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Electrical conductivity, dielectric constant and phase transitions in pure and doped diammonium hydrogen phosphate

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Abstract. DC and AC electrical conductivity measurements in single crystals of diammonium hydrogen phosphate along the c axis show anomalous variations at 174, 246 and 416 K. The low-frequency dielectric constant also exhibits peaks exactly at these temperatures with a thermal hysteresis of 13 °C for the peak at 416 K. These specific features of the electrical properties are in agreement with earlier NMR second-moment data and can be identified with three distinct phase transitions that occur in the crystal. The electrical conductivity values have been found to increase linearly with impurity concentration in specimens doped with a specific amount of SO_4^{2-} ions. The mechanisms of the phase transition and of the electrical conduction process are discussed in detail.

1. Introduction

A number of crystalline ammonium compounds undergo characteristic phase transitions, resulting in dramatic changes in a variety of physical properties as their temperature is changed. These physical properties have been studied extensively by various techniques such as NMR, EPR, IR and Raman, cold neutron scattering, thermal analysis, ultrasonics and x-ray diffraction. Measurement of the electrical properties of such materials can also yield valuable information about the phase transitions.

Diammonium hydrogen phosphate, $(\text{NH}_4)_2\text{HPO}_4$ (DAHP), is a very interesting crystal belonging to the above category of materials. Previous investigations on this material include x-ray studies (Smith *et al* 1957a, b, Coates and Smith 1967, Khan *et al* 1972), differential thermal analysis (DTA) (Coates and Smith 1967, Watton *et al* 1977), NMR second-moment calculations (Watton *et al* 1977) and spin-lattice relaxation time measurements (Koksal 1981). The first investigation was by Sherwin, who is reported to have used the DTA data from polycrystalline samples to show that this substance undergoes a crystalline transition near 418 K (Coates and Smith 1967, Watton *et al* 1977). This transition temperature was found to be slightly influenced by the presence of water and by repeated cycling through the transition, while it is affected little by the rate of heating and cooling. Later, Coates and Smith (1967) used an x-ray powder diffraction technique to determine that the high-temperature structure is orthorhombic. They have also shown that the high-temperature phase has eight molecules per unit cell and its density is 23% higher than that of the low-temperature phase. Watton *et al* (1977), using

NMR proton second-moment and spin-lattice relaxation time measurements made with a coherent-pulse spectrometer in powdered samples in the temperature range 77 to 430 K, suggested that the relatively high activation energies associated with the different motions of non-equivalent NH_4^+ groups can be attributed to hydrogen bonding between NH_4^+ groups and the surrounding nearest-neighbour oxygen atoms. They also suggested that the unrealistically short interproton distance of 1.47 Å as determined by x-ray diffraction may be due to the angular oscillations of the NH_4^+ groups. In addition, they predicted that there is a possibility of a structural phase transition occurring between 295 and 170 K. Since the results obtained at 215 K are in agreement with the structure at room temperature, this temperature range could be limited to the region between 295 and 215 K.

All these previous investigations were restricted to polycrystalline or powdered samples. No attempt has so far been made to study any of the electrical properties of DAHP. In this paper a detailed investigation of this aspect is carried out on single crystals of pure and SO_4^{2-} -doped DAHP. We also confirm and accurately fix the transition point of the previously indicated high-temperature phase transitions using DC and AC electrical conductivity as well as dielectric data. These measurements have been extended to low temperatures to see whether this substance exhibits any phase transitions between 80 and 303 K and consequently some quite interesting new results have been obtained in this region.

