

# Temperature Dependence of the Spontaneous Polarization and the Dielectric Susceptibility near the Phase Transitions in Ammonium Sulfate

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## ABSTRACT

Spontaneous polarization and the dielectric susceptibility are calculated as a function of temperature close to the paraelectric-ferroelectric phase transition ( $T_C=223$  K) in  $(\text{NH}_4)_2\text{SO}_4$ . This calculation is performed using a mean field model by fitting the expressions derived for the dielectric susceptibility to the experimental data for the dielectric constant at the fixed frequencies of 100, 500 and 2000 Hz in ammonium sulfate.

Our calculations show that an observed first order transition can be described adequately by the mean field model given here for ammonium sulfate.

**Keywords:** Spontaneous polarization. Dielectric susceptibility.  $(\text{NH}_4)_2\text{SO}_4$ .

## 1. INTRODUCTION

Ammonium sulfate exhibits a ferroelectric phase transition at about 223 K from the paraelectric phase with the space group  $D_{2h}^{16}$  to the ferroelectric phase with the space group  $C_{2v}^9$ , as the temperature is lowered. This transition is considered as a first order type.

The ferroelectric phase transition of ammonium sulfate has been studied extensively using various experimental techniques. Dielectric measurements /1-4/, infrared and Raman spectra /5-8/, proton-nitrogen double resonance /9/, measurements of the dipolar relaxation time /10/, NMR /11-15/, neutron diffraction /16/, ESR /17, 18/ EPR and Mössbauer /19/ studies have been reported in the literature. DTA (Differential Thermal Analysis) and TMA (Thermo-Mechanical Analysis) /4/ have been performed for ammonium sulfate, as we have reviewed in our previous work /20/.

The ferroelectric phase transition in  $(\text{NH}_4)_2\text{SO}_4$  has also been studied theoretically by using the modified mean field theory /11/ and the soft mode theory /21/. Observation for the temperature dependence of the spontaneous polarization of  $(\text{NH}_4)_2\text{SO}_4$  /22/ has been explained by a two-sublattice model /2/. The polar phase called the ferroelectric phase with the two oppositely polarized sublattices, occurred below  $T_C$  /23/. The two-sublattice model has been studied to explain the mechanism of phase transitions in  $(\text{NH}_4)_2\text{SO}_4$  by obtaining the critical behavior of the spontaneous polarization and the dielectric susceptibility /24, 25/. Recently, we have calculated the temperature dependence of the dielectric susceptibility in the ferroelectric phase of  $(\text{NH}_4)_2\text{SO}_4$  /20/ using the two polarizations  $P_1$  and  $P_2$  with their quadratic coupling in a mean field model. We have also calculated the phase diagram of a mixture of  $(\text{NH}_4)_2\text{SO}_4/\text{H}_2\text{O}$  /26/ using our mean field model.

In this work we investigate the mechanism of the ferroelectric-paraelectric phase transition in ammonium

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sulfate by calculating the temperature dependence of the dielectric constant and the spontaneous polarization using our mean field model. Our calculation is performed by fitting the relation for the dielectric constant which we derive from our mean field model to the experimental data [4] at constant frequencies. By determining the coefficients in the free energy expansion, we then calculate the temperature dependence of the spontaneous polarization at constant frequencies for  $(\text{NH}_4)_2\text{SO}_4$ .

## 2. THEORY

We give here a mean field model which can describe the ferroelectric-paraelectric phase transition for ferroelectric materials. We simply expand the free energy in terms of the spontaneous polarization  $P$  (order parameter) as,

$$F = a_0 + a_2 P^2 + a_4 P^4 + a_6 P^6 \quad (2.1)$$

where we assume that  $a_0$  and  $a_6$  are constants,  $a_2$  and  $a_4$  depend on temperature. We assume the temperature dependence of the coefficients  $a_2$  and  $a_4$  for the ferroelectric and paraelectric phases, separately as given below. When Eq. (2.1) describes a first order phase transition, we have  $a_4 < 0$  and  $a_6 > 0$  in the Landau phenomenological theory.

