Chapter VI

DC AND AC ELECTRICAL CONDUCTIVITY, DIELECTRIC CONSTANT, IONIC THERMOCURRENT AND PHASE TRANSITIONS IN PURE AND DOPED (NH₄)₂Cr₂O₇ CRYSTALS

Abstract

Ammonium dichromate (AD) crystal has been investigated by dc and ac electrical conductivity, dielectric constant and ionic thermocurrent measurements. These measurements carried out along c-axis in the temperature range 80K to 435K show three distinct anomalous reversible changes at temperatures 128, 156 and 268K. Similar and supportive data were obtained with DSC measurements performed in the same temperature range. These experimental results indicate that (NH₄)₂Cr₂O₇ undergoes three phase transitions below room temperature. The mechanism of phase transition and of electrical conduction process in this material have been discussed and the activation parameters are evaluated.
6.1 INTRODUCTION

Ammonium containing crystals have been studied extensively using nuclear magnetic resonance. The proton resonance line shapes and second moments of various ammonium salts [1-8] show interesting changes as a function of temperature. Some of these changes can be interpreted readily in terms of the crystal structure of the salt and of various types of molecular motion occurring in them. Some of the salts, however, have nuclear resonance spectra which are not so easily interpreted, and more experimental and theoretical work is necessary to understand them. Careful measurements of spin lattice relaxation times as a function of temperature might very well provide important and detailed information about the molecular motion in these substances.

Gutowsky, Pake and Behrson [1] have investigated the second moments of the hydrogen resonance of ammonium chloride and ammonium bromide as a function of temperature and they found that this method is very suitable for determining the N-H distances in these compounds. The hindered rotation of \( \text{NH}_4^+ \) in ammonium compounds has been well investigated by the measurement of proton spin lattice relaxation time \( T_1 \) in the laboratory frame and \( T_{1\rho} \) in the rotating frame. However, because of the poor natural abundance of \( ^{17}O \)
(0.037%), it is very difficult to study the motion of oxygens by NMR. Shimomura et al. [6] reported that the temperature dependence of the dipolar relaxation time $T_{1D}$ goes through minimum values in $\text{NH}_4\text{ClO}_4$, $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and $(\text{NH}_4)_2\text{Ce(NO}_3)_6$. They have proposed a spin-rotational model to explain these $(T_{1D})_{\text{min}}$, in which it is considered that the rotation of $\text{NH}_4^+$ is triggered by the reorientation of the anions.

The reorientational motion of ammonium ions in $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ was thoroughly studied by Richards and Schaefer [9] using proton magnetic resonance. They have suggested a low barrier for the reorientational motion for the $\text{NH}_4^+$ ions. The neutron scattering cross section values [10,11] showed a much greater freedom of rotation and weaker hydrogen bonding for ammonium ions in this compound than in $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$. Vibrational spectra of $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ have been reported at room temperature by various investigators [12-15] and the temperature dependence of the infrared studies by Schutte and Heyns [16]. The first attempt to study the phase transitions in $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ was carried out by Jaffray [17] using differential thermal analysis and specific heat measurements. These measurements show that this material undergoes anomalous changes which may correspond to phase transitions at temperatures 128, 155 and 268K.
The temperature dependence of the relaxation time in the laboratory frame $T_1$, and in the rotatory frame $T_{1\rho}$ in pure and deuterated $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ (the concentration of deuterons is about 75%) have been reported by Morimoto [18]. The values of relaxation time in the laboratory frame for deuterated $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ are about three times larger than those in pure $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ below 143K suggesting that the inter molecular dipolar interaction of protons among $\text{NHD}_3^+$ in deuterated $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ is responsible for this change. On the other hand the temperature dependence of $T_{1\rho}$ in deuterated $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ shows minimum values between 313K and 299K. The minimum values of $T_{1\rho}$ observed in ammonium perchlorate and in ammonium dichromate by the same author [18] are about $10^5$ times larger than the theoretical predictions, suggesting that the origin of the $(T_{1\rho})_{\text{min}}$ can be understood as the effect of dipolar interaction between protons ($^1\text{H}$) of ammonium ions and $^{17}\text{O}$ of the anions. Further, the large anions will re-orientate about the symmetrical axes and then modulate the dipolar interaction between $^1\text{H}$ and $^{17}\text{O}$ causing the corresponding decrease in the values of $T_{1\rho}$. Eventhough Morimoto [18] studied the spin lattice relaxation times in pure and deuterated $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ in the temperature range 80K to 400K, no anomalous change has been observed in $T_1$ as well as in $T_{1\rho}$ values of these species at the
transition points reported earlier from specific heat and differential thermal analysis investigations. Moreover, no attempt has hitherto been done to investigate the electrical properties of this material as a function of temperature.

