STRUCTURAL PHASE TRANSITION IN IMPROPER FERROELECTRIC AMMONIUM SULPHATE

Parmendra Kumar Bajpai

DEPARTMENT OF PHYSICS
SCHOOL OF PHYSICAL SCIENCES
NEHU

A THESIS
SUBMITTED
IN
FULFILMENT OF THE REQUIREMENTS OF THE DEGREE OF

DOCTOR OF PHILOSOPHY

To

THE NORTH-EASTERN HILL UNIVERSITY

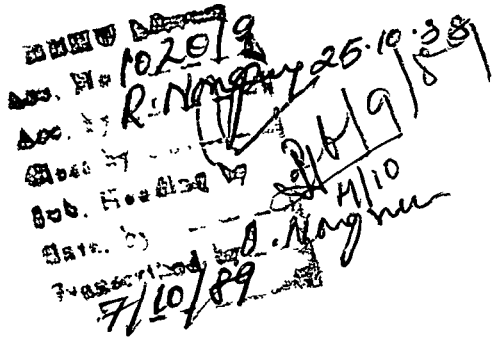
SHILLONG

INDIA

JULY 1987

phy

DS
536.401
BAJ



to my parents

Dr. Y. S. Jain
READER

DEPARTMENT OF PHYSICS
North-Eastern Hill University
SHILLONG 793 003

July 1987

I certify that the thesis entitled "**Structural Phase Transition in Improper Ferroelectric Ammonium Sulphate**" *submitted by Shri Parmendra Kumar Bajpai for the degree of Doctor of Philosophy of the North-Eastern Hill University, Shillong embodies the record of original investigation carried out by him under my supervision. He has been duly registered, and the thesis presented is worthy of being considered for the award of the Ph.D. degree. This work has not been submitted for any degree of any other University.*

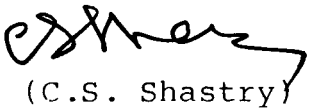
Y. S. Jain

(Dr. Y.S. Jain)
Supervisor

CERTIFICATE

This is certified that Shri Parmendra Kumar Bajpai has cleared the following four Pre-Ph.D. courses obtaining on average 'A' grade.

Courses	Grades
1. Group theory and molecular physics	A
2. Elementary Particle Physics	A
3. Instrumentation techniques (School level)	A
4. French language course (University level)	A



(C.S. Shastry)
Professor and Head
Department of Physics,
North Eastern Hill University
Shillong 793 003

ACKNOWLEDGEMENTS

I express my deepest sense of gratitude to Dr. Y.S. Jain for his keen interest, invaluable suggestions and inspiring guidance throughout the course of this research. I am grateful to him for his encouragement, advice and affection.

I am thankful to Prof. R.K. Mishra, Vice-Chancellor, NEHU for his keen interest in the completion of the work. Thanks are due to Prof. C.S. Shastry, Head, Department of Physics, NEHU, for his encouraging help.

Thanks are also due to Dr. P.N. Ram for useful discussion and valuable suggestion. I am indebted to Prof. P.N. Asthana (B.B. College, Jhansi) for inspiring me to choose the research career.

I am grateful to Prof. H.D. Bist, IIT, Kanpur, for his manifold help including the facilities at his laser Raman Laboratory where laser Raman spectra were recorded. I thank Mr. P.K. Khulbe for his help in recording the spectra.

I wish to thank Profs R.P. Bajpai, H. Junjappa, K.K. Gupta, A.M. Dwivedi, S.N. Dube, P. Shukla, Y.S.T. Rao, and Drs. P.N. Pandita, R. Singh, D.T. Kathing, Vinod Singh, P.K. Mandal and S.K. Mishra for their interest and encouragement.

I am thankful to Prof. G. Schaak, Univ. of Würzburg (W. Germany) for helpful communication.

My thanks are also due to my colleagues Dr. R. Bhattacharjee, S/Shree R.L. Gupta, A. Saxena, Akhilesh Gupta, V.R. Rao, M. Sudarshan and Miss M. Sarkar for their help at various stages.

This column remains incomplete if I forget to acknowledge the help and encouragement which I got from my elder brother Shri S.K. Bajpai and my other family members and friends Mr. G.P. Sinha and S.K. Sharma.

contd..

I thank Mr. N.Paul Choudhury for his adept typing and Mr. Warjary for fine xeroxing.

Financial help from North-Eastern Hill University and the University Grants Commission, New Delhi is gratefully acknowledged.

SHILLONG

Dt.....30.7.....'87

Parmendra Kumar Bajpai

PARMENDRA KUMAR BAJPAI

CONTENTS

SYNOPSIS

STRUCTURAL PHASE TRANSITION IN IMPROPER FERROELECTRIC AMMONIUM SULPHATE

P K Bajpai
Research Scholar
Department of Physics

Over the past few decades, there has been a growing interest in the study of structural phase transitions in Solids[1-4]. Ferroelectric phase transitions are particularly of great importance for the phenomenon of the onset of spontaneous polarization. In addition ferroelectrics have their wide application in modern technology[5], as transducers, frequency controllers, amplifiers and many other appliances used in electronic circuits.

Ammonium Sulphate (AS) undergoes a structural phase transition at 223K[6] below which it becomes ferroelectric. However, AS is a typical ferroelectric that exhibits several peculiar phenomenological properties not common to normal ferroelectrics. The crystal has, therefore, been widely studied to find the detailed nature of its transition but the basic issue of concluding the nature of the microscopic mechanism of its transition has not yet been resolved. We, therefore, decided to undertake a systematic study of the system and report our findings in the form of present thesis.

The experimental work reported in the thesis uses Infrared and Raman spectroscopy as tools to investigate the changes in symmetry, structure and dynamics of the crystal. It particularly

exploits the inferences:

i) that all the changes in mode strength and frequencies in IR/Raman spectra around an SPT are some how related to the change of the structure and/or, to the spontaneous value of the order parameter below T_c.

ii) that the spectra of partially deuterated species are capable of revealing the changes in the dynamics of individual H-atoms in the molecular unit, having H-atoms as their constituent particles.

The thesis also presents the critical analysis of the temperature dependence of crystallographic data reported by Hasebe[7] with an aim to investigate the changes in the structure of individual molecular ions in terms of changes arising due to freezing of their internal as well as external degrees of freedom.

The analysis of our experimental observations and the crystallographic data alongwith the inferences of several other studies leads to conclude a new model of the microscopic mechanism of the phase transition in the crystal. Accordingly, the type of transition occuring in AS is different from the well known displacive/order-disorder type and it should be given a different name; we call it as " molecular distortion type". The transition is triggered by molecular distortion in SO_4^{2-}ion structure as a result of the freezing of its internal modes (particularly the asymmetric S-O stretch ν_3 mode) with finite amplitude. The model accurately accounts for the observed heat of transition. It has also been used to formulate and discuss the phenomenological theory of the phase transition which explains the temperature

dependence of dielectric constants, spontaneous polarization and order parameter.