By minimizing the free energy with respect to the spontaneous polarization, we get

$$P(2a_2 + 4a_4 P^2 + 6a_6 P^4) = 0 \quad (2.2)$$

The above equation can be solved for the spontaneous polarization  $P$ . The  $P=0$  solution defines the paraelectric phase. The quadratic solution gives

$$P^2 = \frac{-a_4 \pm (a_4^2 - 3a_2 a_6)^{1/2}}{3a_6} \quad (2.3)$$

which describes the ferroelectric phase. By using the temperature dependencies of the coefficients  $a_2$  and

$a_4$ , the spontaneous polarization can be calculated as a function of temperature according to Eq.(2.3).

The temperature dependence of the dielectric susceptibility  $\chi$  can also be derived from the free energy (Eq.2.1). By taking the second derivative of the free energy with respect to the polarization,

$$\chi = \left( \frac{\partial^2 F}{\partial P^2} \right)_T$$

or the first derivative of the electric field,  $E = \left( \frac{\partial F}{\partial P} \right)_T$  with respect to the polarization, we

get the temperature dependence of the dielectric susceptibility as

$$\frac{1}{\chi} = 2a_2 + 12a_4 P^2 + 30a_6 P^4 \quad (2.4)$$

By equating the spontaneous polarization to zero ( $P=0$ ) in the paraelectric phase the expression,

$$\frac{1}{\chi} = \frac{1}{\epsilon - 1} = 2a_2 \quad (2.5)$$

represents the temperature dependence of the dielectric susceptibility or equivalently, the dielectric constant  $\epsilon$  in the paraelectric phase ( $T > T_C$ ), whereas Eq.(2.4) is the  $\chi$  relation in the ferroelectric phase ( $T < T_C$ ).

Eq.(2.4) can be expressed in terms of the coefficients  $a_2$ ,  $a_4$  and  $a_6$  by substituting Eq.(2.3), the  $P^2$  solution (with the minus sign in root square) into Eq.(2.4). Using the ansatz  $\frac{a_2 a_6}{a_4^2} \ll 1$  and by expanding the root square term in Eq.(2.3) as

$$(a_4^2 - 3a_2 a_6)^{1/2} = a_4 - \frac{3 a_2 a_6}{2 a_4} \quad (2.6)$$

the reciprocal dielectric susceptibility (Eq.2.4) can be expressed as

$$\frac{1}{\chi} = \frac{1}{\epsilon - 1} = -12a_2 + \frac{16 a_4^2}{3 a_6} \quad (2.7)$$

Thus, Eq.(2.7) represents the temperature dependence of the dielectric constant in the ferroelectric phase.

Finally, using the ansatz  $\frac{a_2 a_6}{a_4^2} \ll 1$  given above, the spontaneous polarization (Eq.2.3) can be easily calculated as a function of temperature. By expanding again the root square term in Eq.(2.3) as given by Eq.(2.6), Eq.(2.3) can be obtained as

$$P^2 = -\frac{2a_4}{3a_6} + \frac{a_2}{2a_4} \quad (2.8)$$

### 3. CALCULATIONS AND RESULTS

We calculated here the temperature dependence of the spontaneous polarization  $P$  and the dielectric susceptibility  $\chi$  or the dielectric constant  $\epsilon$  for the ferroelectric-paraelectric phase transition in  $(\text{NH}_4)_2\text{SO}_4$ . This calculation was performed for the three constant frequencies, namely, 100, 500 and 2000 Hz using the experimental data for  $(\text{NH}_4)_2\text{SO}_4$  [4]. We fitted the expressions for the dielectric constant (Eqs. 2.5 and 2.7) which we derived from the mean field model, to the experimental data for  $(\text{NH}_4)_2\text{SO}_4$  [4]. For our fits, we

$$\frac{1}{\epsilon - 1} = \frac{16}{3} \frac{a_{40}^2}{a_{60}} + \left( \frac{32}{3} \frac{a_{40} a_{41}}{a_{60}} - 12a_{20} \right) (T - T_c) + \frac{16}{3} \frac{a_{41}^2}{a_{60}} (T - T_c)^2 \quad (3.5)$$

in the ferroelectric phase.

