

## ELECTRICAL CONDUCTIVITY, DIELECTRIC PROPERTIES AND PHASE TRANSITION IN ETHYLENEDIAMMONIUM SULPHATE SINGLE CRYSTALS

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**Abstract**—D.C. and a.c. electrical conductivities, dielectric constant and dielectric loss factor in single crystals of ethylenediammonium sulphate,  $(\text{H}_3\text{NCH}_2\text{CH}_2\text{NH}_3)(\text{SO}_4)$ , have been measured axiswise as a function of temperature. Anomalous variations in all the above properties at 480 K indicate the occurrence of a phase transition in the above material at this temperature. The existence of such a phase transition is also confirmed by DSC measurements. Electrical conductivity results are analysed and the activation energies of conduction at different temperature regions have been evaluated from the  $\log \sigma$  vs  $10^3 T^{-1}$  plot. Possible mechanisms for the electrical conduction process are discussed, the available results being in favour of a proton transport model.

**Keywords:** Ethylenediammonium sulphate, electrical conductivity, dielectric constant, phase transition, protonic conduction.

### INTRODUCTION

Ethylenediammonium sulphate,  $(\text{H}_3\text{NCH}_2\text{CH}_2\text{NH}_3)(\text{SO}_4)$  (EDS), is a structurally interesting material and is known for its strong optical rotatory power [1]. The structural details of this material were investigated by Sakurai [2]. The dimensions of the tetragonal unit cell eight formula units are  $a = 8.47 \pm 0.02 \text{ \AA}$ ,  $c = 18.03 \pm 0.04 \text{ \AA}$ , and the space group is  $D_4^4 - C_{4,22}$  or  $D_4^8 - C_{4,22}$ . Ratcliffe [3] studied the proton spin-lattice relaxation time of the ethylenediammonium ion in EDS as a function of temperature from which the activation energies for the reorientation of the  $-\text{NH}_3^+$  groups were evaluated. The results also indicated a phase change setting in at 476 K on heating with the presence of a hysteresis effect on cooling. So far, there exists no report on any studies made on the electrical properties of EDS. In the present communication we report the results of measurements of d.c. and a.c. electrical conductivity, dielectric constant and dielectric loss of single crystals of this material. These measurements clearly reveal the occurrence of a high temperature phase transition which is also confirmed by differential scanning calorimetry.

### EXPERIMENTAL

Microcrystals of EDS were prepared by mixing freshly distilled ethylenediammine (Glaxo Laboratories) and sulphuric acid (British Drug House, Analar grade) in 1:1 mole ratio and the subsequent evaporation of the solution on a water bath. Large

single crystals were grown by slow evaporation of the saturated solution of the material in double distilled water at ambient temperature. Doped samples were prepared in a similar manner from aqueous solution of EDS containing a known amount (0.1 mole%) of  $(\text{H}_3\text{NCH}_2\text{CH}_2\text{NH}_3)\text{HPO}_4$ . The crystals were plate-like and were not hygroscopic. They exhibit a nearly perfect cleavage parallel to the (001) plane [2]. Samples in the form of rectangular plates about  $36 \text{ mm}^2$  in area and 1 mm in thickness were cut with faces parallel to the cleavage plane, and perpendicular to it, so that measurements could be made along the  $c$ -axis and  $c^*$ -axis, respectively. Silver electrodes were evaporated on to the broad faces of the samples to ensure good electrical contact and to remove air gaps between the crystal and the electrode surface.

D.C. electrical conductivity measurements were carried out by the two-probe method using a Keithley Electrometer Model 617. The sample holder used in the present investigations has been described elsewhere [4]. The d.c. conductivity measurements were made with voltage gradients ranging from 100 to  $1000 \text{ V cm}^{-1}$ . The measurements were made for both directions of current flow. The conductivity proved to be independent of direction and voltage gradient. Measurements of d.c. conductivity in pure and doped single crystals of EDS were carried out as a function of temperature in the range 100–495 K. All the measurements were carried out in vacuum to avoid any moisture absorption on the surface of the sample. Moreover, care was taken to anneal the sample at  $100^\circ\text{C}$  for 30 min before each experiment. The temperature dependence of the conductivity was

measured at a uniform heating rate of  $0.1 \text{ K min}^{-1}$  near the phase transition temperature and  $1 \text{ K min}^{-1}$  in other temperature regions. Measurements were repeated to ensure reproducibility.