The thesis is divided into six Chapters. Chapter I, presents various aspects of structural phase transitions, basic theories of ferroelectricity (e.g. mean field theory and soft mode theory) and experimental techniques like IR/Raman spectroscopy relevant to the present investigation.

Chapter II, reviews the experimental and theoretical work reported in the literature on this system.

Chapter III, presents a brief discussion of the experimental details of recording the temperature dependence of IR and Raman spectra. The temperature dependence of D-modes of partially deuterated NH_4^+ ions and internal modes of SO_4^{2-} ion has been critically analyzed. The results reveal that the changes in NH_4^+ ions and H-bonds at T_c are minor and gradual. In contrast the SO_4^{2-} ion undergoes a significant and sudden change[8].

In Chapter IV, we present an analysis of the crystal structural data reported by Hasebe[7] at different temperatures around T_c. This has been accompanied by calculating the polar distortion in the ions. The analysis reveals a new microscopic mechanism of phase transition[9].

Chapter V, describes the phenomenological theory for the phase transition in Ammonium sulphate, using SO_4^{2-} ion distortion as order parameter; linear coupling between SO_4^{2-} ion distortion and polarization has been introduced to account for the occurrance

of spontaneous polarization. The temperature dependence of the order-parameter, spontaneous polarization and dielectric constants are also discussed[10].

Summary of the thesis and its important conclusions are given in Chapter VI alongwith certain observations regarding the usefulness of our conclusions and inferences in understanding the phase transition in other similar systems.

References

1. Scott J.F. (1974) Rev. Mod. Phys. **46** 86.

2. Fleury, P.A. and Lyons, K. (1981) In "Structural Phase Transitions I" (K.A. Müller and H. Thomas. eds.) **23**, 9, Springer-Verlag, Berlin and New York).

3. Currat, R., and Pynn, R. (1979) In "Neutron Scattering in Materials Science" (G. Kostorz, ed.) **23**, 93, Springer-Verlag, Berlin and New York.

4. Iqbal, Z., and Owens, F.J. (1984) "Vibrational Spectroscopy of Phase Transitions", Academic Press, New York.

5. Lines, M.E., and Glass, A.M. (1977) "Principles and Applications of Ferroelectrics and related Materials", Oxford University Press (Clarendon).

6. Matthias, B.T., and Remeika, J.P. (1956) Phys. Rev. **103**, 262.

7. Hasebe, K. (1981) J. Phys. Soc. Japan, **50**, 1266.

8. Bajpai, P.K., and Jain Y.S. (1987) J. Phys. C.-Solid State Phys. **20**, 387.

9. Jain, Y.S., Bajpai, P.K., Bhattacharjee, R., and Chowdhury, D. (1986) J. Phys. C. – Solid State Physics, **19**, 3789.

10. Bajpai, P.K., Jain, Y.S. and Ram, P.N,. (1987) J. Phys. C.-Solid State Phys. **20**, 0000.

INTRODUCTION

1.1 General

Research in Structural Phase Transitions(SPTs) has grown manifold during last several decades[1-11]. Particularly, the study of ferroelectrics has emerged as an interesting subject, since it provides a better understanding of the microscopic interparticle interactions governing the phenomenon of SPTs as well as the onset of spontaneous polarization. Ferroelectrics have found wide applications in modern technology for their large piezoelectric constant and non-linear properties[6,12-14]. These are used as transducers, frequency controllers, filters, amplifiers, computer memory components, electronic appliances in electronic circuits, etc[15-17].

The SPTs are accompanied by changes in the structure and symmetry of the crystals. The crystal lattice dynamics, therefore, plays an important role in understanding the microscopic behaviour of transitions[18-24]. For the same reasons the crystal symmetry also becomes vital for the understanding of the phenomenon[25-31]. Phase transitions have their signatures on the experimental values of physical quantities such as specific heat, dielectric susceptibility, light scattering, ultrasonic attenuation, etc[32]. Obviously, the analyses of such measurements reveal the nature of the physical changes that follow the transition.

Theoretical analysis of phase transitions using thermodynamic principles was given by Landau[33]. The work was later extended by Lifshitz[28], Pippard[34] and Tizza[35] for λ-type transitions, by Devonshire[36-38] for ferroelectrics by Kittel[39] for antiferro-electrics and by Dvořák[40-42] and others[43-47] for improper ferroelectrics. Some other extensions and modifications for varied conditions have been worked out later on and reviewed by several authors[8,16,17,26,29]. Cochran[20,21,48] and Anderson[22] used entirely different approach to understand the phenomenon of phase transition. Their theory is based on the lattice dynamics of the systems and is known as soft mode-theory.

Two mechanicms for the phase transitions i.e. order-disorder type and displacive type are commonly considered to account for the phase transition in large number of crystals[9,49,50]; a crossover from displacive to order-disorder limit is observed in certain cases[51]. However, in some cases, none of these mechanisms describes the transition fully (see for example, $(NH_4)_2SO_4$)[52]. In recent years the nature of the soft mode and its coupling with other modes has been widely used to explain the complex transitions[23,53-55]. Observation of the central peak in the scattering experiments has also attained significant attention[56,57].

SPTs are studied by various experimental techniques like absorption and scattering of light[9,58-62], magnetic

resonance spectroscopy[63-66], Mössbauer spectroscopy[67], dielectric measurements[68], Brillouin[69] and neutron scattering[70], ultrasonic measurements[71], DTA[72], X-ray[73], electron and neutron diffraction[74,75]. Significant informations about the SPTs are also obtained by measuring the temperature variation of macroscopic properties such as specific heat, dielectric constants, elastic stiffness constants, etc. The informations are often complementary and each measurement and technique has its own importance. However, spectroscopic techniques using light scattering and Infrared absorption provide some of the most important and crucial informations regarding the lattic dynamical aspects of the phase transitions. If these informations are examined alongwith the temperature variation of crystallographic data, one can draw some definite conclusions regarding the mechanism of phase transitions.

In the present chapter we discuss the basic aspects of structural phase transitions, ferroelectrics and the fundamentals of experimental techniques such as light scattering and IR absorption.

