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Electrical resistivity of single-crystal lithium ammonium sulphate between 300 and 500 K

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The d.c. electrical resistivity, ρ, of pure $LiNH_4SO_4$ single crystals has been measured between 300 and 500 K in three successive runs. Anomalous behaviour before and at the transition point was observed and thermal annealing was necessary for reproducible results. The temperature dependence of ρ along the polar axis yielded the values $\Delta E = 0.54$ and 1.48 eV and $\Delta E = 1.95$ eV for the energy activating the charge transport mechanisms in the ferroelectric and the paraelectric phases, respectively. A "pre-transition" phenomenon was observed while measuring ρ along the *a*- and *b*-axes. The *J–E* characteristics indicated possible space-charge effects at low measuring fields. The mechanism of electrical conduction in the measuring range has been discussed.

1. Introduction

Lithium–ammonium sulphate, $LiNH_4SO_4$ (LAS), is known to have, at room temperature, orthorhombic symmetry with a pseudohexagonal structure and space group $P2_1cn$ [1]. The lattice parameters are $a = 0.5280$ nm, $b = 0.9140$ nm, $c = 0.8786$ nm and $z = 4$. Between 283 K and 459.5 K, LAS is ferroelectric along the *a*-axis. The low-temperature polymorph, below 283 K, is monoclinic with space group $P2_1/a$. Many investigations have been performed on LAS including dielectric [2–4], optical [5, 6], thermal [4, 7, 8], magnetic resonance [3, 5, 6, 9], elastic constants and Brillouin scattering [10, 11], and pressure studies [4, 5, 12, 13]. The transition at 283 K is first order, with abrupt changes in the electrical conductivity [14]. Recently, it was suggested, on the basis of elastic and specific heat data [15], that another phase transition may take place just above the Curie temperature, T_c (459.5 K). There have been few studies of d.c. electrical resistivity, ρ, in LAS crystals. Syamaprasad and Vallabhan [14] studied the d.c. electrical conductivity of pure, quenched, Zn^{2+} and Cu^{2+}-doped LAS crystals over a wide temperature range.

The present work studied the d.c. electrical resistivity of LAS up to a temperature higher than that at which the new phase transition was suggested (up to 500 K). The effect of thermal annealing on the behaviour of $\rho(T)$ has also been examined, along with the effect of the measuring field on the conduction mechanism in LAS crystals.

2. Experimental procedure

Single crystals of $LiNH_4SO_4$ were grown from saturated aqueous solution containing equimolar amounts of Li_2SO_4 and $(NH_4)_2SO_4$. The slow evaporation method was found to be suitable for growing such crystals. Over a period of about 5 weeks, large (4 cm × 3.5 cm × 2 cm), transparent, colourless and well-defined single crystals could be obtained. Samples in the form of thin slabs 6 mm × 6 mm × 1–2 mm were cut parallel to the *a*- or *b*-axis. Silver conducting solution was painted on the two largest surfaces and the sample suspended freely in a holder with Teflon insulating supports. Temperature was measured and controlled with an accuracy of about ± 0.1 K using a chromel–alumel thermocouple and a d.c. microvoltmeter (Philips type PM 2434). The temperature was changed at a rate of about $3\,K\,h^{-1}$ in the region of the phase transition, otherwise the rate was about $20\,K\,h^{-1}$. The sample resistance was measured directly using a Keithley electrometer type 610c. The temperature dependence of ρ was investigated in three successive runs while heating between 300 and 500 K. All experiments were performed under a vacuum of about 10^{-3} torr (1 torr = 133.322 Pa). The *J–E* characteristics were measured using a d.c. regulated power supply (Pasco model 1030 A) and a Keithley electrometer type 610 c. The overall accuracy was of about 3%.

3. Results and discussion

The current density, *J*, was measured against the electric field intensity, *E*, along the two crystallographic directions *a* and *b* in both the ferro- and paraelectric phases. Figs 1 and 2 show the *J–E* dependence before (at 300 K) and above (at 470 K) the phase transition. The maximum field intensity was about $350\,kV\,m^{-1}$.

Before transition, the results along both the *a*- and *b*-axes on an ln–ln scale can be represented by two

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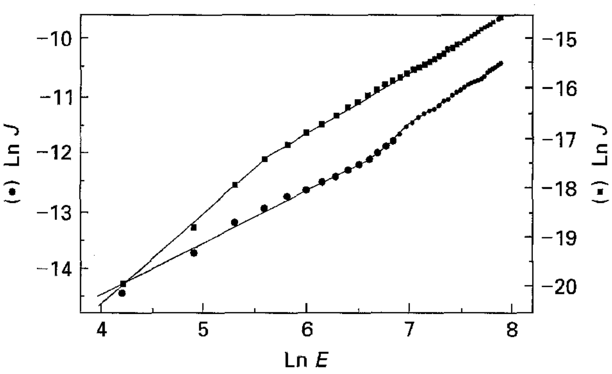

Figure 1 Relation between the current density and the electric field intensity across the *a*-axis: (■) ferroelectric phase, (•) paraelectric phase.

