

## EFFECT OF DEUTERATION ON THE ELECTRICAL CONDUCTIVITY, DIELECTRIC CONSTANT AND PHASE TRANSITIONS IN $\text{LiNH}_4\text{SO}_4$

U. SYAMAPRASAD and C.P.G. VALLABHAN

*Department of Physics, University of Cochin, Cochin 682022, India*

Received 5 November 1981

Revised manuscript received 17 February 1982

Measurements of dc conductivity and dielectric constant show that deuteration causes an upward shift of the high temperature phase transition point from 186.5 to 191°C and a downward shift of the low temperature transition point from 10 to -1.5°C in  $\text{LiNH}_4\text{SO}_4$ . Mechanisms of phase transitions and of electrical transport in the crystal are discussed.

In this letter we present the first report on the effect of deuteration on the electrical conductivity, dielectric constant and phase transitions in lithium ammonium sulphate (LAS) which is an extremely interesting room temperature ferroelectric material exhibiting two phase transitions of the first order at atmospheric pressure with symmetry changes: phase I (Pnam) (paraelectric)  $\xrightarrow{186.5^\circ\text{C}}$  phase II (Pna2<sub>1</sub>) (ferroelectric)  $\xrightarrow{10^\circ\text{C}}$  phase III (P2<sub>1</sub>/a) (ferroelastic) [1-9]. Recent investigations on this material include the NMR studies at high pressure [10,11], the electrical conductivity [12,13] and ionic thermo-current [14] measurements.

Solution grown single crystals of  $\text{LiND}_4\text{SO}_4$  (DAS) were prepared from high purity LAS by repeated recrystallisation using heavy water of isotopic purity 99.8%. The details of sample preparation and measurement of conductivity made under vacuum ( $10^{-3}$  Torr) conditions have been reported earlier [12]. The dielectric measurements were carried out under the same vacuum conditions using a direct reading LC meter having a provision to annul the effect of lead and fringe capacitances which in the present case were estimated accurately [15]. The LC meter readings were counter checked by a Marconi Universal bridge. The rates of temperature variations used were 1°C/h in the vicinity of the transition points and 5°C/h in the other regions.

Fig. 1 shows the  $\log \sigma$  versus  $10^3/T$  plot for DLAS

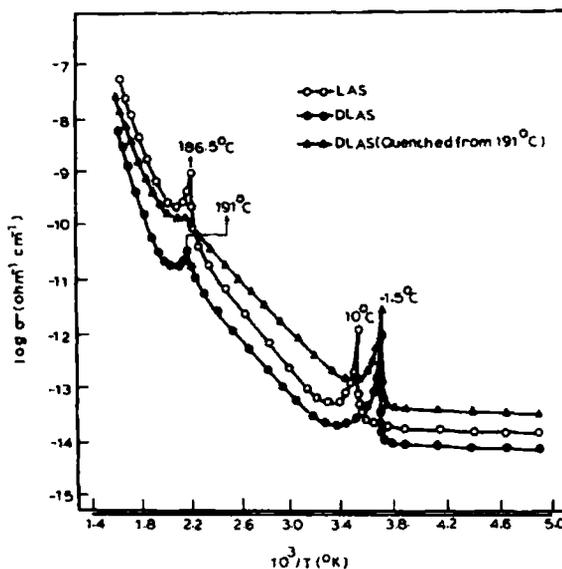


Fig. 1.  $\log \sigma$  versus  $10^3/T$  plots for LAS and DLAS.