1.2 Phase Transitions and Order Parameter

A phase transition is generally characterized by a quantity known as order parameter (η). It is an observable, quantitative parameter which changes with some field variable such as temperature, pressure, electric field, etc[76]. In

some cases it also depends on the conditions such as relative humidity, vapour pressure, etc[77]. In the present work we would be dealing with a kind of transition where the order parameter changes with temperature and vanishes identically above the transition point. In such cases the order parameter is expressed as $\eta(T)$. In many cases $\eta(T)$ is well defined physical entity such as magnetization of a spin system undergoing a magnetic phase transition, spontaneous polarization in the case of a ferroelectric phase transition, etc. The order parameter is also considered as a measure of the extent to which atomic geometry in the less symmetrical (low temperature) phase differs from the more symmetrical (high temperature) phase. In SPTs approaching the order-disorder limit it measures the degree of long range ordering of constituent entities (atoms/molecules/ions) while in the displacive limit it measures the amplitude of relative displacement of two units. The functional dependence of η on the field variable characterizes the order of transition. However, in the thermodynamic theories of phase transition η is an entity of central importance because the stability limits of the system are decided by the free energy(G) expressed as a series expansion of η.

1.3 Structural Phase Transitions and Their Classifications

A structural phase transition(SPT) in a solid follows finite changes in the positions of constituent particles. The transition may be induced by change of temperature, pressure

or some other parameters such as applied electric or magnetic field. Macroscopic as well as microscopic properties of the systems are influenced by the transitions. Consequently, below the transition temperature they acquire distinct properties such as spontaneous polarization, magnetization, nonlinearities in their electromagnetic behaviour, etc[78-80]. Several properties of the system, sometime, attain large changes in their magnitude near T_c. These changes are normally known as anomalies. Anomalous change in elastic coefficients, dielectric constants, expansivities and specific heat is commonly observed[32].

A single well defined basis of classification of SPTs is not possible because changes that follow a SPT differ widely from system to system. However, in the following we briefly describe some common classifications.

1.3.1 The General Classification

The most widely accepted classification is summarized in Fig.1.1. The important features of each class of SPT mentioned in the figure are as follows:

1.3.1a Reconstructive Type

In the process of the reconstructive phase transition the original linkages of the net are disrupted and the constituents of the solid reconstruct a new lattice; a typical example of such SPT is the transformation of Aragonite (Pnma)

to Calcite (R3c) in $CaCo_3$ at 723K[81]. Due to inherent matter transport, these transitions are often slow; further because of discontinuous symmetry change, these are of first order.

1.3.1b Martensitic Type

A class of transitions with certain characteristic structural features, observed in both metallic and non-mettalic systems, are known as martensitic type. Such transitions occur through the shearing of discrete volumes of material without changing the chemical composition[81-84]. The transitions often occur with extremely high velocities and exhibit large temperature hysteresis. These are reversible and generally polymorphic in nature. An example is Fe-29% Ni alloy in which martensitic transition takes place at -30°C[85].

1.3.1c Distortive Type

In a distortive phase transition the linkages of the net are not disrupted, but the lattice is only slightly distorted. These transitions can further be classified into three categories, viz. electronically induced type, order-disorder type and displacive type.

The energy of electronic excitation in certain systems couples with the phonons, leading to a possibility of a change that can be induced by the electronic excitations of certain constituents[86-87]. If the coupling is a sensitive function of temperature, the transition may be triggered with change

in temperature. Such transitions are referred as electronically induced transitions. The cooperative Jahn-Teller transitions[88,89], Band Jahn-Teller transitions[90,91] are some such transitions that fall in the class of electronically induced transitions.

A transition is known to be displacive if the distortive phase can be described through the superposition of the atomic displacement in some coordinate Q over the parent phase. The atomic displacement may occur through longitudinal/transverse as well as optic/acoustic mode; the transition is accordingly classified in various subcategories. An order-disorder transition takes place due to long range ordering of atoms/molecules/ions.

Distinction between order-disorder and displacive transition can be understood in terms of single cell potential[92]

$$V(Q) = \underline{a}\, Q^2 + \underline{b}\, Q^4 \qquad (1.1)$$

Here $\underline{a} < 0$ and $\underline{b} > 0$ and Q refers to generalized coordinate which could stand for displacive motion of atoms, orientation of molecule, etc. Eqn.(1.1) is shown schematically in Fig.1.2. In the figure V(Q) shows a double well potential with an energy difference ΔE between two minima and the central maxima. When $\Delta E >> kT_c$, the transition would be associated with a dynamic ordering in the position/orientation of atomic/molecular units. This situation characterizes the order-disorder

limit of the transition. However, for $\Delta E << kT_c$ a cooperative displacement of the units occurs and the situation defines the displacive limit. The nature of Q specifies the physical nature of transition and helps in identifying the different types of order-disorder and displacive transitions.

In positional order-disorder transitions ordered state refers to situation in which atoms/molecules occupy either of the two positions selectively (position 1 or 2; of Fig.1.2a), while the disordered state arises when atoms occupy position 1 and 2 randomly. The examples of positional order-disorder transitions are AgI[93], CuZn[94], etc. In orientational order-disorder transition Q is associated with the orientational dynamics of molecular units such as CN^- in KCN[95], NO_2^- in $NaNO_2$[96] and NH_4^+ in NH_4Cl[97]. One can also identify Q with spin orientations in magnetic transitions[98] and electric dipoles in ferroelectric and antiferroelectric transitions.

Cooperative displacement of atoms in displacive limit occurs in three distinct ways leading to ferrodistortive type, antiferrodistortive type and thermoelastic type transitions. If Q is an optical phonon of long wavelength (i.e. $\vec{q} \rightarrow \vec{0}$), the transition is ferrodistortive type. On the other hand an optical phonon at Brillouin zone boundary results in anti-ferrodistortive type transition. In thermo-elastic transition Q is an acoustic phonon of long wavelength. Phase transition in $BaTiO_3$[99], $SrTiO_3$[100] and TeO_2[101] are respectively

the typical examples of the above mentioned transitions.

1.3.2 First Order and Second Order SPTs

A first order phase transition involves a sharp and discrete change in the internal energy of the system at T_c, which is the origin of discontinuity in several physical properties of the system. The transition exhibits non-zero heat of transition. The order parameter (η) and the first derivative of Gibbs free energy(G) with respect to η also changes discontinuously (see Fig. 1.3a, 1.4a). At the transition point the two states of the system remain in equilibrium with no predictable relationship between their symmetry. However, there can be some relationship in certain cases. Stability limits of high and low temperature phases do not coinside.

In second order phase transition the entropy and volume of the system do not change at T_c, while the heat capacity, thermal expansivity and compressibility undergo discontinuous changes. The second derivative of G also goes through discontinuous change at T_c. The order parameter increases monotonically from zero (at T_c) towards certain magnitude on lowering the temperature (see Fig.1.3b, 1.4b). Two states of the system tend to become identical as the transition point is reached, implying that the symmetry of the system at T_c contains all the elements of both the phases[26]. The temperature defining the limits of two phases coinside with each other as well as with T_c. The symmetry of the low tempe-

rature phase is the subgroup of the symmetry of high temperature phase.