In the present chapter a detailed investigation carried out in single crystals of pure and $SO_4^{2-}$ doped $(NH_4)_2Cr_2O_7$ along c-axis in the temperature range 80K to 435K using dc and ac electrical conductivity, dielectric constant, ionic thermocurrent and differential scanning calorimetric studies is presented.

6.2 EXPERIMENTAL DETAILS

The method suggested by Kozlova et al. [19] to grow single crystals of $(NH_4)_2Cr_2O_7$ from solution by lowering the temperature of the aqueous solution near 24° from 53°C could not produce good transparent single crystals of suitable dimensions for the electrical measurements. We have used the method of slow evaporation to grow single crystals of this materials. The starting material after three times recrystallization using triply distilled water is used for the growth process. The saturated solution of the recrystallized material is kept in a constant
temperature water bath at 36°C. After three to four weeks large transparent single crystals of \((\text{NH}_4)_2\text{Cr}_2\text{O}_7\) will be obtained. \(\text{SO}_4^{2-}\) doped single crystals of \((\text{NH}_4)_2\text{Cr}_2\text{O}_7\) were prepared by adding appropriate amounts of \((\text{NH}_4)_2\text{SO}_4\) into the solution containing the pure material. The specimen used for the electrical measurements were prepared by cutting slices from large single crystals with typical dimensions 5x5x1 mm\(^3\) and by polishing it with zero grade emery and ground glass. Electrical contacts were made using aluminium electrodes evaporated on to the broad faces of the specimen parallel to (001) faces of the specimen. The electrical measurements were carried out in the cell with the normal procedures described in chapter II. The DSC studies were made in a Perkin Elmer Delta Series DSC7 calorimeter with a heating rate of 10°C/m in the temperature range 100K to 300K.

6.3 EXPERIMENTAL RESULTS

6.3.1 DC electrical conductivity measurements of pure and doped \((\text{NH}_4)_2\text{Cr}_2\text{O}_7\)

The dc electrical conductivity measurements carried out in single crystals of pure and doped specimens of \((\text{NH}_4)_2\text{Cr}_2\text{O}_7\) along c-axis in the temperature range 80K to 435K are shown in figure 6.3a. The results obtained were found to be very well reproducible for different samples
Figure 6.3a. Log $\sigma$ vs $10^3/T$ plot for ammonium dichromate crystals. (1) - pure, (2) - $SO_4^{2-}$ doped.
as well as for different heating and cooling cycles. The log$\sigma$ vs $10^3/T$ plot obtained for pure and doped specimens of ammonium dichromate shows three distinct A-shaped peaks at temperatures 128, 156 and 269K respectively. These anomalous changes in the conductivity plot divides the entire temperature range into four distinct straight line regions (Let us denote these regions as I, II, III and IV in the decreasing order of temperature). The transitions observed in pure $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ at 128 and 156K are quite abrupt and there is an enormous increase in conductivity observed at these points. Here the magnitude of the conductivity rises to more than one order, while the peak observed at 269K is less sharp and the increase in conductivity is about one order of magnitude. It is observed that for slower rate of variation of temperature the peaks are found to be sharper. No measurable thermal hysteresis has been observed in the transition regions. The activation energy values obtained from the straight line regions are 0.72, 0.34 and 0.08 eV respectively, for phases I, II and III in pure $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ (Since the IV phase does not yield measurable slope, no activation energy calculation has been done).

In the higher temperature region the conductivity plots for both pure and $\text{SO}_4^{2-}$ doped specimens merge
together which indicates that the same electrical conduction process are operative in both these materials. However, in the lower temperature region the conductivity of $SO_4^2-$ doped specimens is approximately one order of magnitude less compared to that in pure $(NH_4)_2Cr_2O_7$. No shift in the transition temperatures were observed in doped specimens in the range of doping concentrations used here. The activation energy values obtained in the case of $SO_4^2-$ doped specimens of $(NH_4)_2Cr_2O_7$ are 0.73, 0.37 and 0.085 eV respectively for first three phases.

