

High-temperature phase transitions in pure and deuterated ammonium dihydrogen phosphate: Conductivity and dielectric measurements

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(Received 10 August 1982; accepted for publication 5 November 1982)

Results of axiswise measurements of the electrical conductivity (dc and ac) and dielectric constant of $\text{NH}_4\text{H}_2\text{PO}_4$ confirm the occurrence of the recently suggested high-temperature phase transition in this crystal (at 133 °C). The corresponding transition in $\text{ND}_4\text{D}_2\text{PO}_4$ observed here for the first time takes place at 141.5 °C. The mechanism involved in these transitions and those associated with the electrical conduction and dielectric anomalies are explained on the basis of the motional effects of the ammonium ions in these crystals. Conductivity values for deuterated crystals give direct evidence for the predominance of protonic conduction throughout the entire range of temperatures studied (30–260 °C).

PACS numbers: 77.80.Bh, 77.80. — e

I. INTRODUCTION

Recently Viswanath and Miller¹ suggested the occurrence of a new high-temperature phase transition in ammonium dihydrogen phosphate (ADP) from their studies employing infrared spectroscopy, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and dc conductivity. Even though extensive investigations^{2–7} have been made on the well known transition occurring in this material at a low temperature (–125 °C), no attempt has so far been made in clarifying some of the important features of the newly suggested high-temperature transition. Naturally, the first report on this transition¹ indicated the need for further work especially due to the following reasons.

(1) The above authors have not made any attempt to explain the mechanism involved in this newly found transition.

(2) There appears to have no consistency regarding the transition temperature with respect to the different techniques they used to detect this transition, viz., IR spectroscopy, DSC, TGA, and dc conductivity. In other words, the correct transition temperature is yet to be finalized.

(3) ADP being a hydrogen bonded crystal containing ammonium groups, a direct way of obtaining information on the newly observed transition is to make measurements on the deuterated analogue of ADP, viz., $\text{ND}_4\text{D}_2\text{PO}_4$ (DADP) and this crucial measurement has not been done so far.

(4) Even though dielectric measurement has been accepted as the final and confirmatory test for the detection of a new phase transition, this method has not been used in the present case.

(5) Axiswise measurements are essential in the case of ferroelectric and antiferroelectric crystals undergoing phase transition and these have to be carried out.

Consideration of these aspects has prompted us to take up an axiswise study of dc and ac electrical conductivity and dielectric constants of ADP and DADP above room tem-

perature giving special care in the region of the newly observed transition.

II. EXPERIMENT

Single crystals of ADP were grown by slow evaporation at a constant temperature (32 ± 0.01 °C) of a saturated solution prepared with triply distilled water. Single crystals of DADP were grown in a similar way using heavy water of isotopic purity 99.8%. Finished specimens measuring $5 \times 5 \times 1$ mm³ were prepared with their broad faces normal to the different crystallographic axes. The experimental details of the measurement of dc conductivity made under vacuum conditions (10^{-3} Torr) and of temperature have been reported earlier.⁸ In the case of dc conductivity measurements a potential difference of 9 V was applied across the crystal from dry batteries and the resulting current was measured. For ac measurements, a stable L.F. Oscillator of low output impedance was employed to obtain the alternating potential (10–25 V rms, 90 Hz) which was applied across the crystal. A digital ac millivoltmeter (rms) of high input impedance along with an appropriate standard resistance was used for the current measurements through the crystal. The dielectric measurements (the details of which have been reported earlier⁹) were also carried out under the same vacuum conditions using a direct reading LC meter having a provision to annul the effects of lead and fringe capacitances. The rates of temperature variations used were 2 °C h⁻¹ in the vicinity of the transition point and 10 °C h⁻¹ in the other regions.

III. RESULTS

Figures 1 and 2 show the $\log \sigma$ vs T^{-1} plots for ADP and DADP from 30 to 125 °C along the *a* and *c* axes, respectively. The curve for the *b* axis is almost identical with that for the *a* axis. Above 125 °C, as noted earlier,¹⁰ some anomalous variations are observed for the current through the crystal. The current measuring instrument in this case shows large fluctuations and it is not possible to take readings even with an applied voltage as low as 1.5 V across the sample. An