1.3.3 Incommensurate-Commensurate Phase Transitions

Incommensurate transitions are fundamentally different from the normal commensurate transitions. In the incommensurate phase the system does not have any space symmetry, whereas outside the temperature interval of this phase the structure is crystalline. However, this does not imply that an incommensurate phase is amorphous. Infact it has an ordered structure with periodic distortion which, however, does not fit with any crystal periodicity[102].

Pynn[103] has suggested a model to conceive the difference between commensurate and incommensurate phases. To illustrate his point of view, we depict a chain of equally spaced atoms (separation 'a_o') in Fig. 1.5a. A sinusoidal displacement (Fig.1.5b) of wavelength '$4a_o$' when modulated over the chain, results in a structure (Fig.1.5c) which can be described in terms of a unit cell of dimension '$4a_o$'. However, it is not necessary for a lattice modulation to always have a periodicity which is a rational multiple of a_o. Such a modulation (Fig.1.5d) over the chain of atoms results into a structure shown in Fig.1.5e, which obviously loses the translational symmetry. This structure cannot be defined in terms of original lattice constant 'a_o' and is referred to be incommensurate.

Incommensurate SPTs are thus characterized by an order/distortion corresponding to a wavevector ($\vec{q}_i$) that cannot be expressed as a rational fraction of a reciprocal lattice vector. Recently these transitions have been explained by soliton waves[104,105], where the dispersion curve splits into two branches known as **amplitudon** with ordinary soft mode behaviour and **Phason** which describes phase distortion whose frequency vanishes at a zone point $\vec{q}_c$ (a rational fraction of reciprocal vector) where the incommensurate phase vanishes. The phase diagram of such transitions is given by Cowley and Bruce[102] (Fig.1.6). In this figure 'c' represents a field potential parameter whose minimum value defines a point known as **Lifshifz point** below which INC phase will occur.

1.3.4 Reversible and Irreversible Phase Transitions

A phase transition in which the system returns to its initial phase, on withdrawal of the agency that causes the phase transition, is known as a reversible phase transition. On the contrary, the transition is called irreversible. A prominent example of an irreversible phase transition is that of TiO_2 (Antase) to TiO_2 (Rutile)[106].

1.4 Ferroelectrics

Ferroelectrics are materials in which the transition from the high to low temperature phase is accompanied by spontaneous polarization. The direction of this polarization

can be reversed (or atleast reoriented) by applying a suitable electric field. The reversal of polarization is always accompanied by some hysteresis[107] (Fig.1.7). These materials are also known as Seignette electrics, after P.de la Seignette, who was first to prepare Rochelle salt as a Laxative (at La Rochelle in the seventeenth century) which was later discovered to be the first ferroelectric[108]. Since then more than hundred ferroelectrics and many ferroelectric solid solutions have been discovered.

These materials are electrical analogue of ferromagnetic materials and the word 'ferroelectrics' arises from this analogy. It should be noted that ferroelectrics are nonmatellic materials which do not have Fe^{+++} ion as an essential ingradiant as the word 'ferro' seems to imply. Moreover in many practical ways ferroelectrics differ from ferromagnetics and are totally different on microscopic basis. Anomalous change in some physical properties of the ferroelectrics, i.g. dielectric constant, specific heat etc. is a commonly observed feature. It may be mentioned that to a good approximation, the temperature variation of a component of dielectric constant ε above T_c follows Curie-Weiss law

$$\varepsilon = \varepsilon_o + \frac{C}{T - T_c} \qquad (1.2)$$

Here C is known as Curie-constant T_c* is often referred as

*Jona and Shirane[109] call T_c as transition temperature also, while Megaw[118] and others refer T_o for transition temperature. The former notations are followed. It should be noted that T_c is equal to transition temperature for first order transition, while it may be few degrees low in other transitions.

Curie temperature and defined as the temperature where dielectric constant tends to approach infinity.

A large number of ferrolectrics have been discovered. They have been classified and reviewed extensively[108-119].

1.5 Symmetry Aspects of Ferroelectricity

Symmetry aspects play an important role in theoretical understanding of ferroelectricity. The change in crystal symmetry alongwith the crystallography of domain structure determines to a large extent the properties of ferroelectrics[30]. Landau and Lifshitz[28] applied symmetry properties for the first time to the transitions of second order. According to their analysis, the necessary conditions for the occurrence of second order transitions are:

i) The space group of low temperature phase is a subgroup of the space group of high temperature phase.

ii) The change of the symmetry of the crystal corresponds to a single irreducible representation (excluding identity representation) of the space group of high temperature phase.

iii) There are no third order terms in the expansion of free energy, and

iv) The unit cell of the crystal below T_c is a simple multiple of the original unit cell.

The knowledge of the symmetry of high temperature phase clearly helps to predict the appropriate form of the

expansion of free energy G and the possible symmetries of the low temperature phase.

Aizu[25] concludes that their exists a prototype phase (may be hypothetical for certain cases) which can be symmetrically correlated with possible phases of a system. Symmetry considerations can also help in finding out all possible ferro- and antiferro-electric subgroups for any paraelectric[43] and such results have been worked out by Blinc and Žekš[26].

It may be mentioned that the low temperature phase is the result of the superposition of frozen-in soft mode displacement over the high temperature phase. In view of this fact, the symmetry of the soft mode involved in the transition can be worked out by using the symmetry of the two phases[26].

1.6 Thermodynamic Approach To The SPTs

The thermodynamic approach of SPTs has been developed by Landau[33]. The transition is described by an order parameter whose value is zero in the high temperature phase; below T_c it rises monotonically to a constant value. Devonshire[36-38] applied Landau theory to ferroelectrics considering the spontaneous polarization as order parameter and expressed the free energy as

$$G(T,P) = G_o(T) + \tfrac{1}{2}\, a(T)P^2 + \tfrac{1}{4}b(T)P^4 + \tfrac{1}{6}C(T)\, P^6 \qquad (1.3)$$

The equilibrium value of spontaneous polarization P_s, at a temperature T is obtained by

$$\left.\frac{\partial G}{\partial P}\right|_{P=P_s} = 0 \qquad (1.4)$$

which gives

$$P_s=0 \quad \text{or} \quad P_s = \pm\{-\frac{b}{2c}\,[1-\sqrt{1-\frac{4ac}{b^2}}]\}^{\frac{1}{2}} \qquad (1.5)$$