6.3.2 AC electrical conductivity measurements in pure and doped $(NH_4)_2Cr_2O_7$

The ac electrical conductivity measurements carried out in pure and $SO_4^2-$ doped specimens of $(NH_4)_2Cr_2O_7$ at 90 Hz in the temperature range 80K to 435K is shown in figure 6.3b. The log$\sigma$ vs $10^3/T$ plot shows three distinct variations at temperatures 128, 156 and 269K respectively in both pure and doped $(NH_4)_2Cr_2O_7$ crystals. The magnitude of conductivity in the $SO_4^2-$ doped specimens is found to be less compared to that in pure material. However, the magnitude of ac conductivity is about one order of magnitude higher than that of the corresponding dc conductivity value in the whole temperature range studied here.
Figure 6.3b. Log $\sigma$ vs $10^3/T$ plot for pure (●●●) and $SO_4^2-$doped (○○○) specimen from ac conductivity measurements.
6.3.3 Dielectric Measurements

The dielectric constant measurements carried out in single crystals of pure ammonium dichromate along c-axis at 1 kHz in the temperature range 80K to 300K is shown in figure 6.3c. The plot gives anomalous variations exactly at the same temperatures where the dc and ac conductivity anomalies occur viz., 128, 156 and 269K. The dielectric constant increases gradually from 5.2 at 80K and reaches a maximum value of 10.1 at 128K and decrease thereafter as the temperature increases and attains another maximum of 16.25 at 156K. As the temperature increases the dielectric constant decreases and remains constant at 6.2 upto 200K and then slowly increases and attains a third maximum (12.8) forming a \( V \)-shaped dielectric anomaly at 269K. On further increase in temperature the dielectric constant slowly increases and attains a value about 12.5 at room temperature. On the cooling cycle no appreciable deviation was observed in dielectric values from that obtained in the heating runs and hence it is not shown in figure 6.3c. Also, the dielectric constant values obtained for 0.1 mole \% \( \text{SO}_4^{2-} \) doped specimens of \((\text{NH}_4)_2\text{Cr}_2\text{O}_7\) do not deviate much from the values obtained for pure \((\text{NH}_4)_2\text{Cr}_2\text{O}_7\) and hence they are not in the figure 6.3c.
Figure 6.3c. $\varepsilon_c$ vs $T$ plot for pure ammonium dichromate crystal.
C.3.4 Ionic thermocurrent measurements

The ionic thermocurrent measurements carried out in single crystals of pure \((\text{NH}_4)_2\text{Cr}_2\text{O}_7\) by polarising the specimens at 300K with a field of 3 KV/cm for 5 minutes are shown in figure 6.3d. The ITC spectrum obtained with a heating rate of 0.07 K/sec shows three distinct current peaks at temperatures 130, 159.5 and 271K. Let these peaks be denoted as A, B and C in the increasing order of temperature. The height of the peak B is twice that of A while peak C is approximately the same magnitude as that of peak A. The peaks A and B are quite sharp whereas the peak C is fairly broad. The height of the current peak is found to be slightly increased with increase in the poling field. However no change in magnitude has been observed for these peaks with the change in poling temperature and poling time.

C.3.5 Differential scanning calorimetric studies

Figure 6.3e shows the DSC spectrum recorded for pure \((\text{NH}_4)_2\text{Cr}_2\text{O}_7\) in the temperature range 100K to 300K with a heating rate of 10°C/m. The spectrum obtained shows three distinct variations in the heat flow at temperatures close to the point where earlier electrical and dielectric anomalies were observed.
Figure 6.3d. Ionic thermocurrent spectrum obtained for pure ammonium dichromate crystal.
Figure 6.36. DSC spectrum of ammonium dichromate material.
6.4 DISCUSSION

The results obtained for pure and doped (NH$_4$)$_2$Cr$_2$O$_7$ from various experimental techniques employed, it is clear that this material undergoes three anomalous variations at temperatures 128, 156 and 269K. Also there exists complete agreement between the dc and ac conductivity measurements and dielectric measurements as far as the temperature corresponding to the anomalous variations are concerned. The shift in the temperatures in ITC and DSC measurements is probably due to the higher heating rates employed in these measurements. Though the experimental results obtained for (NH$_4$)$_2$Cr$_2$O$_7$ from the present investigations are in complete agreement with results reported by Jaffray [17] from DTA and specific heat measurements and Schuttle and Heyns from infrared studies [16], no correlation has been observed from the results of NMR spin lattice relaxation time measurements [18]. Again, these earlier results could not explain the origin of the observed anomalous variations in these materials occurring at different temperatures. The transitions observed at the lower temperatures can in fact, be explained by considering the nature of hydrogen bonding in this material.