along the *a*-(ferroelectric) axis. Here the corresponding variation for LAS [12] is also shown alongside for comparison. As in the case of LAS, DLAS also exhibits two prominent  $\Lambda$ -type conductivity anomalies occurring at -1.5°C and 191°C (No such anomalies are observed along the *b* or *c*-axes and hence the plots are not given here. Also no measurable thermal hysteresis is noted in the heating and cooling runs.) It is to be noted that for DLAS there is a downward shift of the

low temperature transition point (lower  $T_c$ ) by  $11.5^\circ\text{C}$  and an upward shift of the high temperature transition point (upper  $T_c$ ) by  $4.5^\circ\text{C}$  when compared with the transitions in LAS. The height of the peak at the low temperature transition point is found to be unaffected by deuteration; but that for the high temperature transition is reduced significantly. Also, the magnitude of electrical conductivity along all the axes in DLAS is found to be much lower than those in LAS in all the three phases, where as the general shapes of the conductivity plots are the same. The conduction activation energies for the DLAS sample show only a very slight variation in all the phases (1.60, 0.57, and 0.023 eV for DLAS compared with 1.51, 0.58 and 0.025 eV for LAS in phases I, II and III, respectively). The distinct straight line regions corresponding to the conductivity plots along the  $a$ -axis for DLAS representing the three different phases of the crystal can be described by the following equations:

$$\sigma(\text{I}) = 8.50 \times 10^4 \exp(-18573/T), \quad (1)$$

$$\sigma(\text{II}) = 2.45 \times 10^{-5} (\exp(-6598/T)), \quad (2)$$

$$\sigma(\text{III}) = 2.82 \times 10^{-14} \exp(-267/T), \quad (3)$$

From these equations it is evident that the lower value of conductivity observed in all the three phases of DLAS is mainly due to the decrease in the value of the pre-exponential factors for conduction ( $8.50 \times 10^4$ ,  $2.45 \times 10^{-5}$  and  $2.82 \times 10^{-14}$  for DLAS against  $1.19 \times 10^6$ ,  $1.09 \times 10^{-4}$  and  $5.01 \times 10^{-14}$  for LAS [12] in phases I, II and III, respectively). The values of pre-exponential factors for the  $b$  or  $c$ -axes are  $2.3 \times 10^4$ ,  $7.5 \times 10^{-6}$  and  $1.1 \times 10^{-14}$  in phases I, II and III, respectively (activation energies are the same as for the  $a$ -axis).

The plot corresponding to a DLAS sample quenched from  $191^\circ\text{C}$  (the high temperature transition point) shows a much higher conductivity (fig. 1) than that for the as grown sample in phases II and III. In phase II this increase in conductivity due to quenching is more than one order of magnitude with only a very slight decrease in the activation energy. Furthermore quenching has the effect of flattening the peak at  $191^\circ\text{C}$  while the peak at  $-1.5^\circ\text{C}$  is unaffected.

The temperature variation of dielectric constant ( $\epsilon$ ) of DLAS along the  $a$ -axis at 1 kHz is shown in fig. 2a in which two sharp peaks (at  $-1.5^\circ\text{C}$  and  $191^\circ\text{C}$ ) occur exactly at the same position of the conductivity

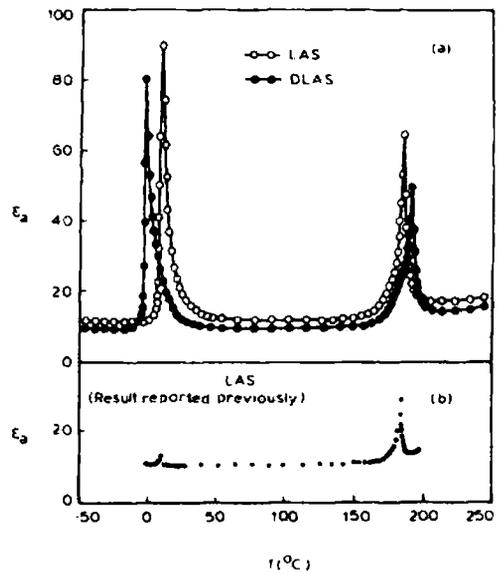


Fig. 2.  $\epsilon$  versus  $T$  plots for LAS and DLAS.