The solution $P_s=0$, identifies paraelectric phase while $P_s \neq 0$ characterizes ferroelectric phase, with the stability condition

$$\left.\frac{\partial^2 G}{\partial P^2}\right|_{P=P_s} > 0 \qquad (1.6)$$

From eqn (1.6) we have

$$\left.\frac{\partial^2 G}{\partial P^2}\right|_{P=P_s} = \chi^{-1} = a(T)+3b(T)P_s^2 + 5c(T)P_s^4 \qquad (1.7)$$

and $$\chi^{-1} = a(T) \qquad (1.8)$$

when $P_s=0$ representing paraelectric phase. For a paraelectric phase thus a(T) must be positive and at the stability limit with a(T) and χ^{-1} must vanish. Near the stability limit a(T) can, therefore, be expanded into a Taylor series in powers of $(T-T_o)$; T_o is the stability limit of paraelectric phase. Keeping only first order term, we have

$$a(T) = a'(T-T_o) \qquad (1.9)$$

with $$a' = \left(\frac{\partial a}{\partial T}\right)_{T=T_o} > 0$$

Eqn(1.8) thus gives rise to Curie-Weiss law which is expected to hold good in the paraelectric phase near T_o. In certain

cases it might hold over wide range of $T>T_o$ indicating that $a(T) = a'(T-T_o)$ is rigorously valid for the system. Since the variation of b(T) and c(T) is slow around the transition temperature T_c, we can write

$$b(T) = b(T_c) = b;\ c(T)=c(T_c)=c \qquad (1.10)$$

depending upon the value of b, three distinct cases can be exhibited by the system.

1.6.1 The Second Order Transition

The system exhibits phase transition of second order if b>0. In such situation P^6 term in G expansion can be neglected and we have

$$P_s = \pm\sqrt{\frac{-a}{b}} = \pm\sqrt{\frac{a'(T_o-T)}{b}} \qquad (1.11)$$

Clearly P_s below T_o is real and it increases monotonically from $P_s=0$ at $T=T_o$ (as η in Fig. 1.3b) to $P_s = \sqrt{a'T_o/b}$ at $T=0K$. The transition temperature T_c for this case represent the state of the system in which G vs P curve is identical to case II of Fig. 1.8b and is same as T_o.

1.6.2 First Order Transition

The transition will be of first order if b<0. In this case P^6 term has to be retained to characterize the stability of the phase. In this situation we have two real solutions

$P_s(I)$ and $P_s(II)$ of P_s

$$P_s(I) = \pm\{-\frac{b}{2c}\,[1+\sqrt{(1-\frac{4a'c}{b^2}\,(T-T_o)]}\}^{\frac{1}{2}} \qquad (1.12)$$

and

$$P_s(II) = \pm\{-\frac{b}{2c}[1-\sqrt{(1-\frac{4a'c}{b^2}\,(T-T_o)}\}^{\frac{1}{2}} \qquad (1.13)$$

$P_s(I)$ is real at all temperatures below T_o^- — which is given by

$$T_o^- = T_o + \tfrac{1}{4}\,\frac{b^2}{4a'c} \qquad (1.14)$$

and defines the stability limit for the ferroelectric phase with $P_s=P_s(I)$. The solution $P_s=P_s(II)$ has real values only in the range of $T_o<T<T_o^-$. However, it corresponds to a maximum in G and therefore defines an unstable phase. The temperature viariation of P_s in such a case, as revealed by Eqn.(1.12) jumps suddenly and than varies monotonically like order parameter η in Fig. 1.2a. The transition temperature T_c for this case refers to a situation represented by G vs P curve (Case III in Fig. 1.8a) and is given by

$$T_c = T_o + \frac{3}{16}\,\frac{b^2}{a'c} \qquad (1.15)$$

1.6.3 Critical Transitions

If for a given system b vanishes, we have critical transition. Such transitions are characterized by large fluctuations in the neighbourhood of T_c, since the free energy G varies as P^6.

Ferroelectrics, where transition is triggered by onset of spontaneous polarization as the order parameter, are known as proper ferroelectrics. However, there are certain

ferroelectrics where the order parameter is different from the spontaneous polarization. It is the coupling between the order parameter and polarization which results in a non-vanishing order parameter (η) and spontaneous polarization (P_s) simultaneously. These ferroelectrics are known as improper ferroelectrics[120-121]. Improper-ferrolectrics can be put into two categories:

i) where P_s and η both have same symmetry properties (e.g. KH_2PO_4), and

ii) where the two have different symmetries (e.g. $Gd_2(MoO_4)_3$)[26,121].

Phenomenological theories of these ferroelectrics have been developed in terms of Landau type mean field theory and have been reviewed.

1.7 Soft Mode Theory

Cochran[20,21] and Anderson[22] suggested that the phase transitions in certain ferroelectrics might result from an instability of one of the normal vibrational modes of the lattice. Accordingly, the frequency of the relevant phonon decreases on approaching T_c because the restoring force for the mode displacement tends to zero until the phonon condenses at the stability limit. The static atomic displacements on going from the paraelectric to the ferroelectric phase thus represent the frozen-in displacements of the unstable phonon. The order parameter of such a transition is the static component

of the eigenvector representing the unstable phonon. Since the ferroelectric state is characterized by a macroscopic spontaneous polarization, the soft mode must be polar (i.e. IR active) and should have corresponds to $\vec{q} \to 0$.

The soft mode concept is consistent with the Landau mean field theory, in which the equilibrium condition $\frac{\partial G}{\partial \eta} = 0$ gives $\eta^2 = a/c$. Since a near T_o can be written as $a=a'(T-T_o)$ order parameter η behaves like

$$\eta = \sqrt{\frac{a'}{c}} (T-T_o)^{\frac{1}{2}} = \eta_s (T-T_o)^{\frac{1}{2}} \qquad (1.16)$$

Here c is assumed to be temperature independent.

The connection between a soft phonon frequency ω and the corresponding order parameter (η) follows from the equation of motion of a simple harmonic oscillation i.e.

$$m\omega^2 = \partial^2 G/\partial \eta^2 \qquad (1.17)$$

where G is the oscillator potential and η corresponds to a small displacement. Since $\partial^2 G/\partial \eta^2 = a$ obviously

$$\omega = \omega_o (T - T_o)^{\frac{1}{2}} \qquad (1.18)$$

This defines the concept of soft mode as a mode of vibration whose frequency goes to zero at T_o. The low temperature distorted structure can then be thought of as resulting from the condensation of the soft mode eigenvector.