2. Experimental procedure

Single crystals of DAHP were grown by slow evaporation from an aqueous solution containing the compound (E Merck, India). The material was further purified by repeated recrystallisation using triply distilled water. SO_4^{2-} -doped samples were prepared by adding a specific amount of $(\text{NH}_4)_2\text{SO}_4$ (between 0.02 and 0.1 mol%) into the solution. Samples of typical size $5 \times 5 \times 2 \text{ mm}^3$ were cut from large single crystals and the broad faces of the specimens were coated with quick-drying silver conducting paint. Details of the cryostat, sample holder and method of temperature measurement have been described previously (Syamaprasad and Vallabhan 1980a). For the DC electrical conductivity measurements, a potential difference of 10–100 V from dry batteries was applied across the specimen which was kept under vacuum (10^{-3} Torr) conditions, and the resulting current was measured using a programmable electrometer (Keithley model 617). For the AC conductivity measurements a LF oscillator of low output impedance was used to provide a sinusoidal voltage of 10–25 V RMS at 90 Hz across the sample. An AC microvoltmeter of high input impedance along with an appropriate standard resistance was used for the current measurements. The dielectric measurements were carried out using a direct reading capacitance meter (Vasavi Electronics India, Model VLC1) and the lead and fringe capacitances were eliminated using the method suggested by Ramasastry and Syamasundara Rao (1979).

3. Results

The results of the DC electrical conductivity measurements carried out in pure and SO_4^{2-} -doped single crystals of diammonium hydrogen phosphate in the temperature

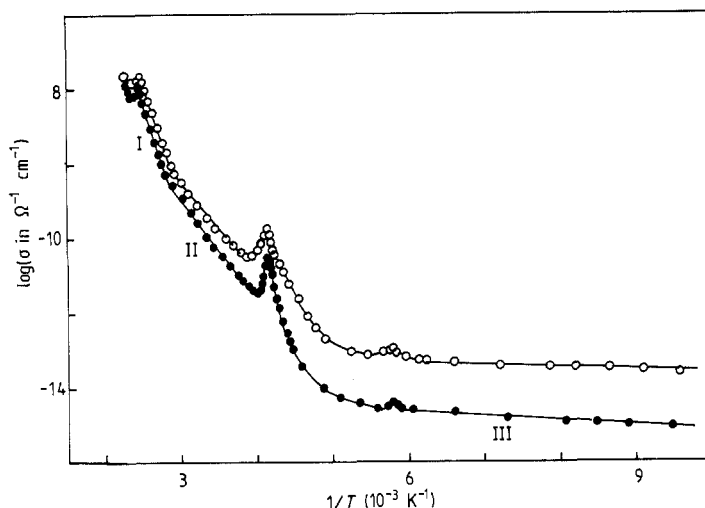


Figure 1. DC conductivity plots for DAHP along the *c* axis: ●, pure DAHP; ○, SO_4^{2-} -doped (0.1 mol%) DAHP.

range 80 to 423 K are shown in figure 1. The results were found to be easily reproducible for different samples. The $\log \sigma$ against $10^3/T$ plot for pure and doped DAHP shows prominent conductivity anomalies with distinct Λ -shaped peaks, one at 246 K and the other at 416 K. Another anomalous variation of much smaller magnitude occurs at 174 K. The peak at 246 K is abrupt and a very large variation in conductivity is observed on the low-temperature side of this peak. It is found that the conductivity rise in this region covers about four orders of magnitude. On the other hand, the high-temperature conductivity anomaly observed at 416 K is confined to less than one order of magnitude. Below 416 K the conductivity plots have three straight-line regions designated by I, II and III (boundaries of the regions are specified elsewhere in the text) which are characteristic of ionic crystals. It is also found that in pure and doped DAHP crystals in dry nitrogen atmosphere the magnitudes of the conductivities in the respective samples are the same as those obtained under vacuum conditions.

In the low-temperature range the conductivity for SO_4^{2-} -doped specimens is found to be greater than that for undoped specimens. However, the temperatures at which the anomalies occur are found to remain unshifted in the doped samples for the concentrations used here. In the high-temperature regions the conductivity plots for both pure and doped samples merge together, which indicates that the same mechanisms are operative in both materials.

A plot of σ against SO_4^{2-} concentration for the doped samples at 303 K is shown in figure 2. This gives a straight line, from which the mobility, μ , of the defects created by the addition of the SO_4^{2-} ions (as will be discussed later) can be calculated using the equation $d\sigma/dn = e\mu$, where n is the concentration of SO_4^{2-} defects, yielding a value of $\mu = 1.27 \times 10^{-12} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. The activation energy values calculated using the straight-line regions of the conductivity plots are 1.48, 0.49 and 0.01 eV respectively for regions I, II and III. These are quite close to the corresponding values (1.47, 0.46 and 0.01 eV) obtained for the SO_4^{2-} -doped DAHP.