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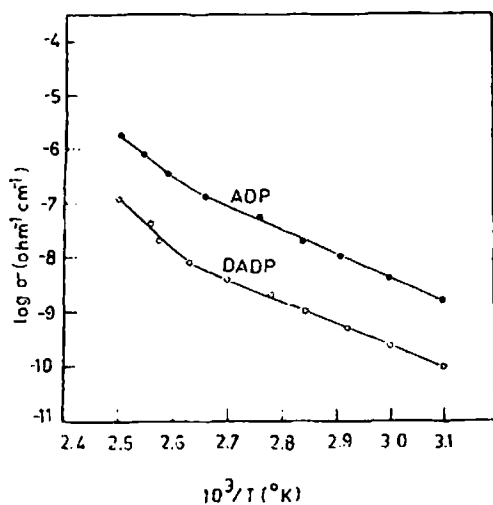


FIG. 1. dc conductivity plots (*a* axis) for ADP and DADP.

X-Y recorder connected to the output of the current measuring instrument along with the thermocouple voltage gives a large number of spikes above this temperature (125 °C). The heights of these peaks are found to increase with further rise in temperature. In spite of the occurrence of these fluctuations it is possible to recover the clear and transparent crystal without any damage even after heating it up to 160 °C. From 30 to 125 °C, the dc conductivity plots have two distinct straight line regions with a "knee" around 90 °C. The straight line regions of the curve corresponding to the *c* axis of the ADP crystal can be represented by the following equation:

$$\sigma_{\text{ADP}} = 2.41 \times 10^2 \exp(-0.70 \text{ eV}/kT) + 1.6 \times 10^6 \exp(-1.78 \text{ eV}/kT) \Omega^{-1} \text{ cm}^{-1},$$

giving activation energy values 0.70 and 1.78 eV in the lower and upper straight line regions, respectively.

Axiswise ac conductivity measurements have been made from 100 to 160 °C and the $\log \sigma$ vs T^{-1} plots for the crystals along the *a* and *c* axes are shown in Figs. 3 and 4. It is

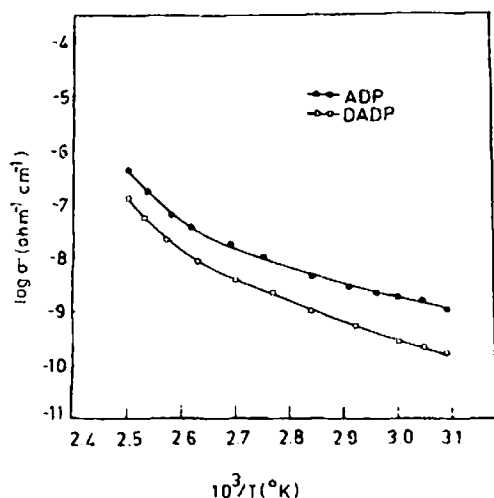


FIG. 2. dc conductivity plots (*c* axis) for ADP and DADP.

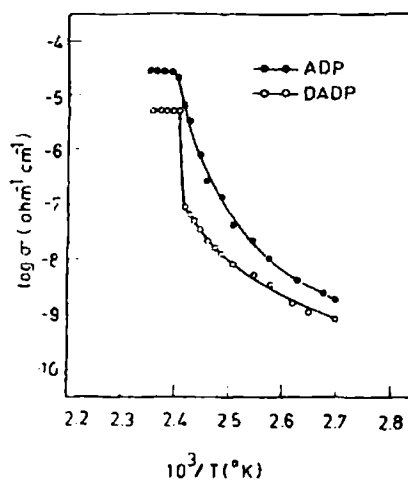


FIG. 3. ac conductivity plots (*a* axis) for ADP and DADP.

notable that the plots corresponding to the *c* axis of ADP and DADP show well defined peaks at 133 and 141.5 °C, respectively, which are clearly indicative of the phase transitions occurring in these crystals. The upward shift of the transition temperature by 8.5 °C is of particular importance. Along the *a* axis, the respective conductivities abruptly rise up to large values at these temperatures and level off beyond these points. Results for *b* axis are the same as those for *a* axis and they are not shown here. Generally, the deuterated crystals show smaller values of conductivity when compared to ADP crystals.