From the lattice dynamical point of view, the soft mode concept can be realized directly from Lyddne-Sachs-Teller (LST) relationship

$$\Pi_i \ \omega_{LO}^2 / \omega^2_{TO} = \varepsilon(0)/\varepsilon(\infty) \qquad (1.19)$$

Since $\varepsilon(0)$ diverges at T_c for a $\omega_{i\,TO}$ ferroelectric SPT, it is clear that $\omega_{TO}^2 \to 0$. Cochran and Anderson[20-22,48] brought the concept of soft mode within the framework of the harmonic lattice dynamics of dielectric crystals treating all positive and negative ions as point charges of magnitude $\pm Ze$ and $\varepsilon(\infty)$ as unity, ω_{TO} and ω_{LO} are then given by

$$m\,\omega_{TO}^2 = \beta - (Ze)^2/3V\varepsilon(0) \qquad (1.20)$$

$$m\,\omega_{LO}^2 = \beta + (2Ze)^2/3V\varepsilon(0) \qquad (1.21)$$

where β represents the short range repulsive interaction and V the primitive cell volume. It is clear that ω_{TO} can vanish if short range force becomes equal to long range Coulomb force. Thus only a TO type soft phonon is possible[24].

The above described soft mode character is applicable to displacive systems only. Mode coupling and the onset of relaxational modes occur for transitions of mixed character and order-disorder type. In such cases the theory has been modified by including anharmonic phonon-phonon interactions[23,122]. Anharmonicity leads to a broadening of the response (decrease in phonon lifetime) and changes the frequency which is given by

$$\omega_s^2 = \omega_{s(h)}^2 + \Delta \qquad (1.22)$$

where $\omega_{s(h)}$ is the purely harmonic frequency. Δ is proportional to the density of states into which the phonon decays. The temperature dependence of soft mode is given by

$$\omega_s^2 = a'T + a'(T-T_o) \qquad (1.23)$$

1.8 The Central Peak

In certain scattering experiments an intense peak is observed with an extremely narrow linewidth ($\sim 5 \times 10^9$Hz) and zero energy shift. This peak known as central peak dominates the scattering close to T_c. This phenomenon was observed for the first time by Riste **et al**[123] in $SrTiO_3$ in the neutron scattering experiment and was earlier predicted theoretically by Cowley[23]. Later the phenomenon has been observed in several other systems, for example lead germenate[124], KH_2PO_4[125].

There have been several attempts to explain the phenomenon[89,126-129], the phenomenon, particularly the extremely narrow linewidth ($<2 \times 10^7$Hz)[130], is yet not clearly understood.

Blinc and Žekš[26] developed a classical picture of the phenomenon in terms of the damping of soft mode due to anharmonic interactions. Among the other three classes of models, one considers the coupling of soft mode with thermal relaxation processes[127]. The second considers impurities[57] and surface effects[131] as the origin of the phenomenon. In these models, the central peak arises as an extrinsic property resulting from localised distortions. In other models central peak is regarded as an intrinsic property associated with the formation of clusters of low temperature phase in the high temperature phase in the temperature region around T_c. In other words, the central peak arises due to scattering of relaxating domain walls or solitons of these long lived

clusters.

1.9 Infrared Absorption

A phonon mode at $\vec{q} \to 0$ absorbs radiation in the IR spectral range if the mode displacements are associated with finite change in dipole moment ($\vec{\mu}$). IR absorption may also arise due to change in electric moments of higher order, magnetic moments, etc. However, the intensity of such absorption is very weak. For example if a typical transition induced by electric dipole moment is assumed to take place at a rate 10^8 Sec^{-1}, the transitions induced by magnetic dipole and electric quadrupole moments are expected to take place at a rate 10^3 and 1 Sec^{-1}, respectively[132]. Since frequencies of vibrations of molecules in crystal fall in the IR range, enough informations (such as force constants, nature of intra- and inter-molecular interactions, symmetry and structure, etc.) about these systems can be obtained from IR absorption spectra which is rightly recognized as an important tool to investigate SPTs.

1.10 Raman Scattering

Inelastic scattering of photons is known as Raman Scattering. The frequency of the scattered light changes by a quantum necessary for the excitation of the system. The excitation could be associated with vibrational or electronic states. The important feature of the phenomenon is that the

scattered light carries informations about the structure and dynamics of the scatterer. The scattered light of lower frequencies is called **Stokes** scattering and that at higher frequencies as **antistokes**. **Antistokes** emission is weaker than **stokes** emission because it arises from the first excited state which is less populated than the ground state from where **Stokes** Raman scattering can be explained in terms of energy transfer between the scattering system and the incident radiation. When a system (in ground state) interacts with radiation of wave number $\tilde{\nu}_i$, it makes an upward transition from its lower energy level E_1 to an upper energy level E_2 (Fig.1.9a). In the process the system gains energy, $\Delta E = E_2 - E_1$, from the incident radiation. If the wavenumber difference associated with two levels is $\tilde{\nu}_v$, then $\Delta E = hc\tilde{\nu}_v$. This energy is made available by annihilation of a photon ($E = hc\tilde{\nu}_i$) of incident radiation and creation of a photon of lower energy, $hc(\tilde{\nu}_i - \tilde{\nu}_v)$; in the process the system is excited to a higher state. On the other hand, the interaction of incident radiation with the system in excited state may cause a downward transition from a higher energy level E_2 to a lower energy level E_1 (Fig.1.9b). In this case, an amount of energy $E_2 - E_1 = hc\,\tilde{\nu}_v$ is made available by the system. In the process a photon of energy $hc\,\tilde{\nu}_i$ is annihilated and another photon of energy $hc(\tilde{\nu}_i + \tilde{\nu}_v)$ is created; the system deexcites to its lower energy state.

Raman scattering is usually weak in intensity hence a strong source of incident radiation is needed for its

observation. Stimulated interest in its study and applications therefore arose only after the invention of high power and highly monochromatic continuous laser sources. Developments in the field have since been very fast and several new phenomena, such as resonance-, surface enhanced-, stimulated-, hyper-, inverse-, coherent anti-**Stokes**, coherent **Stokes**-Raman scattering have been discovered. Stimulated Raman gain spectroscopy, photoacoustic Raman spectroscopy, Raman induced Kerr effect spectroscopy, asterisk spectroscopy have also been developed[134-136] and several of them have been used in investigating the SPTs.