peaks. (Such anomalies are absent along the  $b$ - and  $c$ -axes. Also no measurable thermal hysteresis occurs for either transitions.) Unlike the  $\epsilon$  versus  $T$  plot for LAS (fig. 2b) obtained by Mitsui et al. we have here observed much larger anomalies at the transition points of DLAS. This has prompted us to reinvestigate the dielectric constant of LAS also. As a result we have found that the dielectric constant of LAS along the  $a$ -axis reaches much higher values (90 and 65 at  $10^\circ\text{C}$  and at  $186.5^\circ\text{C}$  respectively) than those (12 and 26) indicated in the plot given by Mitsui et al. [3]. The general dielectric behaviour of DLAS with temperature is found to be the same as that of LAS with the difference that the peak heights for the former (85 and 50 at  $-1.5^\circ\text{C}$  and  $191^\circ\text{C}$ , respectively) are slightly smaller. The value of the room temperature dielectric constant of LAS is found to be the same as that reported previously [3]. The reason for the low values of the dielectric maxima observed at the transition points in the previous study on LAS due to Mitsui et al. [3] might have been due to a higher heating rate or due to the use of a bridge (which requires repeated balancing) instead of a direct reading instrument for capacitance measurements.

The very recent studies [16–20] on electrical conductivity and dielectric constant of several ammonium containing ionic crystals and their deuterated analogues

have given direct evidences regarding the phase transition mechanisms in these crystals. Here the experimental results from conductivity and dielectric measurements conclusively show that DLAS undergoes two phase transitions at  $-1.5^{\circ}\text{C}$  and  $191^{\circ}\text{C}$  corresponding to the two transitions in LAS occurring at  $10^{\circ}\text{C}$  and  $186.5^{\circ}\text{C}$ . The transition at  $10^{\circ}\text{C}$  in LAS is a structural one (accompanied by a unit cell doubling along the  $a$ -direction) which has already been studied in detail [6,7]. On the other hand no serious attempt has so far been made in studying the mechanism involved in the recently observed high temperature transition in this crystal except that due to Syamaprasad and Vallabhan, who suggested from electrical conductivity and ionic thermo-current studies [12–14] that this transition can be attributed to the onset of free rotation of the  $(\text{NH}_4)^+$  ions in the crystal. Here the experimentally observed result that the high temperature transition point shifts upwards in DLAS is completely in agreement with the above suggestion and the observed increase in transition temperature by  $4.5^{\circ}\text{C}$  corresponds to the additional energy required in the case of  $(\text{ND}_4)^+$  to change over into a state of free rotation in DLAS. Also, the earlier proposal [12] that the sudden release of a large number of protonic defects generated due to the unrestricted rotation of the  $(\text{NH}_4)^+$  ions leading to the high temperature conductivity anomaly in LAS, is confirmed here by the experimental result that in deuterated samples the peak height corresponding to the high temperature transition point has only a much lower value as expected because of the lower mobility of the deuterons.

From the experimental results it is evident that compared with LAS, the lower conductivity observed in all the phases of DLAS is mainly because of a decrease in the values of the pre-exponential factors rather than due to a change in the values of conduction activation energies. The decrease in the pre-exponential factors can be readily accounted as due to the lower mobility of deuterons in the crystal when compared to that of protons. Hence it can be concluded that in addition to the cationic Frenkel defects [12], protons detached from ammonium groups also contribute to the electrical conduction process in all the three phases of LAS.

The quenching of the DLAS sample from  $191^{\circ}\text{C}$  leads to the freezing of the newly generated carriers (the deuterons) produced at the transition point. This

is also evident from the flattening of the peak in quenched sample. These frozen in defects are responsible for the increase in conductivity of the quenched sample.