The a.c. conductance  $G$ , capacitance  $C$  and dielectric loss  $\tan\delta$  were measured as a function of frequency using a Hewlett Packard LF Impedance Analyzer (Model 4192A), in the temperature range  $100\text{--}495 \text{ K}$ .  $G$  and  $\tan\delta$  for EDS single crystals were found to be below the detection limit of the instrument except in the high temperature region near the phase transition. The value of the a.c. conductivity was calculated using the known dimensions of the sample. The dielectric constant was derived from the measured capacitance, after eliminating the lead and fringe capacitances using standard methods [5]. Differential scanning calorimetry traces were recorded using a Perkin Elmer DSC-7 instrument in a nitrogen atmosphere at a scanning speed of  $10 \text{ K min}^{-1}$ .

## RESULTS

The variation of d.c. electrical conductivity with temperature in pure and phosphate doped single crystals of EDS is illustrated in Fig. 1. The increase of  $\sigma_{\text{d.c.}}$  with temperature is extremely small up to about  $340 \text{ K}$ . A careful analysis of the  $\log \sigma_{\text{d.c.}}$  vs  $10^3/T$  plot above this temperature reveals that it is linear up to about  $408 \text{ K}$ . Thereafter it shows a continuous curvature up to  $480 \text{ K}$ , where a prominent conductivity anomaly indicative of a phase transition occurs. The conductivity of the doped sample is found to be slightly higher than that of pure sample in the entire temperature range. Again the conductivity along the  $c^*$ -axis is found to be higher than that

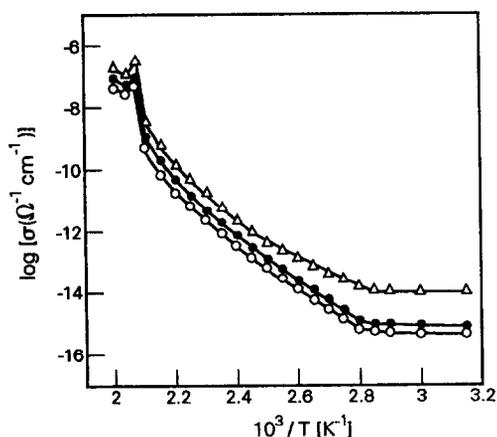


Fig. 1. D.C. conductivity vs temperature plots.  $\circ$ —pure EDS along the  $c$ -axis;  $\bullet$ —phosphate-doped (0.1 mole%) EDS along the  $c$ -axis;  $\triangle$ —pure EDS along the  $c^*$ -axis.

Table 1. Activation energy  $E_a$  for d.c. conductivity of EDS single crystals along the  $c$ - and  $c^*$ -axes

Sample	Axis	Temperature range (K)	Activation energy (eV)
EDS (pure)	$c$	340–408	1.25
		408–454	1.86
	$c^*$	340–408	0.95
		408–454	1.71
EDS (phosphate doped)	$c$	340–408	1.36
		408–454	1.90

along the  $c$ -axis. The activation energy values calculated from the Arrhenius plots are given in Table 1. The prominent conductivity anomalies with distinct  $\Lambda$ -shaped peaks at about  $480 \text{ K}$  is a clear indication of a phase transition taking place at this temperature.

The temperature dependence of the a.c. conductivity and the dielectric loss in EDS single crystals along the  $c$ -axis are shown in Fig. 2. The abrupt change in  $\tan\delta$  and a  $\Lambda$ -shaped anomaly in  $\sigma_{\text{a.c.}}$  indicate again a phase transition at  $480 \text{ K}$  in conformity with the d.c. conductivity results.

