuki 1979) studies on this remarkable crystal have appeared in the literature, many of its other details still remain to be investigated. This Letter reports the results of our studies on the electrical conductivity of pure and doped TAHDS single crystals along the  $c^*$  axis from liquid nitrogen temperature to  $200^\circ\text{C}$ . We also report the detection of a new phase transition in TAHDS at  $-26^\circ\text{C}$  without applying any external pressure.

Single crystals of TAHDS were grown by slow evaporation from an aqueous solution containing a 3:1 mole fraction of  $(\text{NH}_4)_2\text{SO}_4$  and  $\text{H}_2\text{SO}_4$ . Doping of the crystal with  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  was done by adding specific amounts of  $\text{CuSO}_4$  and  $\text{ZnSO}_4$  in the solution. Crystals obtained were plates of pseudo-hexagonal shape with predominant (001) faces. Quick drying silver paint was applied on these faces to act as electrodes, and the electrical conductivity perpendicular to the (001) plane ( $\sigma_{c^*}$ ) was measured by using an electrometer (Electronic Corporation of India Ltd, EA 815). The same was checked by means of a DC microvoltmeter (Marconi TF 2655). A steady voltage of 10–100 V was applied to samples of typical size  $5 \times 5 \times 0.5 \text{ mm}^3$ . The sample holder, the chamber for tem-

perature variation studies, the measurement of temperature and the other details have been described previously (Syamaprasad and Vallabhan 1980a). The rate of temperature variation was  $2^{\circ}\text{C h}^{-1}$  in the transition regions and  $5^{\circ}\text{C h}^{-1}$  in other regions. No polarisation effect was observed for the current densities used here. To avoid surface conduction effects the samples were annealed at  $100^{\circ}\text{C}$  for 3 h in vacuum ( $10^{-3}$  Torr) before each measurement and all the measurements were done under the same vacuum condition.



**Figure 1.** DC electrical conductivity plots for  $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$  single crystals along the  $c^*$  axis: A, for pure sample in the heating run; B, for pure sample in the cooling run; C, for  $\text{Zn}^{2+}$  doped sample; D, for  $\text{Cu}^{2+}$  doped sample (concentration of  $\text{Zn}^{2+}$  and  $\text{Cu}^{2+}$  is less than 0.1 molar fraction). Curves E, F, and G show the details of the conductivity peaks corresponding to the different phase transitions.

Curves A and B in figure 1 (A, temperature rising; B, temperature falling) show the variation of  $\sigma_{c^*}$  with temperature for pure TAHDS single crystals in the conventional  $\lg \sigma$  versus  $10^3/T$  plot. In both the heating and the cooling runs the curves have four unmistakable peaks at 140,  $-26$ ,  $-132$  and  $-140^{\circ}\text{C}$  which evidently correspond to four distinct phase transitions occurring in the crystal. The corresponding five phases obtained here are denoted as phases I, II, III, IV and V in order of decreasing temperature. The transition at  $-140^{\circ}\text{C}$  is accompanied by a thermal hysteresis of  $4^{\circ}\text{C}$  during heating and cooling cycles. The detailed shape of each peak in the heating cycle is separately shown in curves E, F and G given in the inset of figure 1. In contrast to the dielectric results reported by Gesi (1976a, b), we have obtained here a very sharp peak at  $-26^{\circ}\text{C}$  without applying any external pressure (the contact pressure applied to the crystal was only about  $300 \text{ g cm}^{-2}$ ). On the other hand, no conductivity anomaly was observed at  $-8^{\circ}\text{C}$  even though a temperature variation of  $2^{\circ}\text{C h}^{-1}$  was used in this region. Except in the vicinity of these four peaks the plots have straight line regions in the various phases characteristic of ionic crystals (Lidiard 1957). Phase IV is so narrow that no linear region can be perceived here. By taking the average values in the heating and cooling cycles the

straight line regions for the pure crystal can be represented by the following equations:

$$\sigma_I = 9.97 \times 10^8 \exp(-16442/T) \quad (1)$$

$$\sigma_{II} = 1.07 \times 10^2 \exp(-8101/T) \quad (2)$$

$$\sigma_{III} = 1.34 \times 10^{-10} \exp(-714/T) \quad (3)$$

$$\sigma_V = 2.63 \times 10^{-12} \exp(-133/T). \quad (4)$$

These equations give activation energy values 1.43, 0.71, 0.062 and 0.012 eV, corresponding to phases I, II, III and V respectively. Conductivity measurements were extended to samples doped with divalent cationic impurities (curves C and D in figure 1) with a view to explaining the mechanism of electrical conduction in the crystal. It is found that doping in general has the effect of enhancing the conductivity of the crystal. The effect is more pronounced in phases III, IV and V. The activation energy of the doped samples does not significantly change in these phases, while it shows a decrease in value in phase II. In phase I the conductivity and activation energy of all the samples coincide and this region may be considered as the intrinsic region.

Recent investigations show that electrical conductivity measurement is a very sensitive method for the detection of a phase transition in improper ferroelectrics containing ammonium groups, since in such materials the change in conductivity at the transition point is much greater than the variation in dielectric constant (Syamaprasad and Vallabhan 1980a, b, c, 1981). The results reported here on TAHDS are entirely in accordance with the above conclusion. The very sharp peak observed at  $-26^\circ\text{C}$  should definitely correspond to a new phase transition in the crystal at atmospheric pressure. Even though the details have not been published, Pepinsky *et al* (1958) have mentioned a dielectric anomaly at  $-26^\circ\text{C}$  which is in support with our observation.

Several mechanisms were suggested by various authors for the electrical conduction in ionic crystals containing ammonium groups (Herrington and Stavely 1964, Kroger 1969, Murti and Murthy 1973, Murti and Prasad 1974a, b, Syamaprasad and Vallabhan 1980a, b, c, 1981). The conductivity data for pure TAHDS single crystals above  $-196^\circ\text{C}$  fall into different straight line regions, which show that several defect mechanisms are involved in the conduction process. Usually in ionic crystals containing ammonium groups, the possible types of point defects are normal ionic and electronic defects and protonic defects. Of these electronic defects, electrons and holes are very small in number. As noted earlier (Syamaprasad and Vallabhan 1980a, b, c, 1981), in crystals containing  $(\text{NH}_4)^+$  and  $(\text{SO}_4)^{2-}$  the contribution to the electrical conduction process by these ions and their vacancies can be neglected on considerations based on their sizes. The experimentally well confirmed result that the addition of divalent cationic impurities into the crystal enhances the conductivity of the crystal proves that the positive charge carriers in the crystal are responsible for the conduction process, thereby eliminating the role of positive ion vacancies. Hence it is concluded that the mechanism of electrical conduction in TAHDS single crystal is the migration of protons in the interstitial position and of the inherent cationic impurities in the crystal (the 'pure' sample obtained after five recrystallisations of extra pure BDH Analar salt using triply distilled water was known to contain positive and negative ion impurities of the order of  $10^{-6}$  molar fraction).

We should also consider the effect of association of inherent impurity ions with the more significant charge compensators in the crystal, viz. the interstitial protons and their vacancies in the formation of complexes. In phase I these complexes will be entirely in

dissociated states providing a greater number of mobile defects resulting in a higher conductivity. In phase II these complexes are only partially dissociated and hence the conductivity will be comparatively smaller. In phases III, IV and V, the existing impurity content may exceed the solubility limit and the impurity may precipitate out as a separate phase. This leads to a reduction in carrier concentration, which explains the remaining portion of the curve.

The anomalous peaks in the conductivity plots can be related to phase transitions of structural as well as reorientational types. The protonic defects in TAHDS are of two categories: the hydrogen ions and their vacancies belonging to the ammonium groups and those associated with the rest of the molecular unit. The onset of free rotation of ammonium groups or the beginning of random reorientation of axes of its torsional oscillation in the crystal can lead to a sudden increase in the concentration of protonic defects of the former type, and this can lead to an anomalous rise in the conductivity. As the peak at 140°C is certainly due to structural phase transitions as revealed by earlier studies, it is reasonable to assume that the next peak found at -26°C may be due to the motional effects of ammonium groups. Gesi's observation of maximum value of dielectric constant around -28°C is in support with this conclusion (Gesi 1976a).

Further measurements on deuterated and quenched samples are in progress and it is hoped that these data will throw more light on the various phase transitions in this crystal.

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