The results of the AC electrical conductivity measurements in pure and SO_4^{2-} -doped specimens of DAHP are shown in figure 3. It can be seen that the $\log \sigma$

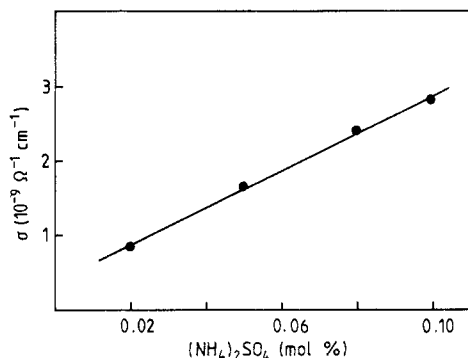


Figure 2. DC conductivity against concentration of SO_4^{2-} (in mol%) for DAHP.

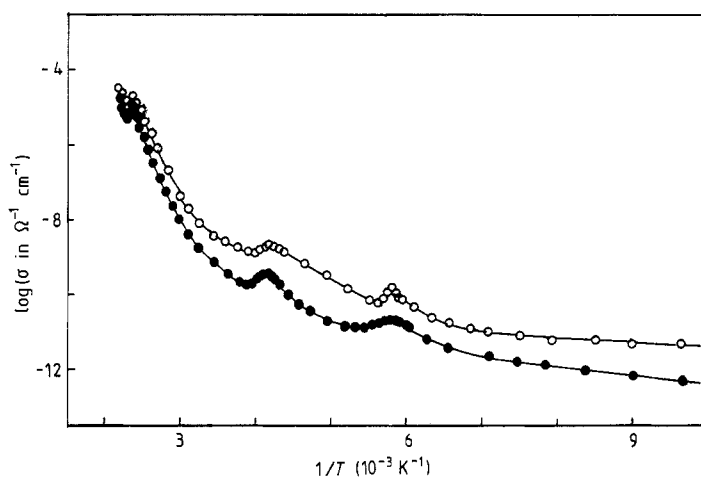


Figure 3. AC electrical conductivity plots for DAHP along the c axis: ●, pure DAHP; ○, SO_4^{2-} -doped (0.1 mol%) DAHP.

against $10^3/T$ plot shows three distinct variations at temperatures of 174, 246 and 416 K respectively in both pure and doped samples of DAHP. Here the magnitude of the AC conductivity is far higher than that of the DC conductivity in both pure and doped samples. In this case also no appreciable change in conductivity was observed when the experiments were performed in a dry nitrogen atmosphere.

The results of dielectric measurements carried out in DAHP single crystals at 1 kHz in the temperature range 80 to 303 K are shown in figure 4, and the ϵ_c against T curve for the high-temperature region (303 to 423 K) is shown in figure 5. The ϵ_c against T plot gives abrupt variations at exactly the same temperatures at which the conductivity anomalies occur, namely 174, 246 and 416 K. The dielectric constant increases gradually and reaches a maximum of 13.6 at 174 K. It decreases thereafter as the temperature increases and again attains another maximum (14.5) giving a second peak at 246 K. On further increasing in temperature ϵ_c remains constant at the value of 10.6 up to 375 K. Above this temperature the dielectric constant changes abruptly from its steady value of 10.6 to 320 at 416 K and then levels off beyond this temperature. On cooling cycle the above change reverses with a thermal hysteresis of about 13 °C. However, below room

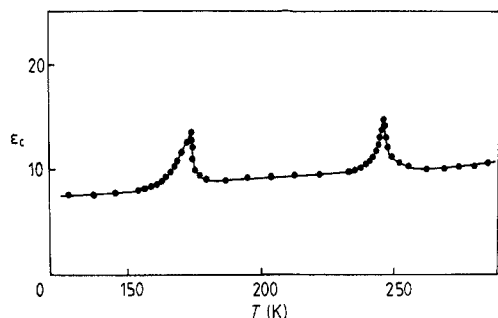


Figure 4. ϵ_c against T for DAHP in the low-temperature region.