Figure 3 illustrates the variation of dielectric constant along the  $c$ - and  $c^*$ -axes at different frequencies. The value of dielectric constant at  $300 \text{ K}$  is  $7.29$  along the  $c$ -axis and  $9.27$  along the  $c^*$ -axis (at  $1 \text{ kHz}$ ). The increase in  $\epsilon_c$  and  $\epsilon_{c^*}$  is extremely small up to the phase transition temperature. Both  $\epsilon_c$  vs  $T$  and  $\epsilon_{c^*}$  vs  $T$  plots exhibit  $\Lambda$ -shaped peaks exactly at the same temperature where the conductivity anomalies occur viz.  $480 \text{ K}$ . The height of the peak is notably suppressed at higher frequencies. Figure 4 shows the temperature dependence of the dielectric constant along the  $c$ -axis around the transition temperature recorded on heating and cooling cycles, the measuring frequency being  $10 \text{ kHz}$ . The anomaly shows a thermal hysteresis of about  $5 \text{ K}$ , which is indicative of

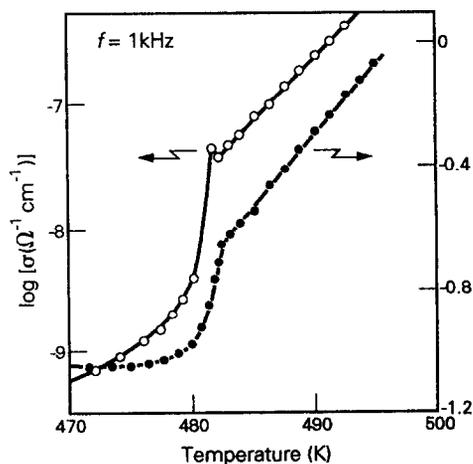


Fig. 2.  $\bullet$ —variation of  $\tan\delta$  with temperature along the  $c$ -axis for EDS;  $\circ$ —variation of a.c. conductivity with temperature along the  $c$ -axis.

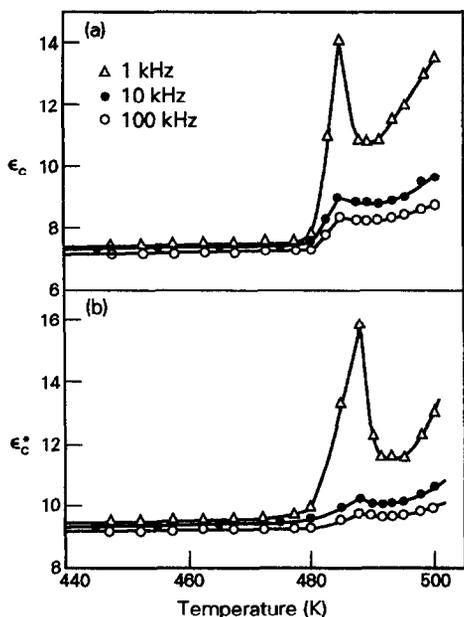


Fig. 3. Dielectric constant of EDS as a function of temperature at different frequencies along: (a) the  $c$ -axis and (b) the  $c^*$ -axis.

first order phase transition. Figure 5 shows the DSC thermograms of EDS in the heating and cooling runs which reveal the following characteristics. The compound apparently decomposes following melting at about 554 K. The sharp peak preceding decomposition is presumably due to melting of the sample. The peak with an onset at 482 K is due to a phase transition. The enthalpy change ( $\Delta H$ ) for this phase transition is  $14.1 \text{ kJmole}^{-1}$ . This transition shows a thermal hysteresis characteristic of a first order phase transition. The compound does not exhibit any transformation in the temperature range 300–400 K, confirming that it is not a hydrate.

