CHAPTER 2

A STUDY OF LOW TEMPERATURE PHASE TRANSITION IN AMMONIUM DIHYDROGEN PHOSPHATE USING DC ELECTRICAL CONDUCTIVITY MEASUREMENTS.

2.1. ABSTRACT.

Results of dc electrical conductivity measurements carried out on single crystals of tetragonal ammonium dihydrogen phosphate (ADP) along c-axis in the temperature range 100 K to 400 K have been presented. The log $\sigma$ vs $10^3 / T$ plot obtained for this material shows anomalous variation at 147K with a hysteresis of 1.1 indicating that this material undergoes a first order phase transition at this temperature unlike other ionic crystals of this category. ADP is found to exhibit a clear pyroelectric behavior at the transition point. The mechanisms of electrical conduction process in this material are discussed along with that for phase transition. The activation energy values obtained from the straight line regions of the Ahrenius plot are also given.
2.2. INTRODUCTION

Studies on the properties of crystals containing ammonium groups have been of great interest in recent years in view of their optical, dielectric, ferroelectric and thermal behavior. The hydrogen bonds in these materials play a critical role in deciding many of these properties. The above mentioned properties have been studied extensively using various techniques such as NMR [1], EPR [2,3], IR [4], DTA [5] and neutron diffraction [6]. In this context it must be said that the measurements of the electrical properties like dc and ac conductivities also have yielded valuable informations about the transport processes and phase transitions occurring in these materials. ADP is a scientifically important photonic material used in the phenomenon of second harmonic generation. Second harmonic generation are now standard equipments for use with visible and IR lasers. Recently considerable advances have been achieved in harmonic generation, and in particular, ADP has sufficiently large nonlinear coefficients and high optical breakdown thresholds, it become an attractive material for the generation of higher order harmonics which is useful for obtaining laser radiation in the UV region with visible range lasers. Optical bistability has also been observed in ADP crystals. Optical bistability leading to bistable devices which are important in the digital circuit used in communications, signal processing and computing. They are also used as switches, logic gates and memory elements. Two wave mixing process occur in ADP can be employed in real time holography. Wave mixing has numerous applications in optical data processing, including image amplification, the removal of image aberrations, cross correlation of images and optical interconnections.
ADP occupies a prominent position among the numerous isomorphous of potassium dihydrogen phosphate (KDP). It has been observed that the replacement of potassium ion by the ammonium group in KDP causes a radical change in the nature of the phase transition in ADP converting it into an antiferroelectric at low temperature [7]. Mason and Matthias have shown that this material undergoes a sharp first order antiferroelectric transition at 148 K accompanied by a discontinuous drop in dielectric susceptibility [8]. However, the dielectric and piezoelectric measurements show that the transition is not a ferroelectric one but an order disorder transition as was suggested by the specific heat measurements [9,10]. Since, the specific heat anomaly occurring at this transition is much larger than those observed in other ammonium containing materials, the above transition was believed to be due to the interaction of the distorted NH₄⁺ ions which deviate from a spherically symmetrical configuration. X-ray studies by E.A.Wood show that the crystal structure change accompanying the transition in pure and deuterated ADP is caused by a quadratic distortion proportional to square and even powers of the spontaneous polarization. Hence below \( T_c \), the structure is antiferroelectric. Several authors reported the temperature dependence of the thermal parameters extrapolated at \( T=0 \) K. They obtained the following results; the P atom has a two-site distribution along the c- axis and the N atom along a(b) axis. The two-site distribution of the P and N atoms respectively means that the \( \text{PO}_4^{3-} \) and \( \text{NH}_4^+ \) ions have dipole moment that is parallel to the distribution direction [11]. Even though extensive investigations have been done to study this material near the well known transition using DSC and TGA, no attempt has hitherto been made to study the electrical
properties, particularly the dc electrical conductivity around this low temperature phase transition. In this paper we present the results of our studies on the low temperature electrical conductivity of ADP and discuss the implications of some of our findings.

2.3. EXPERIMENTAL

Single crystals of pure ADP were grown by slow evaporation from a saturated solution prepared with triply distilled water. Samples of the typical sizes 10 x 10 x 1 mm³ were cut from large single crystals and the broad faces (C-axis) of the specimens were coated with silver using vacuum coating technique. Details of the cryostat, sample holder and temperature control and measurements have been described in chapter 1. DC conductivity data were obtained on single crystals of ADP using an electrometer (Keithley model 642) along with a constant voltage source. A potential difference of the order of 10 - 40 V has been applied across the specimen which was kept under vacuum conditions.