Most of the H-bonded ferroelectrics especially those belonging to the KDP-type show large upward shifts of their lower  $T_c$  when D is substituted for H; and it is well known that the ordering of protons in the H-bonds is the mechanism involved in these transitions. However there are some instances where the lower Curie point is shifted downwards (eg. Rochelle salt) or is unaffected as in ammonium sulphate by deuteration. The results of NMR [21] and ESR [22] studies show that the low temperature transition occurring in LAS at  $10^{\circ}\text{C}$  is essentially due to the distortion of  $\text{LiO}_4$  tetrahedra. The pressure temperature phase diagram of LAS [10] indicate that the lower  $T_c$  of the crystal shifts downwards with increase in pressure. The downward shift of the lower  $T_c$  observed in DLAS could possibly be due to an increase in internal pressure arising as a secondary effect of deuteration, which reduces the mean amplitude of vibration of the hydrogen atom with the consequent change in the effective length of the hydrogen bonds in the crystal [23]. However in KDP-type crystal, the previous result that  $T_c$  shifts upward on deuteration and downward under pressure, may be the result of compensation of the secondary effect (pressure effect) by the primary one viz. the upward shift of  $T_c$  due to the involvement of D atoms in the transition mechanism.

The authors are thankful to Dr. K. Sathianandan for his interest and encouragement during the progress of this work. One of the authors (U.S.P.) gratefully acknowledges the award of a Senior Research Fellowship by University Grants Commission, New Delhi.

#### References

- [1] R. Pepinsky, K. Vedam, Y. Okaya and S. Hoshino, *Phys. Rev.* 111 (1958) 1467.
- [2] W.A. Dollase, *Acta Crystallogr.* B25 (1969) 2298.
- [3] T. Mitsui et al., *J. Phys. Soc. Japan* 39 (1975) 845.
- [4] A.I. Kruglik, K.S. Aleksandrov and M.A. Simonov, *Kristallografia* 23 (1978) 2.
- [5] B.O. Hildman, Th. Hahn, L.E. Cross and R.E. Newnham, *Appl. Phys. Lett.* 27 (1975) 103.
- [6] K.S. Aleksandrov et al., *Izv. Akad. Nauk SSSR, Ser. Fiz.* 39 (1975) 943.

- [7] I.P. Aleksandrova, I.S. Kabanov, S.V. Melnikova, T.I. Chekmasova and V.I. Yuzvak, *Krystallografia* 22 (1977) 321.
- [8] I.M. Iskornev and I.N. Flyorov, *Fiz. Tverd. Tela* 19 (1977) 1040.
- [9] V.I. Yuzvak, L.I. Zerebstova, V.B. Shkuryaeva and I.P. Aleksandrova, *Krystallografia* 19 (1974) 773.
- [10] T.I. Chekmasova, I.S. Kabanov and V.I. Yuzvak, *Phys. Stat. Sol. (a)* 44 (1977) K155.
- [11] T.I. Chekmasova and I.P. Aleksandrova, *Phys. Stat. Sol. (a)* 49 (1978) K185.
- [12] U. Syamaprasad and C.P.G. Vallabhan, *Solid State Commun.* 34 (1980) 899.
- [13] U. Syamaprasad and C.P.G. Vallabhan, *Nat. Acad. Sci. Lett. (India)* 3 (1980) 364.
- [14] U. Syamaprasad and C.P.G. Vallabhan, to be published.
- [15] C. Ramasastry and Y. Syamasundara Rao, *J. Phys.* E12 (1979) 1023.
- [16] U. Syamaprasad and C.P.G. Vallabhan, *Solid State Commun.* 38 (1981) 555.
- [17] U. Syamaprasad and C.P.G. Vallabhan, *Proc. Nuclear Phys. and Solid State Phys. Symp. I.I.T. (New Delhi)* Paper No. SLA10 (1980).
- [18] U. Syamaprasad and C.P.G. Vallabhan, *J. Phys.* C14 (1981) L571.
- [19] U. Syamaprasad and C.P.G. Vallabhan, *J. Phys.* C14 (1981) L865.
- [20] U. Syamaprasad and C.P.G. Vallabhan, *Solid State Commun.*, to be published.
- [21] Yuzvak et al., *Sov. Phys. Crystallogr.* 19 (1975) 480.
- [22] B. Jayaram, Ph.D. Thesis, Indian Institute of Technology, Madras (1982).
- [23] D. Hadzi, *Hydrogen bonding* (Pergamon, New York, 1959).