The structure of (NH$_4$)$_2$Cr$_2$O$_7$ is monoclinic with space group $C_{2h}^3$ or $C_{2h}^6$ according to Gossner and Mussgnug [20]. The determination of the unit cell parameters from
powder photographs (Cr-K radiation, \( \lambda a = 2.2909 \, \text{Å} \)) gives the following cell dimensions agreeing well with Gossner's and Mussgnug's values: \( a = 13.26 \, \text{Å} \), \( b = 7.54 \, \text{Å} \), \( c = 7.74 \, \text{Å} \) and \( \beta = 93.2^\circ \) with four formula units in the unit cell.

The crystal structure of \((\text{NH}_4)_2\text{Cr}_2\text{O}_7\) is shown in figure 6.4a. The chromium atoms are surrounded by four oxygen atoms, situated at the corners of a distorted tetrahedron. The \( \text{Cr}_2\text{O}_7^2- \) group is formed by the sharing of one corner oxygen atom by the two distorted tetrahedra. The \( \text{Cr}-\text{O}_4\text{-Cr} \) angle is 115° and the \( \text{Cr}-\text{Cr} \) distance in the bridge is 3.2 Å. The \( \text{Cr}-\text{Cr} \) distances between different \( \text{Cr}_2\text{O}_7^2- \) groups are much longer being 4.8 Å. The stable arrangement of the \( \text{Cr}_2\text{O}_7^2- \) group, consists of two \( \text{Cr} \) atoms and the shared oxygen atoms. The strong distortion of the dichromate group in the material is considered as due to the formation of strong N-H-O bonds but the accuracy of the \( \text{NH}_4-O \) (or rather N-O) distances is so low that it is not possible to decide whether this explanation is likely to be true or not. It is highly probable that the \( \text{NH}_4 \) tetrahedra in \((\text{NH}_4)_2\text{Cr}_2\text{O}_7\) also are highly distorted to give distinct orientations at lower temperatures where the lattice is found to be more rigid as in the case of \((\text{NH}_4)_2\text{SO}_4\) [21] and \((\text{NH}_4)_2\text{HPO}_4\) [22].

As observed in the infrared studies, the spectra obtained below 268K phase transition point differs very little
Figure 6.4a. The crystal structure of ammonium dichromate viewed along c-axis.
from that obtained at room temperature. When temperature is varied, a very broad band develops gradually in the region 1750 cm$^{-1}$ and 1600 cm$^{-1}$ and it splits into two weak broad bands at 1720 cm$^{-1}$ and 1650 cm$^{-1}$ below this transition point. It is also observed that the $\nu_4$ band of the NH$_4^+$ ion also becomes more asymmetric on the high frequency side as the temperature decreases below 268K. On further decrease in temperature below 155K just below the second phase transition a definite shoulder appears in the infrared spectrum at 1430 cm$^{-1}$ ($\nu_{4a}$) and a change in intensities of the Cr$_2$O$_7^{2-}$ bands is observed. As the temperature decreases below the phase transition point at 128K, the 875 cm$^{-1}$ band of the Cr$_2$O$_7$ ions is split into two components at 868 cm$^{-1}$ and 878 cm$^{-1}$ and abrupt changes occur in the intensities of some of the Cr$_2$O$_7^{2-}$ absorptions. From these experimental results it is concluded that NH$_4^+$ begins to execute free rotations (as observed in NH$_4$I [23]) at and above 128K. At lower temperatures because of the hindrance to the rotational motion and change in the torsional mode different variety of orientations are taking place. The distorted NH$_4^+$ ions are expected to possess a significant electric dipole moment. The high value of dielectric constant observed at temperatures 128, 156 and 269K can be attributed to the dipolar contribution to dielectric constant of (NH$_4^+$)$_2$Cr$_2$O$_7$ as a result of motional effect of NH$_4^+$ ions. This is in accordance with the results of NMR investigations. Similar effects
have been found to occur in ammonium sulphate [24], diammonium hydrogen phosphate [22] and in ammonium dihydrogen phosphate [25]. A detailed study of NMR measurements and low temperature structural studies preferably with neutron diffraction will be required to get a better understanding of the nature of reorientation of the various ion groups in this material.