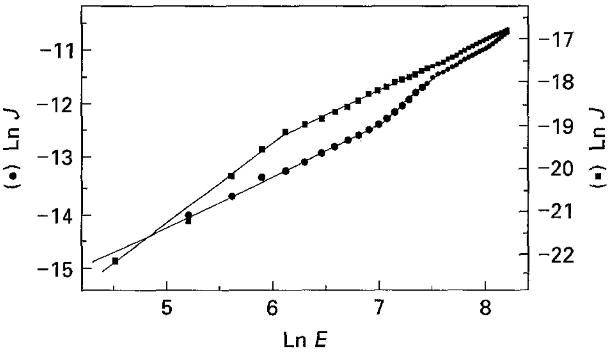

Figure 2 Relation between the current density and the electric field intensity across the *b*-axis: (■) ferroelectric phase, (•) paraelectric phase.

straight lines described by the following equations

Direction	Low-field region	High-field region	
a	$J = 12.2\times10^{-13}E^{1.79}$	$J = 4.38\times10^{-11}E^{1.17}$	(1)
b	$J = 0.4\times10^{-13}E^{1.91}$	$J = 0.36\times10^{-11}E^{1.16}$	(2)

The low-field region ends at $32 \pm 1\,\mathrm{kV\,m^{-1}}$ for the *a*-direction and at $41 \pm 1\,\mathrm{kV\,m^{-1}}$ for the *b*-direction.

After transition, the J–E dependence can be represented by three equations of the form

Direction	Low-field region	Intermediate-field region	High-field region	
a	$J = 1.1\times10^{-8}E^{0.96}$	$J = 6.9\times10^{-11}E^{1.7}$	$J = 3.3\times10^{-9}E^{1.15}$	(3)
b	$J = 0.5\times10^{-8}E^{0.96}$	$J = 3.0\times10^{-11}E^{1.7}$	$J = 1.4\times10^{-9}E^{1.18}$	(4)

The fields separating the low from the intermediate regions have the values 87 ± 2 and $117 \pm 3\,\mathrm{kV\,m^{-1}}$ for the *a*- and *b*-axes respectively, while the intermediate-field region joins the high-field region at fields of 115 ± 3 and $177 \pm 4\,\mathrm{kV\,m^{-1}}$ for the *a*- and *b*-directions, respectively.

In the ferroelectric phase, up to about 32 and $41\,\mathrm{kV\,m^{-1}}$ for the *a*- and *b*-directions, respectively, the J–E characteristics have a nearly quadratic relationship. This may be due to the fact that the effect of the electric field on the ferroelectric domains and their wall motion is still weak in addition to the negligible effect of the rotational motion of SO_4^{2-} groups at room temperature and so, the effect of the space charge may be dominated in this region.

After the phase transition at 459.5 K, it is clear from the equations that the current density follows (approximately) an ohmic relationship with the field intensity, except between 87 and $115\,\mathrm{kV\,m^{-1}}$ for the *a*-direction and between 117 and $177\,\mathrm{kV\,m^{-1}}$ for the *b*-direction. The effect of the field intensity in the two regions may be related to the disordered structure of LAS after the transition at about 459.5 K.

In ionic crystals, electric conduction is a point defect-controlled property. The defect concentration increases exponentially with rising temperature or linearly with increased measuring field and the electrical conductivity correspondingly increases. Possible point defect types in crystals like the double sulphate may be normal ionic and electronic. Protonic defects may also be present if ammonium is one of the two sulphates in such crystals. Consequently, conduction in $LiNH_4SO_4$ crystals may be ionic, electronic or protonic. The most probable conduction may be due to ions, vacancies or interstitials, because this type of crystal contains lithium, ammonium and sulphate ions. Above the transition, the results indicate the presence of an intermediate field region at which $J \propto E^{1.7}$ for both the *a*- and *b*-directions. In this region the dominant effect may be due to protonic defects which may be hydrogen ions generated in high concentrations from ammonium groups while changing from a state of torsional oscillation to one of a free rotation during the rearrangement process of the crystal lattice at T_c.

Figs 3 and 4 show the temperature dependence of the electrical resistivity, ρ, of pure LAS crystals over the temperature range from 300–500 K. Over this range, a linear relationship exists between ln ρ and T^{-1} with more than one segment according to the well-known relationship

$$\rho = \rho_0 \exp\left(w/kT\right) \qquad (5)$$

where the activation energy, w, and the pre-exponent, ρ_o are the two constants which summarize the experimental information for the material. Figs 3 and 4 reveal three bends at about 397, 433 and 459.5 K (the Curie temperature, T_c). The activation energy of conduction in each segment along both the *a*- and *b*-axes are listed in Table I. From the table it is clear that to obtain the steady state the crystal must be annealed at high temperature. Nothing abnormal was detected above T_c in spite of careful measurement in this temperature range. These results fail to confirm the existence of the new phase transition proposed by Wyslouzil *et al.* [15].