$$P^2 = -\frac{2}{3a_{60}} [a_{20} + a_{21}(T - T_c)] + \frac{a_{20}(T - T_c)}{2[a_{40} - a_{41}(T - T_c)]} \quad (3.6)$$

Thus, we fitted first Eq.(3.5) to the experimental data for the dielectric constant [4] and we determined the coefficients  $a_{20}$ ,  $a_{40}$  and  $a_{41}$  at a constant frequency of 100 Hz for  $(\text{NH}_4)_2\text{SO}_4$  in the ferroelectric phase ( $T < T_c$ ). We chose here  $a_{60} = 1$ . Our fitted values of  $a_{20}$ ,  $a_{40}$  and  $a_{41}$  are tabulated within the temperature interval in **Table 1**. We plot  $1/(\epsilon-1)$  as a function of  $T_c - T$

assumed the temperature dependence of the coefficients as

$$a_2 = a_{20} + a_{21}(T - T_c) + a_{22}(T - T_c)^2 \quad (3.1)$$

for the paraelectric phase ( $T > T_c$ ) according to Eq. (2.5).

For the ferroelectric phase, we assumed the temperature dependencies of the coefficients  $a_2$  and  $a_4$  for our fits as

$$a_2 = a_{20}(T - T_c) \quad (3.2)$$

$$a_4 = a_{40} + a_{41}(T - T_c) \quad (3.3)$$

and  $a_6 = a_{60}$ . On the basis of the temperature dependence of the coefficient  $a_2$  (Eq.3.1), the dielectric constant  $\epsilon$  (Eq.2.5) can be written as

$$\frac{1}{\epsilon - 1} = 2[a_{20} + a_{21}(T - T_c) + a_{22}(T - T_c)^2] \quad (3.4)$$

in the paraelectric phase.

Similarly, using the temperature dependencies of the coefficients  $a_2$  (Eq.3.2) and  $a_4$  (Eq.3.3), the dielectric constant  $\epsilon$  (Eq.2.7) can be written as

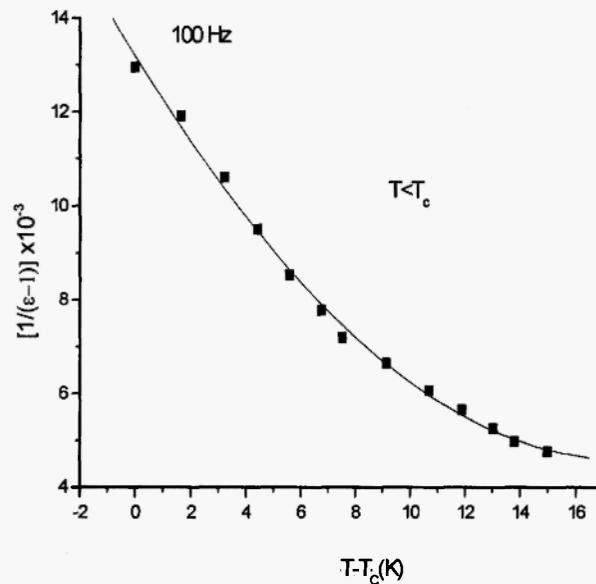
Finally, the temperature dependence of the spontaneous polarization (Eq.2.8) can be expressed in terms of the temperature-dependent  $a_2$  and  $a_4$  terms as

at 100 Hz for  $(\text{NH}_4)_2\text{SO}_4$  in the ferroelectric phase ( $T < T_c$ ) in **Figure 1** with the observed data [4]. We then fitted Eq. (3.4) to the experimental data [4] for  $(\text{NH}_4)_2\text{SO}_4$  at 100 Hz and we calculated the coefficients  $a_{20}$ ,  $a_{21}$  and  $a_{22}$ , for the paraelectric phase ( $T > T_c$ ), as given in **Table 2**. **Figure 2** gives  $1/(\epsilon-1)$  as a function of

**Table 1**

Values of the parameters calculated according to Eq.(3.5) within the temperature interval given for constant frequencies indicated in the ferroelectric phase ( $T < T_c$ ) of  $(\text{NH}_4)_2\text{SO}_4$ . The figure numbers are also given here to indicate the parameters used for each constant frequency.