2.4. RESULTS

The dc electrical conductivity measurements carried out in single crystals of ADP along C-axis in the temperature range 100 K to 400 K are shown in Fig (2.1). The results were found to be very well reproducible for different heating and cooling runs. Curve denoted by (a) in Fig (2.1) shows the log \( \sigma \) vs \( 10^3 /T \) for ADP in the cooling run whereas curve (b) represents the heating run. Conductivity plot shows a single unmistakable peak at 147 K on cooling the sample. In the heating
run it again occurs but is found to be shifted to a temperature of 148.1 K. Paraelectric-antiferroelectric phase transition temperature determined by dielectric, NMR, EPR and DSC techniques for ammonium dihydrogen phosphate shows the thermal hysteresis of the transition to be close to $2^\circ$ in all cases [12]. In the cooling run conductivity plot shows a sharp dip which is two orders of magnitude less compared to the one at 200 K whereas in the heating cycle it shows pronounced upward enhancement which is one order of magnitude greater than that observed at 200 K. This change in direction of the current peaks at the phase transition point is the most striking feature of the results of present measurements. It is also seen that below 300 K the log $\sigma$ vs $10^3 / T$ can be divided into two straight line regions denoted as I and II which are characteristics of ionic crystals. The activation energy values obtained by making use of the respective straight line regions are 0.70 eV and 0.08 eV respectively. The inset of Fig. (2.1) shows the variation of current values as a function of temperature in the heating and cooling runs around this transition point. Fig. (2.2) shows the current $I$ versus $10^3 / T$ plot for ADP in the cooling run and heating run (which are designated as (a) and (b) respectively) without applying any electric field across the sample.

2.5. DISCUSSION.

It is well known that ADP has a tetragonal structure with space group $D_{2d}^{12}$ in the paraelectric phase and it undergoes an antiferroelectric transition to the orthorhombic structure with space group $D_2^4$ [13]. The tetragonal crystal structure was studied in detail by Ueda and Pepinsky [14,15]. The crystal lattice of ADP and
the four hydrogen bonds $H_1, H_2, H_3$ and $H_4$ associated with phosphate group $P_0$ and with ammonium group A in ADP are shown in Figs. (2.3), (2.4) and (2.5) respectively.

Their results show that the $O----O$ distance of the hydrogen bonds connecting the neighboring $PO_4$ groups is 2.49A or 2.51A, smaller than the corresponding value for KDP which is 2.54A. Each nitrogen is surrounded by four oxygen atoms in the form of a flattened tetrahedron and the $N----O$ distance is 2.87A or 2.84A. It has been inferred from this small value of the $N----O$ distance that the formation of $N---H----O$ hydrogen bonds may play an important role in the mechanism of phase transition. However, the sum of the ionic radii of $NH_4^+$ and $O^{2-}$ is nearly equal to the observed $N----O$ distance, leading to the conclusion that such bonds do not play any role in this phase transition mechanism. On the other hand, the experimental investigations conducted on the crystal using dielectric constant, specific heat and infrared absorption evidently show that the antiferroelectric ordering in ADP involves the protons in the hydrogen bonds linking the acid group $H_2PO_4^-$ [8,10]. The specific anomaly at $T_c$ indicates a first order transition with a large isotopic effect on $T_c$ for deuterated samples. This implies that hydrogen bond motions dominate the phase transition dynamics. However, the infrared studies show strong ammonium ion distortions occurring at $T_c$ and this suggests that the $NH_4^+$ ion motions together with the acid group proton motions govern the phase transition dynamics which is fully in agreement with the NMR second moment calculations [16]. The polarized infrared reflectivity spectra of ADP in the paraelectric and antiferroelectric phase are reported for a wide spectral range, including the $PO_4$ and
Fig. (2.1) Temperature dependence of dc electrical conductivity measurements of pure ADP single crystal (a) cooling (b) heating.
Fig. (2.2). Current I vs. $10^3 / T$ plot for ADP in the cooling (a) and heating (b) run without applying any electric field across the sample.
Fig. (2.3). The crystal lattice of ADP.
Fig. (2.4). The four hydrogen bonds H₁, H₂, H₃ and H₄, associated with phosphate group P₀.

(a) view along c-axis (b) along b-axis (c) along a-axis.

The phosphate groups P₀ to P₄ are those shown in Fig. (2.3). Small circles are oxygens of the PO₄ groups.
Fig. (2.5). The four hydrogen bonds $H_1^1, H_2^1, H_3^1$ and $H_4^1$ associated with ammonium group A.

(a) view along c-axis (b) view along b-axis (c) view along a-axis.