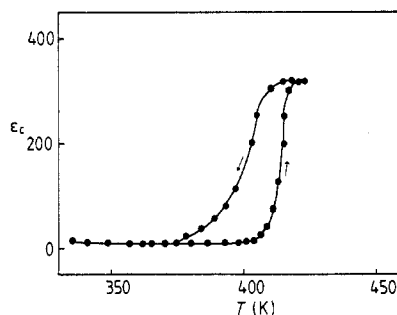


Figure 5. ϵ_c against T for DAHP in the high-temperature region.

temperature no thermal hysteresis has been observed at 246 or at 174 K. For the doping concentrations employed here (0.02 to 0.1 mol %), the dielectric constant values observed for SO_4^{2-} -doped samples are found to be virtually the same as those obtained for pure DAHP and hence are not shown in the figure.

4. Discussion

Previous studies made on a series of ammonium-containing crystals such as $(\text{NH}_4)_2\text{SO}_4$ (Syamaprasad and Vallabhan 1981b, c, 1982a), LiNH_4SO_4 (Syamaprasad and Vallabhan 1980a, b, 1982b, c), NH_4Cl (Murti and Prasad 1975), $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$ (Syamaprasad and Vallabhan 1981a, Devendar Reddy *et al* 1982) and $\text{NH}_4\text{H}_2\text{PO}_4$ (Subhadra *et al* 1983) have unmistakably shown that anomalous variations in the conductivity and dielectric constants of the type observed here are almost always associated with structural, orientational or order-disorder transitions occurring in the crystals at specific temperatures. In the results obtained here, there is complete agreement between the AC/DC electrical conductivity measurements and the dielectric constant data as far as the anomalous variations in these quantities are concerned. It is to be noted that proton second-moment data (Watton *et al* 1977) as a function of temperature also show unmistakable variations near 246 and 174 K, whereas the relaxation time in the laboratory frame T_1 in $(\text{NH}_4)_2\text{HPO}_4$ clearly indicates a dip in the vicinity of 416 K (Watton *et al* 1977). Thus the experimental results obtained for single-crystal samples of DAHP from the above independent measurements conclusively show that this substance undergoes three phase transitions at temperatures of 416, 246 and 174 K respectively. The origin and mechanisms of these transitions can be understood by detailed consideration of the structure of this compound.

At room temperature diammonium hydrogen phosphate forms colourless monocrystals with space group $\text{P2}_1/\text{C}$ having cell constants $a = 11.043 \text{ \AA}$, $b = 6.700 \text{ \AA}$, $c = 8.043 \text{ \AA}$, $\beta = 113.42^\circ$ and $Z = 4$ (Smith *et al* 1957a, b) and is isomorphous to $(\text{NH}_4)_2\text{HAsO}_4$ (Khan *et al* 1970). It was suggested that the structure of DAHP (Khan *et al* 1972) consists of PO_4 and NH_4 tetrahedra connected by $\text{O}-\text{H} \dots \text{O}$ and $\text{N}-\text{H} \dots \text{O}$ bonds which form infinite zig-zag chains parallel to the c axis. In fact, the structure of $(\text{NH}_4)_2\text{HPO}_4$ is determined to a large extent by these hydrogen bonds and their peculiarities. The lengths of the hydrogen bonds, however, are not identical ($\text{H} \dots \text{O}$ distances in $\text{N}-\text{H} \dots \text{O}$ are 1.87, 2.07, 1.96 and 1.930 \AA for the first NH_4 group and 1.86,

2.00, 2.06 and 1.96 Å in the second NH₄ group). The NH₄ tetrahedra in this material are slightly distorted even at room temperature as indicated by x-ray data (Khan *et al* 1972). The H–N–H angles deviate from normal tetrahedral values ranging from 105° to 115° at room temperature. It is likely that the extent of distortion of the NH₄ tetrahedra is much larger at lower temperatures, where the lattice is found to be more rigid and all the hydrogen bonds are intact as suggested by NMR investigation (Watton *et al* 1977). It is to be expected that the hydrogen bonding would become sufficiently weak at high temperatures to allow reorientations of the NH₄ group. Since the strength of these bonds are all different, as indicated by their bond lengths, a variety of reorientations can take place at different temperatures.