Frequency (Hz)	$a_{20} \times 10^{-4}/\text{K}$	$-a_{40} \times 10^{-2}$	$-a_{41} \times 10^{-3}/\text{K}$	$\Delta T (\text{K}) = T_c - T$	Figures
100	1.80	4.98	2.252	$0 < \Delta T < 16$	1
500	5.312	7.45	4.258	$0 < \Delta T < 20$	3
2000	16.268	11.74	7.963	$0 < \Delta T < 20$	5

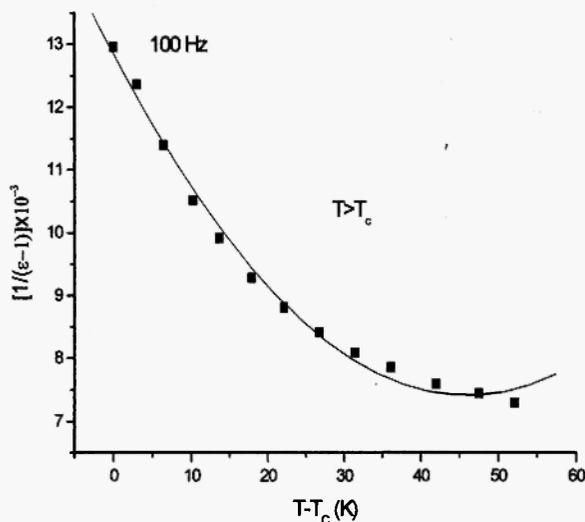


**Fig. 1:** Inverse susceptibility  $\chi^{-1} = 1/(\epsilon - 1)$  where  $\epsilon$  is the dielectric constant calculated from Eq.(3.5) as a function of  $T_c - T$  in the ferroelectric phase ( $T < T_c$ ) of  $(\text{NH}_4)_2\text{SO}_4$  at the frequency of 100 Hz. (■) represents the observed data [4].

**Table 2**

Values of the parameters calculated according to Eq.(3.4) within the temperature interval given for constant frequencies indicated in the paraelectric phase ( $T > T_c$ ) of  $(\text{NH}_4)_2\text{SO}_4$ . The figure numbers are also given here to indicate the parameters used for each constant frequency.

Frequency (Hz)	$a_{20} \times 10^{-3}$	$-a_{21} \times 10^{-4}/\text{K}$	$a_{22} \times 10^{-6}/\text{K}^2$	$\Delta T (\text{K}) = T - T_c$	Figures
100	6.42	1.183	1.288	$0 < \Delta T < 55$	2
500	14.44	6.85	24.55	$0 < \Delta T < 18$	-
500	10.23	0.5967	0.4158	$20 < \Delta T < 85$	4
2000	20.39	2.1988	2.002	$0 < \Delta T < 80$	6



**Fig. 2:** Inverse susceptibility  $\chi^{-1}=1/(\epsilon-1)$  where  $\epsilon$  is the dielectric constant calculated from Eq.(3.4) as a function of  $T-T_c$  in the paraelectric phase ( $T>T_c$ ) of  $(\text{NH}_4)_2\text{SO}_4$  at the frequency of 100 Hz. (■) represents the observed data [4].

$T-T_c$ . The observed data for 100 Hz [4] is also given in **Figure 2**.