According to Aleksandrova *et al.* [16, 17], below the transition at 459.5 K the two groups $(NH_4)^+$ and $(SO_4)^{2-}$ are ordered in their extreme positions. All the

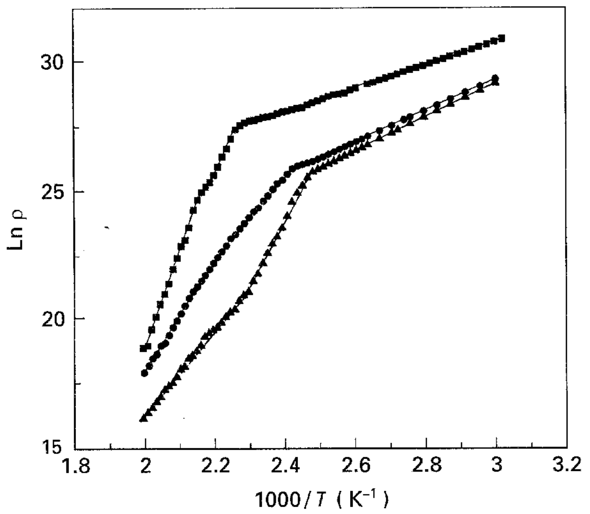

Figure 3 The temperature dependence of the electrical resistivity for LAS crystals along the *a*-axis: (■) first run, (●) second run, (▲) third run.

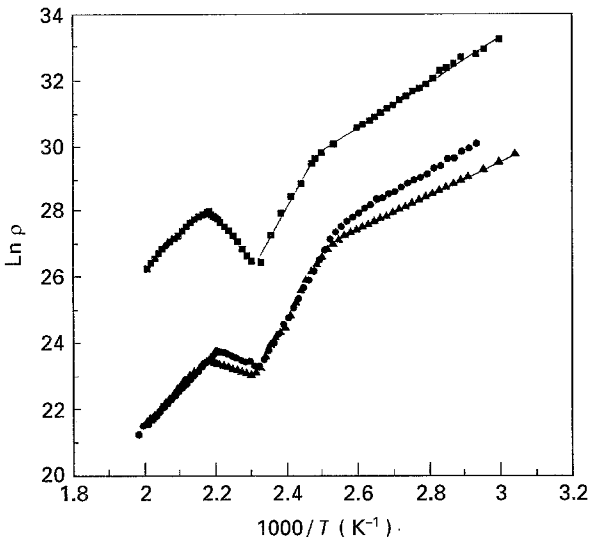

Figure 4 The temperature dependence of the electrical resistivity of LAS crystals along the *b*-axis: (■) first run, (●) second run, (▲) third run.

TABLE I The activation energy, W, of conduction along *a*- and *b*-axes of LAS

Direction	Run	W_1(eV)	W_2(eV)	W_3(eV)	W_4(eV)
a	First	0.39	2.48	3.29	
a	Second	0.56	1.45	2.06	
a	Third	0.54	1.48	1.95	
b	First	0.60	1.74	− 1.09	0.85
b	Second	0.52	1.68	− 0.34	0.98
b	Third	0.48	1.59	− 0.31	0.96

SO_4^{2-} groups rotate about the *a*-axis in the same direction by 20° while the NH_4^+ ions rotate in the opposite direction by 24°. The order–disorder transition is thought to start far below T_c. Because of the rotational motion of the SO_4^{2-} groups, the oxygen atom at the top of the SO_4^{2-} tetrahedra has been found to be disordered and to randomly occupy three positions around the *a*-axis. These three positions are not strongly distinguishable by their free energies [18] and are separated by relatively low energy barriers. It seems possible that, at moderately high temperatures, i.e. at 397 K, rotational disorder may take place. Such rotational motion causes a weakening of the ionic bonds resulting in a reduction of the height of the energy barrier and an increase in the mobility of the ions. When, as a consequence, the frequency of the rotational motion of SO_4^{2-} groups about the *a*-axis increases with increasing temperature above the onset point of this rotational motion, perhaps at 433 K, a disturbance about the *b*-axis causes an increase in the resistivity between about 433 and 459.5 K, Fig. 4. The increase in the frequency of this rotational motion reaches a maximum at the transition temperature, giving rise to the maximum resistivity observed at T_c. The order–disorder process extending over a relatively wide range of temperature may be considered as a "pre-transition" effect previously observed in similar cases [18].

The difference between the results taken in the "pre-transition" region along the *a*- and *b*-axes seems to agree well with the conjecture of the rotational motion about the *a*-axis of the SO_4^{2-} groups leading to an increase in the resistivity along the *b*-axis with temperature up to the Curie point.

From Figs 3 and 4 it is clear that the difference between the results taken in three successive runs indicates that reproducibility is only achieved after the second run, i.e. after the sample was taken to high temperatures and cooled to room temperature for the next run. It is noteworthy that the stability of the measurements in the third run is better than the first and second runs.

The frequency- and temperature-dependence of the a.c. resistivity along both *a*- and *b*-axes of this crystal will be important in clarifying the role of the frequency of the rotational motion of SO_4^{2-} groups on the conduction mechanism of this type of crystal. This will be the subject of another publication.

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