The measurements of d.c. conductivity and dielectric constant do not show any anomalous variation in the temperature region 100–303 K, ruling out the possibility of a phase transition in this region.

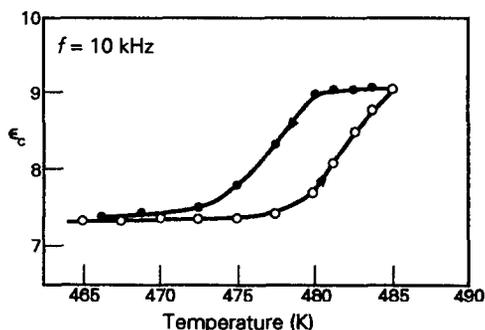


Fig. 4. Dielectric constant vs temperature plot for EDS along  $c$ -axis in the heating and cooling runs.

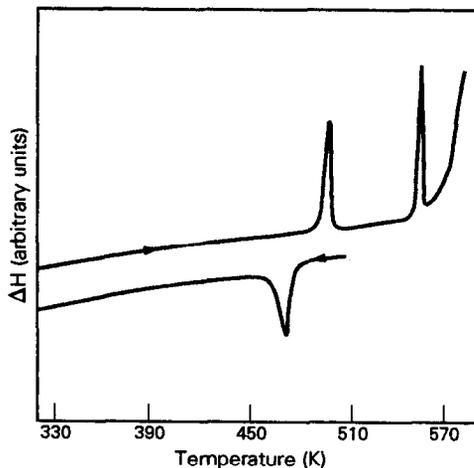


Fig. 5. DSC curve for EDS showing enthalpy change ( $\Delta H$ ) with temperature.

## DISCUSSION

The mechanism of conduction in EDS single crystals can be understood by a detailed consideration of its structure [2]. The crystal structure of this material can be conveniently described as built up of layers, parallel to (001), containing ethylenediammonium and sulphate groups. In each layer these two groups are linked by two sets of hydrogen bonds of lengths 2.80 and 2.81 Å and N...O contacts with distances 3.31 and 3.32 Å, while these layers are held together by hydrogen bonds of length 2.82 Å and N...O contacts with a distance of 3.26 Å. As the number of linkages between layers formed by each nitrogen atom is smaller than that within a layer, a nearly perfect cleavage is observed parallel to (001). The two  $-\text{NH}_3^+$  groups of  $\text{H}_3\text{NCH}_2\text{CH}_2\text{NH}_3^+$  ion are *cis* to each other in EDS. The structure indicates that both  $-\text{NH}_3^+$  groups have symmetrically equivalent positions in the lattice and the hydrogen bonding occurs between the  $-\text{NH}_3^+$  protons and the surrounding oxygen atoms of sulphate groups. This rigid structure could be the cause for the low, almost temperature independent conductivity up to about 340 K. Moreover, unlike typical ionic crystals, EDS contains two ions of large size. Because of the large size of these ions, the probability of occurrence of interstitial ethylenediammonium and sulphate ions or vacancies is very low. Also, the mobilities of these defects are comparatively low. Hence, ethylenediammonium and sulphate ions and their vacancies cannot contribute to the conduction process in any significant manner. As the temperature of the specimen is raised above room temperature, the hydrogen bonds become progressively weaker. It seems appropriate to conceive of a proton-switch mechanism [6–8] to explain the conductivity of EDS single crystals above 340 K. To