On increasing the temperature from 77 K, reorientations of NH₄ tetrahedra about twofold (C₂) and threefold (C₃) as well as simultaneous reorientations about two independent twofold (2C₂) axes can take place depending on the magnitudes of the reorientational activation energies required for the changes. A satisfactory explanation for the observed experimental results from AC/DC conductivity and dielectric constant data can be obtained if we assume that the reorientation of NH₄⁺ ions about the twofold axis is the cause for the transitions at 174 K, since a comparatively low activation energy is required for this type of rearrangement. The transition observed at 246 K can then be attributed to the reorientation about the threefold axis or simultaneous reorientation about two C₂ axes of the NH₄ tetrahedra in the crystal lattice. Thus one may conclude that NH₄⁺ ions in this material undergo sudden reorientations of different kinds at two different temperatures, namely 174 and 246 K, leading to the occurrence of two separate, well defined transitions at low temperatures.

As the temperature of the specimen increases above room temperature the hydrogen bonds become progressively weaker, and at 416 K one may conclude that the hydrogen bonds associated with the ammonium tetrahedra are completely broken and the NH₄⁺ 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, for example (NH₄)₂SO₄ (Syamaprasad and Vallabhan 1981b, c, 1982a), NH₄H₂PO₄ (Subhadra *et al* 1983) and LiNH₄SO₄ (Syamaprasad and Vallabhan 1980a, b, 1982b). The present observations are in complete agreement with the earlier DTA measurements (Coates and Smith 1967, Watton *et al* 1977) except for a slight change in temperature from 418 to 416 K. X-ray measurements (Coates and Smith 1967) which also support our experimental data show that this substance undergoes a change of structure from monoclinic to orthorhombic with unit cell parameters $a = 10.78$, $b = 14.46$ and $c = 9.06$ Å at higher temperatures. Further, the variation of dielectric constant with temperature gives a clear thermal hysteresis of 13 °C showing that the transition at 416 K is first order.

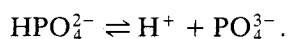
To facilitate an understanding of the conduction mechanisms in pure and doped specimens of DAHP, a brief discussion of the peculiar features of the PO₄ group in ammonium-containing phosphates is required. The phosphate lattice is similar to that of ammonium dihydrogen phosphate (NH₄H₂PO₄) and potassium dihydrogen phosphate (KH₂PO₄) (Tenzer *et al* 1958, Jona and Shirane 1962) with the difference that instead of two hydrogen atoms being associated with the PO₄ tetrahedra (H₂PO₄⁻), only one hydrogen atom is incorporated in the present structure (HPO₄²⁻) and as a result an open hydrogen-bonded network (as shown in figure 1 of Khan *et al* 1972) is formed to accommodate the cations (NH₄⁺ ions) to preserve charge neutrality. Thus each hydrogen-bonded network of the phosphate lattice has on average only one position for its

proton and it is located towards the end of the bond. However, configurations such as H_2PO_4^- or H_3PO_4 may be formed due to the transfer of a hydrogen ion from one HPO_4^{2-} group to the adjacent group or by the transfer of two hydrogen ions to an HPO_4^{2-} group. It is also possible for protons associated with the HPO_4^{2-} group to jump from one group to another along the same bond (intrabond jump) by a resonance tunnelling mechanism (Murphy 1964) which has been found to occur in ADP and KDP (Harris and Vella 1973). These processes are sometimes observed at fairly high temperatures and result in the formation of so called ionisation defects.

Naturally it is also possible for protons to jump from one bond to another bond on the same phosphate group (interbond jump) and this leaves a hydrogen bond without a proton (this is known as an L defect) or produces a bond with an H^+ in each of its proton positions. Such a doubly occupied proton position is known as a D defect (Murphy 1964, Harris and Vella 1973). Thus protons can migrate through the hydrogen-bonded network by a series of interbond and intrabond jumps. Hence, electrical conduction in this class of compounds can be attributed to the combined effect of the individual motions of ionisation defects and of L or D defects.