To the best of our knowledge all the earlier dielectric studies on ADP were limited to temperatures below 100 °C. DADP has been studied only below room temperature. Here, we have measured the dielectric constants (at 100 Hz) of ADP and DADP along the *a* and *c* axes in the temperature range 30 to 160 °C and the results are presented in Figs. 5 and 6. It is found that the dielectric constants at first decrease and then go on increasing. For ADP in the heating run the dielectric constant along the *a* axis (ϵ_a) begins to increase at 85 °C, reaches a maximum value of 72 at 133 °C and levels off beyond this temperature. In the cooling run

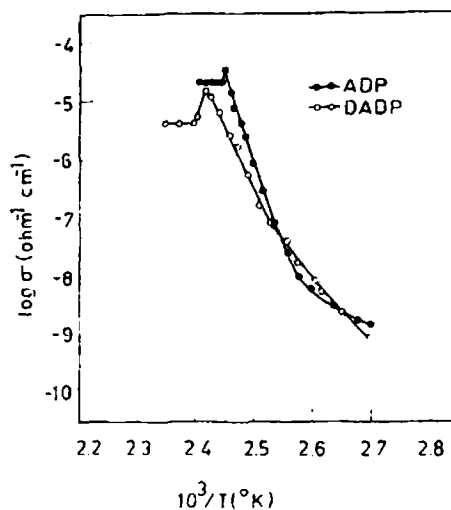


FIG. 4. ac conductivity plots (*c* axis) for ADP and DADP.

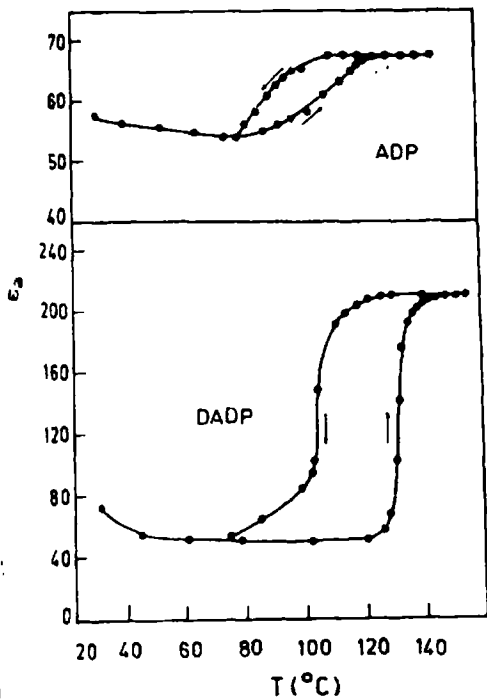


FIG. 5. ϵ_a vs T plots for ADP and DADP.

above change reverses with a thermal hysteresis of nearly 20 °C. The dielectric constant along the c axis (ϵ_c) also shows the same type of variation with the difference that the dielectric maximum in this case has a slightly larger value compared to ϵ_a . The mean value of thermal hysteresis in this case is as much as 40 °C.

For deuterated samples, as observed in electrical conductivity measurements, it is found that the transition point shifts upwards by 8.5 °C. The dielectric constants of DADP along the a and c axes begin to increase around 100 °C and reach maximum values of 215 and 130, respectively, at 141.5 °C. Thermal hysteresis effects in these cases (27 and 55 °C) were found to be much greater than those observed in the case of ADP. The values of room temperature dielectric constants are found to be identical with the values observed previously.²

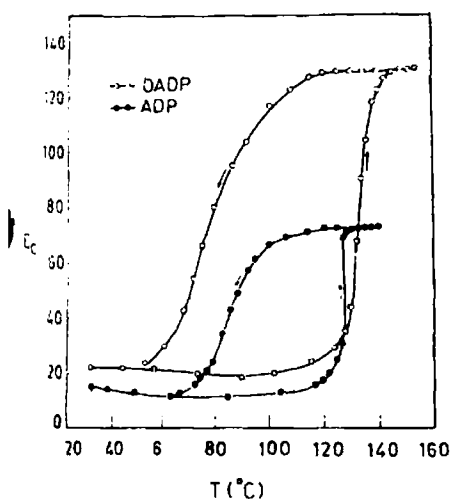


FIG. 6. ϵ_c vs T plots for ADP and DADP.

IV. DISCUSSION

The electrical conductivity and dielectric anomalies observed in ADP and DADP along all the crystallographic axes undoubtedly show that there exist high temperature phase transitions in these crystals at 133 and 141.5 °C, respectively. These results confirm the suggestion of Viswanath and Miller¹ that ADP undergoes a high-temperature phase transition. The present experimental results along with some earlier results^{1,10-15} are indicative of the nature of the mechanism involved in the newly observed transition in ADP. Also, the present results lead to a better understanding of the process of electrical conduction in the different phases of the crystal as well as at the transition point.