1.11 IR Band Intensity

The intrinsic absorption corresponding to a transition between states |m> and |n> is given by

$$dI(\nu) = -hc\nu . I(\nu) . B_{mn}(N_n - N_m)dl \qquad (1.24)$$

where B_{mn} is the Einstein probability of absorption related with the transition moment as

$$B_{mn} = \frac{8\pi^3}{3ch^2} |\langle m|\vec{\mu}|n\rangle|^2 \qquad (1.25)$$

$\nu = \nu_{mn} = (E_m - E_n/hc)$, N_n and N_m are the number of molecules per unit volume in the initial and final states, respectively. $I(\nu)$ is the intensity of light beam at frequency ν after travelling distance dl in the absorbing media and $di(\nu)$ is the absorbed intensity at the same frequency. Eqn (1.24) can be rearranged to give Bouquer's or Lambert's law[137].

$$I(\nu) = I_o(\nu)\ \mathrm{Exp}\ (-a\nu l) \qquad (1.26)$$

where a_ν is the absorption coefficient given by

$$a_\nu = hc\nu\ B_{mn}.N_n \qquad (1.27)$$

1.12 Raman Band Intensity

Raman scattering arises from the ground state polarizability, which depends on molecular vibrations[138]. In polarizability theory, the Raman band intensity in single crystals is generally treated in terms of scattering efficiency S defined as[139]

$$S = \frac{N(\nu_s)d\Omega}{N(\nu_i)} \qquad (1.28)$$

where $N(\nu_s)$ is the number of scattered photons of frequency ν_s produced per unit time per unit cross-sectional area of the crystal in solid angle $d\Omega$ along the direction of observation and $N(\nu_i)$ is the number of incident photons of frequency ν_i per unit time per unit cross-sectional area.

For right angle scattering and unpolarized light S is given as[140]

$$S = \frac{3h\ L\ d\Omega\ (\nu_i-\nu)^4}{2\pi\ \sigma\ c\ \nu}\ |\ \alpha_{mn}|^2.[1-\mathrm{Exp}(-hc\nu/kT)]^{-1} \qquad (1.29)$$

where $\nu = \nu_{mn} = (E_m - E_n/hc)$ and L is effective length of the crystal from which the scattered radiations are received at the slit of the spectrophotometer, σ is the density of scattering centres, k is Boltzmann constant and T is absolute temperature.

The experimentally observed Raman band intensity is of relative importance and the integrated intensity is considered to be more significant than the peak intensity. To a good approximation, integrated intensity can be computed by multiplying the peak height with the FWHMI.

1.13 Band Shapes

IR and Raman band shapes are complex, in general. However in ideal situations they can be expressed as either of the two shapes[136]

(i) for Gaussian shape

$$I(\nu) = I(\nu_o)\ \mathrm{Exp}\ -(\nu-\nu_o)^2\ /\underline{a} \qquad (1.30)$$

and

(ii) for Lorentzian shape

$$I(\nu) = I(\nu_o)\ \frac{\underline{b}^2}{\underline{b}^2+(\nu-\nu_o)^2} \qquad (1.31)$$

here $I(\nu_o)$ is the maximum intensity at peak frequency (ν_o) and $\underline{a}$ and $\underline{b}$ are adjustable parameters. $\underline{b}$ is such that $2\underline{b}$ = FWHMI of the band.

The observed band can in general be resolved into indefinite number of band components of either shapes. Largely one has to guess from the shape of the band about its components. Obviously, this type of resolution is somewhat arbitrary and hence the resolved band may have considerable uncertainties in peak positions, FWHMI and intensity.

1.14 IR and Raman Selection Rules

A transition between |f> and |i> states is allowed only when transition probability defined by

$$M_{fi} = \int \Psi_f \tilde{M} \Psi_i \, d\tau, \qquad (1.32)$$

has non-zero value. In general it is difficult to find out the eigen functions (Ψ) of a system. However from the group theoretical methods the zero and non-zero values of M_{fi} can be predicted and for the non-zero value of M_{fi}, the R.H.S. of Eqn. (1.32) must be totally symmetric. As the depole moment has the character of a polar vector and ground state is totally symmetric the final state Ψ_f should have the symmetry of x/y/z for an allowed IR transition.

Raman scattering occurs through the induced electric dipole moment($\vec{P} = \tilde{\alpha} \vec{E}$; $\tilde{\alpha}$ is a second rank tensor having basis of representation: xx, yy, zz, xy, zx and yz). Obviously for an allowed Raman transition the product of symmetry species of Ψ_f and Ψ_i must be similar to that of any basis of $\tilde{\alpha}$.

1.15 Intensity of Forbidden Modes

During a phase transition, very often new peaks arise in the IR and Raman spectrum. This generally happens because of two reasons -

i) some forbidden modes may become active in low temperature phase, and

ii) the degeneracy of modes could be totally or partially removed in the distorted phase.

The process of a forbidden mode becoming active was qualitatively understood however their was no quantitative theory (except in few specific cases) of the phenomenon until recently when Jain and Bhattacharjee formulated the quantitative relation for the IR/Raman intensity of forbidden modes with the distortion in the molecular unit[141-142].

REFERENCES

1. Currat, R., and Pynn, R. (1979) In "Neutron Scattering in Materials Science" (G. Kostorz, ed.), p.131, Academic Press, New York.

2. Dorner, B. (1981) In "Structural Phase Transitions I" (K.A. Müller and H. Thomas, eds.) Topics in current Phys. **23.** p.93, Springer-Verlag, Berlin and New York.

3. Dorner, B. and Comes, R. (1977) In "Dynamics of Solids and Liquids by Neutron Scattering" (S.W. Lovesey and T. Springer, eds.), p.127, Springer-Verlag, Berlin and New York.

4. Fleury, P.A. and Lyons, K. (1981) In "Structural Phase Transitions I" (K.A. Müller and H. Thomas, eds.), **23.** p.9, Springer-Verlag, Berlin and New York.

5. Iqbal, Z., and Owens F.J. (1984) "Vibrational Spectroscopy of Phase Transitions". Academic Press, New York.

6. Känzig, W. (1957) "Ferroelectrics and Antiferroelectrics" Academic Press, New York, also In Solid State Phys. (F. Seitz and D. Turnbull, eds.) **4**, Academic Press, New York.

7. Petzelt, J., and Dvořák, V. (1976) J. Phys. C-Solid State Phys. **9.** 1571, 1587.

8. Samara, G.A., and Peercy, P.S. (1981) In "Solid State Phys. Advances in Research and Application", **36.** p.1, Academic Press, New York.