In addition to the defects mentioned above, there exist what are known as protonic defects associated with the ammonium group (also known as A defects). It has been suggested that proton vacancies are generated in the NH_4 lattice by the incipient decomposition associated with the formation of NH_3 and H_3PO_4 . This is mainly due to the breaking of the ammonium hydrogen bonds and the transfer of the proton directly to the neighbouring phosphate ion where it is held by electrostatic attraction (Harris and Vella 1973). This process occurs only at a much higher temperature.

Consideration of these phenomena occurring in the crystal can provide a satisfactory explanation of the electrical conduction which is essentially a defect-controlled process. In the intrinsic region below the high-temperature phase transition point (region I, from $T = 416$ to 355 K) the electrical conduction is mainly due to the generation of thermal defects as well as ionisation defects. In this temperature range, protons are transferred from the HPO_4^{2-} group giving rise to a PO_4^{3-} group. The equilibrium condition can be expressed as



This is in accordance with the prediction of Khan *et al* (1972) who suggest that the oxygen atom O(I) (in figure 1 of Khan *et al* 1972) associated with the HPO_4^{2-} acting as a donor in the only O—H . . . O bond in the structure is saturated and is not well qualified to act as an acceptor of a hydrogen bond. Thus it is quite likely that the conduction in this region is essentially due to the migration of these protons from the phosphate group. The activation energy of 1.48 eV obtained for pure DAHP (1.47 eV for SO_4^{2-} -doped DAHP) in this temperature region is in very good agreement with the values reported in the literature for similar crystals in which the mechanism of electrical conductivity is dominated by protonic conduction (Murphy 1964, O'Keefe and Perrino 1967, Murti and Prasad 1975, Syamaprasad and Vallabhan 1981a, Subhadra *et al* 1983).

The region from $T = 355$ K to $T = 246$ K can be designated as region II. This is a region where impurity-controlled conduction dominates over other conductivity mechanisms. This becomes clear from the effect of doping the crystal with sulphate ions. The SO_4^{2-} ions in the lattice replace the PO_4^{3-} ions and a proton hole (L defect) is created for charge compensation. Here, a corresponding increase in conductivity is expected. Indeed, as seen in figure 2, a linear increase in conductivity with SO_4^{2-} ions occurs as a result of generation of L defects in the materials. The activation energy of 0.46 eV for L

defect mobility is in very good agreement with that observed in ADP (0.46 eV and 0.52 eV) crystals (Murphy 1964, O'Keefe and Perrino 1967, Perrino *et al* 1972). The magnitude of mobility of these L defects generated by the doping of SO_4^{2-} in DAHP again compares well with the values reported by several authors for other hydrogen-containing phosphates (Murphy 1964, O'Keefe and Perrino 1967, Perrino and Wentrcek 1974). In the temperature range below 246 K (region III, $T = 174$ K to $T = 100$ K), the small values of conductivity and activation energy observed could be due to the precipitation of the existing defects generated by the impurities or to the freezing-in of defects generated by the impurity ions leading to a corresponding decrease in the number of mobile carriers.

The AC conductivity measured at 90 Hz is higher than the DC conductivity by more than one order of magnitude over the whole temperature range. The higher value is expected in this case because of the additional contribution of the polarisation component of the current. As a result the sharp change from intrinsic to extrinsic region is smeared out and the conductivity plots show much smoother variations with respect to temperature. At still lower frequencies the conductivity plots do exhibit the distinct regions I, II and III as obtained in the case of DC measurements.

5. Conclusions

DC and AC electrical conductivity and dielectric constant measurements in single crystals of $(\text{NH}_4)_2\text{HPO}_4$ show anomalous variations at 174, 246 and 416 K, corresponding to three distinct phase transitions occurring in this crystal. These observations are in good agreement with the earlier DTA and NMR second-moment calculations. The phase transitions occurring at 416 K can be identified with the structural change indicated by the x-ray measurements. The transitions at 246 and 174 K are attributed to the different reorientations of the NH_4^+ groups in DAHP. The activation energy and mobility for carriers in this material show that protonic conduction is the dominant mechanism responsible for the electrical conductivity of this material.

Acknowledgments

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