Similar calculation was also carried out at the frequencies of 500 and 2000 Hz for the ferroelectric and paraelectric phases of  $(\text{NH}_4)_2\text{SO}_4$ . By fitting Eq.(3.5) to the observed data at the frequencies of 500 and 2000 Hz [4], the coefficients  $a_{20}$ ,  $a_{40}$  and  $a_{41}$  were determined within the temperature intervals in the ferroelectric phase, as given in Table 1. Also, by fitting Eq.(3.4) to the observed data [4], the coefficients  $a_{20}$ ,  $a_{21}$  and  $a_{22}$  were determined within the temperature interval in the paraelectric phase, as tabulated in Table 2. **Figure 3** represents our calculated (Eq.3.5)  $1/(\epsilon-1)$  against  $T_c-T$  in the ferroelectric phase ( $T<T_c$ ) with the observed data [4] at 500 Hz. **Figure 4** gives our fit in the temperature interval, as indicated in Table 2, for  $1/(\epsilon-1)$  against  $T-T_c$  in the paraelectric phase ( $T>T_c$ ) at 500 Hz. The observed data [4] is also shown there. A plot of  $1/(\epsilon-1)$  against  $T-T_c$  in the paraelectric phase can also be obtained in the temperature interval ( $0<\Delta T<18$  K) at 500 Hz, as given in Table 2. We plot in **Figure 5** our calculated values of  $1/(\epsilon-1)$  against  $T_c-T$  according to Eq.(3.5) at the frequency of 2000 Hz in  $(\text{NH}_4)_2\text{SO}_4$ . We also plot  $1/(\epsilon-1)$  as a function of  $T-T_c$  in the paraelectric phase at the frequency of 2000 Hz in **Figure 6**,

according to Eq.(3.4). Since we determined the coefficients  $a_{20}$ ,  $a_{40}$  and  $a_{41}$  for the ferroelectric phase at the frequencies of 100, 500 and 2000 Hz (**Table 1**), we were able to evaluate the spontaneous polarization as a function of temperature according to Eq.(3.6) for  $(\text{NH}_4)_2\text{SO}_4$ . **Figure 7** gives our calculated polarization as a function of temperature at the frequencies of 100, 500 and 2000 Hz.

#### 4. DISCUSSION

We calculated here the temperature dependence of the dielectric constant by the relations derived from our mean field model for the ferroelectric and paraelectric phases of  $(\text{NH}_4)_2\text{SO}_4$ . This calculation was carried out at the frequencies of 100, 500 and 2000 Hz for this ferroelectric material. By fitting Eq.(3.5) (obtained from Eq.(2.7) in the ferroelectric phase) and Eq.(3.4) (obtained from Eq.(2.5) in the paraelectric phase) to the experimental data [4], we deduced the values of the coefficients (**Tables 1 and 2**). As we see from the plots (**Figures 1-6**), our quadratic fits (Eqs.3.5 and 3.4) are reasonably good and they are compared well with the observed data [4]. In particular, at the frequency of 100 Hz (**Figures 1 and 2**), the observed data is very well