explain the mechanism of conduction in ammonium chloride, Herrington and Stavely [6] have postulated that there is significant amount of dissociation in these crystals to form molecular species which may be represented as  $\text{NH}_4^+ + \text{Cl}^- \rightarrow \text{NH}_3 + \text{HCl}$ . They proposed a three stage proton switch mechanism in which: (i) the proton leaves the  $\text{NH}_4^+$  ion and joins the  $\text{Cl}^-$  ion forming  $\text{NH}_3$  and  $\text{HCl}$  molecules; (ii) a vacancy and the appropriate molecule exchange positions and (iii) the proton jumps back to  $\text{NH}_3$  forming  $\text{NH}_4^+$  and  $\text{Cl}^-$  ions once again. The possibility of a proton switch mechanism in ammonium salts has further been supported by the work of Fuller and Pattern [7] and Taylor and Lasker [8]. The concepts put forward by Herrington and Stavely also seem to be applicable in explaining the mechanism of conduction in EDS, where the cations and anions are connected by hydrogen bonds. The initial step in the transport process can be the breaking of hydrogen bonds and the transfer of the protons directly to the neighbouring sulphate ion where it is held by the coulombic attraction of the anion. In the second step, the neutral  $\text{H}_2\text{SO}_4$  molecule may migrate to an adjacent vacancy and in the final step a reversal of proton switch may occur. Thus, a net displacement of charge can be achieved in an applied electric field. The activation energy values obtained for pure and phosphate doped EDS in the temperature range 340–408 K (Table 1) are in very good agreement with those reported in the literature for similar materials in which the electrical conductivity is dominated by protonic conduction [8–11]. The higher magnitude of  $\sigma_{\text{d.c.}}$  along the  $c^*$ -axis (Fig. 1) could be due to the higher mobility of the charge carriers along this axis, which is parallel to the cleavage plane. The lower activation energy along this axis in the temperature range 340–408 K could be due to the comparatively smaller barrier in this direction. The conductivity of the phosphate-doped sample is found to be slightly higher than that of the pure sample in the entire temperature range, whereas the activation energy is not significantly altered (Table 1). When EDS is doped with ethylenediammonium phosphate,  $(\text{H}_3\text{NCH}_2\text{CH}_2\text{NH}_3)\text{HPO}_4$ , the  $\text{HPO}_4^{2-}$  ions substitute for  $\text{SO}_4^{2-}$  ions. The enhancement of conductivity in the doped sample may be attributed to the contribution of the protons of the acid phosphate. This observation is also in support of the conclusion that protonic conduction is the dominant mechanism of charge transport in EDS. The results of the electrical conductivity measurements on EDS are quite similar to those obtained in our studies on ethylenediammonium dinitrate single crystals [11], in which protonic conduction was established by chemical methods.

In the NMR spin-lattice relaxation measurements [3], the  $T_1$  minimum of EDS is interpreted in terms of the  $-\text{NH}_3^+$  reorientation. Again it is anticipated that the reorientational barriers decrease with increasing temperature, because of lattice expansion and increased vibrational amplitudes. The change in slope of the conductivity plots above 408 K apparently arises from the initiation of a rotational reorientation of the  $-\text{NH}_3^+$  group of EDS. A varying activation energy above 408 K as observed can also result from the gradual decrease of the reorientational barriers. Thus, some sort of "variable potential barrier" model [12, 13] has to be invoked to explain the experimental result.

As the temperature of the sample increases further, the hydrogen bonds become progressively weaker and at about 480 K, the hydrogen bonds associated with ethylenediammonium ions can be completely broken and the  $-\text{NH}_3^+$  ions, which are assumed to be in a state of torsional oscillation, now change over to a state of free rotation. The onset of such free rotation can cause a significant change in the electrical conductivity as well as the dielectric constant at this temperature. Similar effects have been found to occur in a number of ammonium salts like  $(\text{NH}_4)_2\text{SO}_4$  [14],  $\text{NH}_4\text{H}_2\text{PO}_4$  [15],  $\text{LiNH}_4\text{SO}_4$  [4] and  $(\text{NH}_4)_2\text{HPO}_4$  [16]. The variation of dielectric constant with temperature in the present studies gives a thermal hysteresis of about 5 K, which was reported in the NMR studies also [3]. The abrupt increase in conductivity at the phase transition point and the thermal hysteresis observed in the dielectric measurements and DSC indicate that the phase transition is of first order. The slight difference in temperature for the onset of phase transition as revealed by DSC measurements could be due to the higher heating rate employed.

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