As already discussed in chapter III the mechanism of electrical conduction in the material can also be explained by considering the nature of defect phenomena generally observed in crystals containing ammonium groups. In crystals containing ammonium groups, the types of defects usually observed are normal ionic, electronic and protonic defects. The contribution to the electrical conductivity by the \( \text{NH}_4^+ \) and \( \text{Cr}_2\text{O}_7^{2-} \) group and their vacancies can be neglected in considerations based on their sizes.

From the experimental results obtained for pure and doped material, it has been suggested that the conduction mechanism in the region is predominantly due to the cation vacancies created by thermal generation of the detached ammonium groups in this material or due to the generation of protonic defects. The activation energy values obtained in the phase I, for pure and doped material clearly show that
electrical conduction mechanisms are responsible in this region for both kind of crystals.

The lower value of conductivity observed in the case of $\text{SO}_4^{2-}$ doped specimens of $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ can be explained by considering the nature and role of $\text{SO}_4^{2-}$ ions in the $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ lattice. When a divalent anionic impurity is substituted in an ionic crystal like $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$, the charge compensation is generally accomplished by the creation of anionic vacancies in the host lattice. Since in the $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ lattice, the size of the anions are fairly large compared with that of the impurity ions, the probability of the migration of interstitials as well as vacancies is less likely. Therefore, the $\text{SO}_4^{2-}$ ions form complexes with only the mobile ions viz., hydrogen associated with the $\text{NH}_4^+$ groups in $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$. Complexes thus formed are predominantly $\text{HSO}_4^-$ ions which have lesser mobility. Thus it is clear that the reduction in the magnitude of conductivity at lower phases can be due to the formation of these complexes provided the dominant mechanism of electrical conduction is by migration of interstitial hydrogen ions. The experimental results reveal that the above mechanism is operative in phases II and III causing a significant reduction in the magnitude of conductivity compared to that in pure $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$. At fairly high temperatures probably the dissociation of these complexes can also affect
the electrical conduction process in this material and in this region one can hence expect a higher value for $\sigma^-$. 

As already indicated $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ undergoes phase transitions at different temperatures due to free rotation and hindered rotations of the $\text{NH}_4^+$ ions. This gives rise to free charge carriers, causing a corresponding peaks in the ITC spectrum. Thus the observed peaks in the ITC spectrum attributed to the space-charge formation at the phase transition points. As these peaks are rather sharp they are not likely to be due to reorientation of any I-V dipoles. This result is a further confirmation that ITC measurement is a sensitive technique for the detection of a phase transition in solid.

6.5 CONCLUSIONS

The dc and ac conductivity, dielectric constant ionic thermocurrent and DSC studies carried out in single crystals of pure and doped $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ along c-axis in the temperature range 80K to 435K give the following conclusions.

1. The dc and ac electrical conductivity and dielectric constant measurement show anomalous variations at temperatures 128, 156 and 269K corresponding to three phase transitions.
A small shift in transition temperatures were observed in the ionic thermocurrent and DSC studies.

2. The shift in the transition temperatures observed in ITC and DSC studies could be due to the higher heating rates employed in these techniques.

3. The transition observed in this material at different temperatures could be due to free rotation, reorientation and hindered internal rotation of the NH$_4$ groups in these materials.

4. The activation energy values obtained in phase I in both pure and doped (NH$_4$)$_2$Cr$_2$O$_7$ indicate that the electrical conduction mechanism in this region is predominantly due to protons.

5. The higher magnitude of conductivity observed in ac measurements compared to that in dc measurements is probably due to the additional component of polarization current in the ac measurements.

6. The activation energy values obtained from the straight line regions of the phases I, II and III are 0.72, 0.34 and 0.08 and 0.73, 0.37 and 0.08 respectively for pure and doped (NH$_4$)$_2$Cr$_2$O$_7$. 
6.6 REFERENCES


[23] W. Vedder, "The Infrared Absorption Spectrum of the Ammono­
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