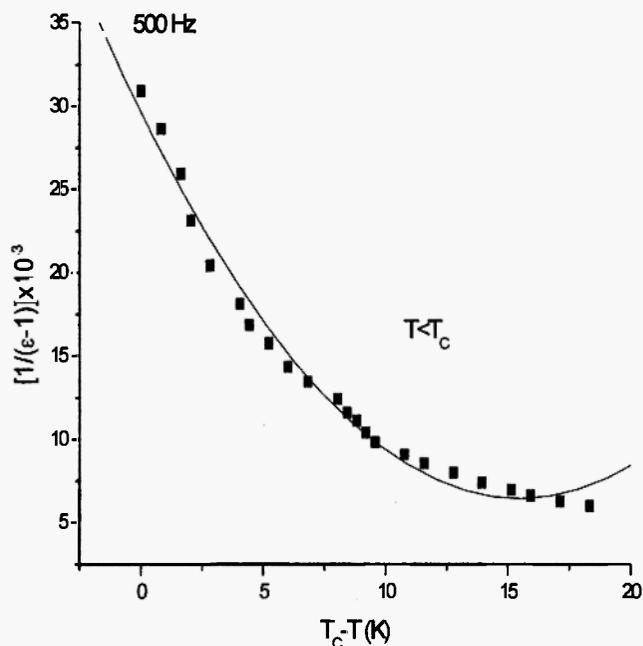


Fig. 3: Inverse susceptibility  $\chi^{-1}=1/(\epsilon-1)$  where  $\epsilon$  is the dielectric constant calculated from Eq.(3.5) as a function of  $T_c-T$  in the ferroelectric phase ( $T < T_c$ ) of  $(\text{NH}_4)_2\text{SO}_4$  at the frequency of 500 Hz. (■) represents the observed data /4/.

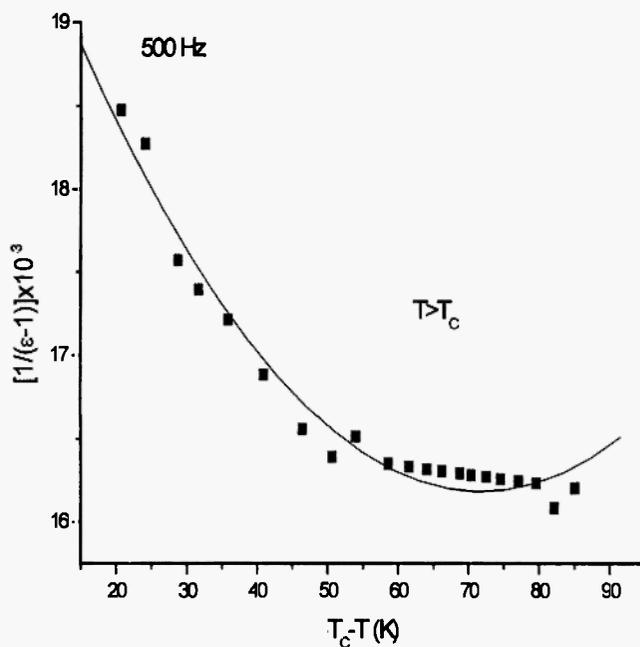
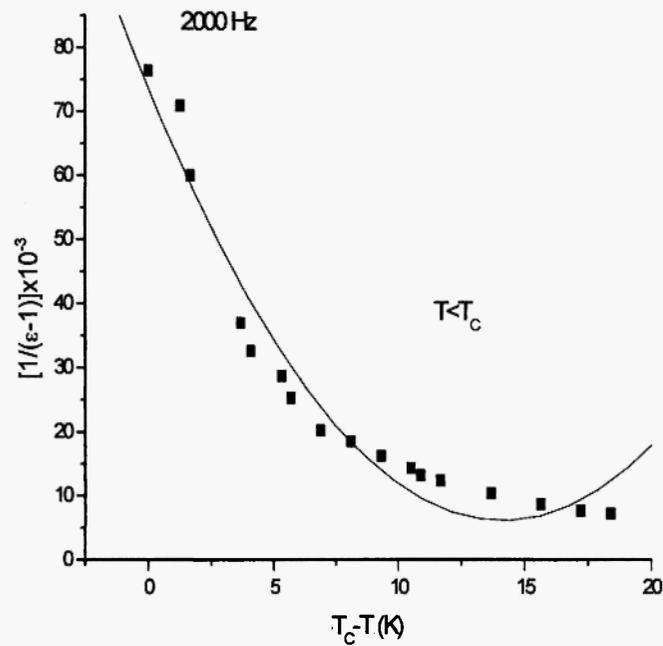
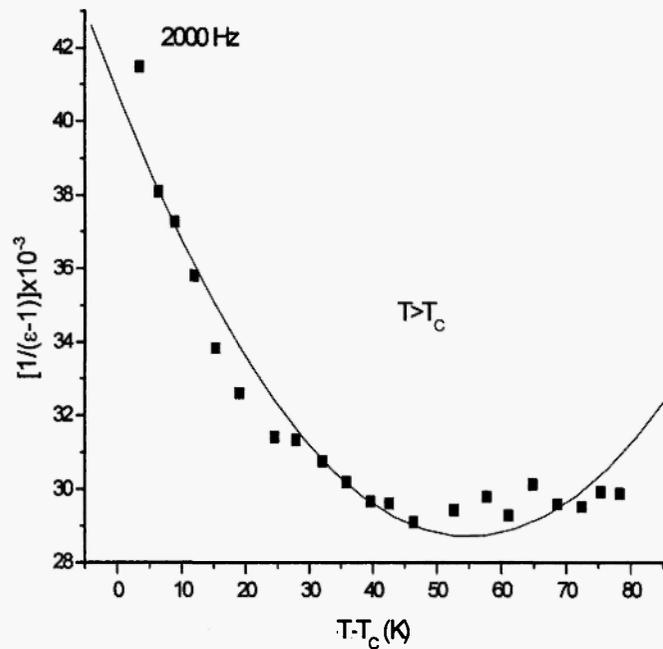