Generally, in ADP-type crystals the possible type of point defects which help the electrical conduction process are the "ionization" defects, viz., $(\text{HPO}_4)^{2-}$ and (H_3PO_4) produced as a result of the proton jumps from one phosphate group to another along the same bond (intrabond jump) and the L and D defects (proton vacancy and doubly occupied proton positions) which are generated as a result of jumps of protons from one bond to another (interbond jumps) of the same phosphate group.¹⁴ In ADP, in addition to the above defects there exist protonic defects associated with the ammonium groups which are called the A defects. In the extrinsic region the conduction process is mainly due to the "ionization defects" and the L and D defects. In the intrinsic region, the A defects, which are generated as a result of gradual release of ammonia gas,¹⁴ dominate over the other kind of defects and this is assigned as the cause of the observed "knee" in between the straight line regions. The present experimental result that the deuterated sample (DADP) has lower conductivity values (Figs. 1-4) compared to ADP along all the crystallographic axes is direct evidence for the existence of predominant protonic conduction in ADP both in the extrinsic and intrinsic regions.

As the temperature of the crystal reaches the high-temperature transition point (133 °C), the $(\text{NH}_4)^+$ ions, which are assumed to be in a state of torsional oscillation up to the transition region, may change over to a state of free rotation. The unhindered rotation of the $(\text{NH}_4)^+$ ions can cause the liberation of a large number of protonic defects (A defects) resulting in a high value of conductivity which is observed at the transition point. The high value of dielectric constant observed at the transition point along all the axes of the crystal arises from the contribution to the orientational polarizability from the freely rotating $(\text{NH}_4)^+$ ions. The mechanism involved in this transition can be related to similar transitions observed recently in many other crystals containing ammonium groups, viz., NH_4Cl and NH_4Br ¹⁶, LiNH_4SO_4 ,^{8,17,18} $(\text{NH}_4)_2\text{SO}_4$,^{9,19,20} and $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$.²¹ The high temperature transitions occurring in these crystals are also attributed to the onset of free rotation of the $(\text{NH}_4)^+$ ions. Even though a similar high temperature transition is known to occur in KDP,²² the mechanism involved in that transition is not exactly of the same type. In KDP, the onset of disordered hindered rotation of $(\text{H}_2\text{PO}_4)^-$ groups around all the three axes, is considered to be the cause of the high-temperature phase transition.

The upward shift of the transition temperature (by 8.5 °C) in deuterated specimen (DADP) gives a direct evidence on the role of $(\text{NH}_4)^+$ ions in the phase transition mechanism. Such an upward shift in the transition point is expected when the rotation of the $(\text{NH}_4)^+$ ions is the cause of the observed transition. Here, the shift in the transition temperature corresponds to the additional energy required for the onset of free rotation of $(\text{ND}_4)^+$ groups in DADP which are heavier compared to the $(\text{NH}_4)^+$ groups in ADP. (Incidentally, the high temperature transition point is found to be lowered in KDP on deuteration.²³)

V. CONCLUSIONS

An axis wise measurement of electrical conductivity (ac and dc) and dielectric constant of $\text{NH}_4\text{H}_2\text{PO}_4$ and $\text{ND}_4\text{D}_2\text{PO}_4$ have been carried out over the temperature range 30–160 °C which confirms the occurrence of high-temperature phase transitions in these crystals at 133 and 141.5 °C, respectively. The onset of free rotation of $(\text{NH}_4)^+$ groups in ADP is suggested to be the mechanism involved in this transition. The rise in conductivity at the transition point is explained as due to the liberation of *A* defects arising from the unhindered rotational effects of the $(\text{NH}_4)^+$ groups. A direct evidence for the predominance of protonic conduction in the crystal throughout the entire region (both extrinsic and intrinsic) has been obtained from the experimental result that the deuterated samples have lower conductivity values in comparison with the undeuterated samples along all the crystallographic axes. The large value of dielectric constant observed at the transition point is explained as due to the contribution to the orientational polarizability from the freely rotating $(\text{NH}_4)^+$ groups. The upward shift of the transition temperature in deuterated crystals confirms the idea of $(\text{NH}_4)^+$ rotation as a cause of the new phase transition.

ACKNOWLEDGMENTS

Thanks are due to Dr. K. Sathianandan for providing the authors with the necessary facilities for carrying out work. The financial assistance from the Department of Science and Technology, Government of India is gratefully acknowledged.

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