The groups A, P_0, P_1 and P_3 are those shown in Fig. (2.3); P_6 and P_8 are at a distance c above P_2 and P_4 in Fig. (2.3), small circles are either oxygens of PO_4 groups or hydrogens of the NH_4 group A.
some of the NH₄ internal modes. Measurements were performed despite the shattering of the samples when undergoing the phase transition. Results evidence the disappearance just below T_c of a highly damped mode, which is observed in the whole paraelectric phase. This mode originates from intersite proton motions and is coupled with the brillouin zone-corner antiferroelectric instability. The other modes are only slightly affected by the phase transition, especially the NH₄ internal modes [17].

For ADP and its deuterated isomorphous DADP, the site symmetries of PO₄³⁻ (or H₂PO₄⁻ or D₂PO₄⁻) and NH₄⁺ (or ND₄⁺) ions have been reported to be C₂ in the paraelectric phase and C₁ in the antiferroelectric phase [15,16]. Although the order disorder mechanism is also expected for ADP and DADP in analogy with KDP, the site symmetry of the molecules or ions (PO₄, NH₄ and so on) in the paraelectric phase is different from that in the antiferroelectric phase. Consequently, the dipole moment produced by electric charges of ions and their distances in the paraelectric phase suggests that this phase has larger dipole moment at the transition point as the temperature decreases from 400 K to 100 K. According to the positional refinements of each atom in ADP by X ray diffraction study, each ammonium ion at the potassium position in KDP structure is shifted to the off center position by forming two shorter and longer bonds with four PO₄ tetrahedra at low temperature phase. When an oxygen is connected with the shorter N---H---O bond, it tends to keep the other proton off in the O---H---O bond and when with the larger N---H---O bond it tends to take the acid proton nearby. Thus the extra hydrogen bonds produce a distorted NH₄ ion lattice at low temperature causing a drastic change in the dipole moment. The
crystal invariably shatter on entry into the antiferroelectric phase because different domains get distorted in different directions. Several authors felt doubt about the coexistence of two phases at the low temperature transition point in the case of ADP crystals [5,6,20,21,22].

With reference to Fig.(2.1), although peaks appear during both cooling and heating runs in the conductivity plots the difference in direction of the peaks is particularly noteworthy. This observation undoubtfully confirm that, at the transition point the crystal shows pyroelectric behavior in addition to the antiferroelectric behavior. The corresponding pyroelectric field produced is directly proportional to the rate of heating of the sample. Hence this field get superposed over the externally applied field and produces peaks of different magnitude during cooling and heating runs, aiding the externally applied field in one case and acting in opposition in the other. Fig.(2.2) gives the recording of the peaks produced without applying any external electric field across the crystal at the transition point. The sharp and narrow nature of the peaks clearly distinguishes it from any ionic thermocurrent phenomenon. This explains the directional change observed in the conductivity plot at the transition point.

To elucidate the mechanism of electrical conduction process observed in ADP below 300 K, a brief discussion of the peculiar features of the PO₄ group in ammonium contain phosphates is required. Various types of defects observed in phosphate lattice is shown in Fig.(2.6). It is well known that in ADP type crystals the generally observed defects enhancing the electrical conduction processes are
(A) Ammonium dihydrogen phosphate lattice

(B) L and D defects.

(C) Ionization defects.

Fig. (2.6). Various types of defects observed in phosphate lattice.
the ionization defects viz: $\text{HPO}_4$ and $\text{H}_3\text{PO}_4$ produced as a result of the proton jumps from one phosphate group to the other along the same bond (intra bond 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 jump) of the same phosphate group. In ADP, in addition to the above defects there exists protonic defects associated with protons belonging to the NH$_4$ group (also known as A defects). In the extrinsic region above 285 K the conduction process is mainly due to the ionization defects and L and D defects corresponding to the activation energy value of 0.7 eV. In the temperature range below 285 K the small value of conductivity and activation energy (0.08 eV) observed could be due to the precipitation of the existing defects generated by the impurities in the conduction process.

2.6. CONCLUSION.

DC electrical conductivity measurements in single crystals of NH$_4$ H$_2$ PO$_4$ show anomalous variation at 147 K corresponding to a phase transition occurring in this material. The directional change observed in the conductivity plot undoubtedfully confirm that, the crystal exhibit pyroelectric behavior at the phase transition point. This observation is in good agreement with the possible coexistence of two phases at low temperature transition point in ADP crystal. Electrical conductivity at low temperature could be mainly due to protonic motion in addition to a small contribution due to impurity dominated extrinsic conduction.
2.7. REFERENCES.