Fig. 4: Inverse susceptibility  $\chi^{-1}=1/(\epsilon-1)$  where  $\epsilon$  is the dielectric constant calculated from Eq.(3.4) as a function of  $T-T_c$  in the paraelectric phase ( $T > T_c$ ) within the temperature interval indicated for  $(\text{NH}_4)_2\text{SO}_4$  at the frequency of 500 Hz. (■) represents the observed data /4/.



**Fig. 5:** Inverse susceptibility  $\chi^{-1}=1/(\epsilon-1)$  where  $\epsilon$  is the dielectric constant calculated from Eq.(3.5) as a function of  $T_c-T$  in the ferroelectric phase ( $T < T_c$ ) within the temperature interval indicated for  $(\text{NH}_4)_2\text{SO}_4$  at the frequency of 2000 Hz. (■) represents the observed data /4/.



**Fig. 6:** Inverse susceptibility  $\chi^{-1}=1/(\epsilon-1)$  where  $\epsilon$  is the dielectric constant calculated from Eq.(3.4) as a function of  $T-T_c$  in the paraelectric phase ( $T > T_c$ ) within the temperature interval indicated for  $(\text{NH}_4)_2\text{SO}_4$  at the frequency of 2000 Hz. (■) represents the observed data /4/.

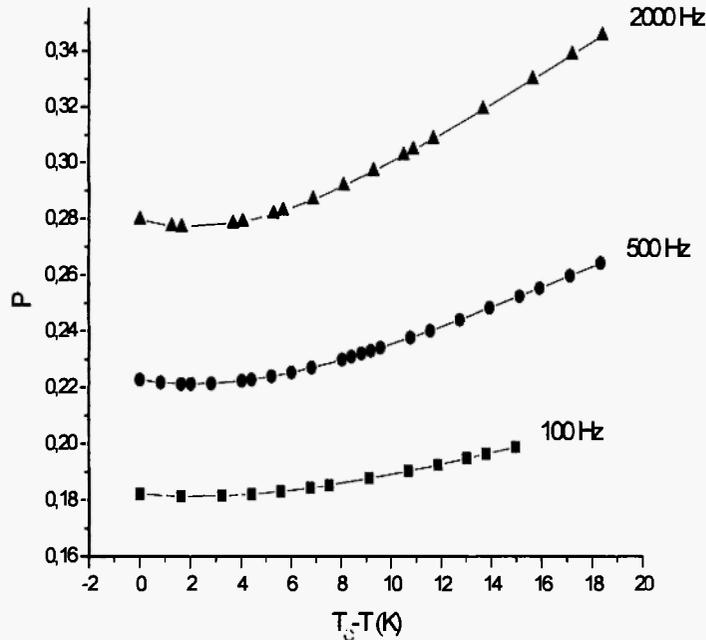


Fig. 7: Spontaneous polarization  $P_S$  ( $T_C = 223$  K) calculated from Eq.(3.6) as a function of  $T - T_C$  for  $(\text{NH}_4)_2\text{SO}_4$  at constant frequencies of 100, 500 and 2000 Hz.

represented by the predictions (Eqs. 2.5 and 2.7) of our mean field model. At higher frequencies (500 and 2000 Hz), our fits (Figures 3-6) are not as good as those for 100 Hz because of some scattered data which is not very well represented by a quadratic function predicted from our mean field model. At the frequency of 500 Hz, we fitted Eq. (3.4) to the experimental data [4] in the paraelectric phase ( $T > T_C$ ) for the two different temperature intervals (Table 2), as plotted here for a wider temperature interval (Figure 4). Since the experimental data was obtained in a relatively large temperature interval ( $T - T_C = 90$  K), one quadratic fit (Eq.3.4) was not appropriate for all the region. So that Eq. (3.4) was fitted to the experimental data in the two temperature intervals. The experimental data was also scattered in the paraelectric phase ( $T > T_C$ ) at the frequency of 2000 Hz within the temperature range of  $T - T_C = 40$  K to 80 K where the inverse susceptibility is almost independent of temperature (Figure 6). It has been reported that a dielectric dispersion (the frequency dependence of the dielectric constant) was detected in

the high temperature phase and that this dispersion was attributed to piezoelectric resonance [4]. The anomalies predicted for the inverse susceptibility, as also observed experimentally (Figures 1-6) are attributed to the reorientations of the ammonium ions. It has been argued that the anomalies are mainly due to distortion of the tetrahedron [27] or change of reorientation time [28]. This follows that the first order character of the phase transition in ammonium sulfate is mainly because of the sulfate groups, as also suggested previously [29].

By knowing the values of the coefficients (Table 1) from the fits of the dielectric constant  $\epsilon$ , we were then able to evaluate the spontaneous polarization for various temperatures at constant frequencies of 100, 500 and 2000 Hz in  $(\text{NH}_4)_2\text{SO}_4$ . As shown in Figure 7, our calculated values of the spontaneous polarization exhibit the expected critical behaviour in the ferroelectric phase. As the temperature decreases, the spontaneous polarization grows which indicates the ordering due to the reorientation of the  $\text{NH}_4^+$  ions. Our prediction for the spontaneous polarization  $P$  (Figure 7) can be

compared with the observed behavior in the ferroelectric phase of  $(\text{NH}_4)_2\text{SO}_4$ . Such a plot of  $P_S$  ( $\mu\text{C}/\text{m}^2$ ) vs  $T(\text{K})$  with the observed data due to contribution of the lattice polarization and its best fit has been reported [29] for the ferroelectric phase of ammonium sulfate. Contribution due to the distortion of all the ions causes the spontaneous polarization decreasing on cooling. Therefore, they have explained the behavior of the spontaneous polarization by two contributions, a lattice part and a part due to distortion of all the ions [29].

Our calculated values of the spontaneous polarization can be properly compared with the experimental measurements at 100, 500 and 2000 Hz. Thus, the measurements of the spontaneous polarization as a function of temperature within the temperature intervals given at constant frequencies of 100, 500 and 2000 Hz, can examine our calculated values (Figure 7).

## 5. CONCLUSIONS

We derived here the temperature dependence of the dielectric constant and of the spontaneous polarization from our mean field model. By fitting our expressions for the dielectric constant to the experimental data for  $(\text{NH}_4)_2\text{SO}_4$ , we calculated the coefficients given in the mean field free energy. This provided us to calculate the temperature dependence of the spontaneous polarization at constant frequencies in  $(\text{NH}_4)_2\text{SO}_4$ . From our calculated values of the dielectric constant and the spontaneous polarization at various temperatures for constant frequencies, we conclude that our mean field model describes satisfactorily a first order transition of  $(\text{NH}_4)_2\text{SO}_4$ , as observed experimentally. Experimental measurements for the spontaneous polarization at a constant frequencies studied, are needed to examine our calculations given here.

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