9. Scott, J.F. (1974) Rev. Mod. Phys. **46.** 86.

10. Shirane, G. (1971) Rev. Mod. Phys. **43.** 437.

11. Subba Rao, E.C. (1974) In "Solid State Chemistry", (C.N.R. Rao, ed.), Marcel Dekker, New York.

12. Burfoot, J.C. (1967) "Ferroelectrics: An Introduction to its physical principles", Von Nostrand, London.

13. McQuarrie, M. (1955) Bull. Amer. Ceram. Soc. **34.** 170.

14. Billeter, T.R., Giarola, A.J., and Bjorkstam, J.L. (1964) J. Appl. Phys. **35,** 2159.

15. Fatuzzo, F., and Merz, W.J. (1967) "Ferroelectricity", John Willey, New York.

16. Müser, H.E., and Peterson, J. (1971) Fortschritte der Physik, **19.** 559.

17. Lines, M.E., and Glass, A.M. (1977) "Principles and Applications of Ferroelectrics and Related Materials". Oxford Univ. Press (Clarendon).

18. Fröhlich, H. (1949) "Theory of Dielectrics". Clarendon, London and New York.

19. Rao, C.N.R., and Subba Rao, G.V. (1968) Rev. Mod. Phys. **40**, 673.

20. Cochran, W. (1960) Adv. Phys. **9**, 387.

21. Cochran, W. (1961) Adv. Phys., **10.** 401.

22. Anderson, P.W. (1959) "Fizika Dielekrikov" (G.I. Skanavi, ed.), Akad. Nauk SSR. Moscow.

23. Cowley, R.A. (1970) J. Phys. Soc. Jap. Suppl. **28.** 239.

24. Stirling, W.G. (1972) J. Phys. C-Solid State Phys. **5.** 2711.

25. Aizu, K. (1967) J. Phys. Soc. Jap. **22.** 1511 and references cited therein.

26. Blinc, R. and Žekš, B. (1974) "Soft modes in Ferroelectrics and Antiferroelectrics", North-Holland, Amsterdam.

27. Bruce, A.D. (1978) In "Solitons and Condensed matter Physics" (A.R. Bishop and T. Schneider, eds.), p.116. Springer-Verlag, Berlin and New York.

28. Landau, L.D., and Lifshitz, E.M. (1959) "Statistical Physics", Pergamon Press, Oxford.

29. Rao, C.N.R. (1974) In "Solid State Chemistry", (C.N.R. Rao, ed.), Marcel Dekker, New York.

30. Shuvalov, L.A. (1970) J. Phys. Soc. Jap. Suppl. **28.** 38 and references cited therein.

31. Zheludev, I.S. (1977) Pramāna. **9.** 385.

32. Petzelt, J., and Dvořák, V. (1984) In "Vibrational Spectroscopy of phase transitions" (Z. Iqbal and F.J. Owens, eds.), p.56, Academic Press, New York.

33. Landau, L.D. (1954) "Collected Papers of L.D. Landau" (D. ter Harr, ed.) Gordan and Breach, New York.

34. Pippard, A.B. (1956) Phil. Mag. **1.** 473.

35. Tizza, L. (1951) In "Phase Transformations in Solids" (R. Smaluchowski, J.E. Mayer and W.A. Weyl, eds.), John Willey, New York.

36. Devonshire, A.F. (1949) Phil. Mag. **40.** 1040.

37. Devonshire, A.F. (1951) Phil. Mag. **42.** 1065.

38. Devonshire, A.F. (1954) Adv. in Phys. **3.** 85.

39. Kittel, C. (1951) Phys. Rev. **82.** 729.

40. Dvorak, V. (1974) Ferroelectrics, **7.** 1

41. Dvořák, V. (1980) In "Modern Trends in theory of condensed matter" (A. Pekalski and J. Przystawa, eds.), lecture notes in Phys. **115,** p.447, Springer-Verlag, Berlin and New York.

42. Dvořák, V. (1984) In "Structural Phase Transitions II" (K.A. Müller and H. Thomas, eds.), Topics In Current Phys. **23,** Springer-Verlag. Berlin and New York.

43. Zheludev, I.S., and Shuvalov, A.L. 1956) Kristallographia, **1.** 681.

44. Sonin, A.S., and Zheludev, I.S. (1959) Kristallographia, **4.** 487.

45. Petzelt, J., and Dvořák, V. (1971) Physica Status Solidi. b**46.** 413.

46. Levanyuk, A.P., and Sannikov, D.G. (1968) Exp. Theor. Fiz. **55.** 256.

47. Levanyuk, A.P., and Sannikov, D.G. (1970) Fiz. Tverd. Tela. **12.** 2997.

48. Cochran, W. (1969) Adv. in Phys. **18.** 157.

49. Samuelsen, E.J. Anderson, E., and Feder, J. (1973) Proc. Nato Advanced Study Institute, Geilo, Norway.

50. Enz, C.P. (1976) "Critical Phenomena" Lecture Notes in Phys. **54.** 103, Springer-Verlag, New York.

51. Bruce, A.D. (1982) In "Nonlinear phenomena at Phase Transitions and instabilities" (T. Riste, ed.), p.35, Plenum, New York.

52. Jain, Y.S. (1974) Ph. D. Dissertation, I.I.T. Kanpur, (India).

53. Rae, A.I.M. (1984) J. Phys. C-Solid State Phys. **15.** 1883.

54. Schneider, T., and Stoll, E. (1973) Phys. Rev. Lett. **36.** 1501.

55. Yoshihara, A. Bernstein, E.R., and Raich, J.C. (1983) J. Chem. Phys. **79**, 445.

56. Cowley, R.A. (1977) In "Proceedings of the International Conference on Lattice dynamics" (M., Balkanski, ed.) p.625, Flammarion, Paris.

57. Halperin, B.I., and Varma, C.M. (1976) Phys. Rev. **B14**, 4030.

58. Crawford, B. Jr. Goplen, T.G., and Swanson, D. (1978) In "Advances in Infrared and Raman Spectroscopy" (J.R.H. Clark and R.E. Hester, eds.) **4**. p.47, Heyden, London.

59. McDowell, R.S. (1978) In "Advances in Infrared and Raman Spectroscopy" (R.J.H. Clark and R.E. Hester, eds.) **5**, p.1, Heyden, London.

60. Volkov, A.A., Kozlov, G.V., and Lebedev, S.P. (1979) Radiotekh. Elektron. **6**, 1405.

61. Volkov, A.A. Kozlov, G.V., and Lebedev, S.P. (1980) J. Phys. Soc. Jap. Suppl. **49**, 78.

62. Proto, S.P.S. (1969). In "Light Scattering Spectra of Solids" (G.B. Wright, ed.) Springer-verlag, New York.

63. Owens, F.J. Poole, C.P., and Farah, H.A. (1979) Magnetic resonance of Phase transitions", Academic Press, New York.

64. Blinc, R. (1968) In "Advances in magnetic resonances" (J.S. Waugh, ed.) **3**, Academic Press, New York.

65. Rao, C.N.R., and Natarajan, M. (1972) "Crystal structure transformations in Binary Halides" NSRDS-NBS monograph 41, National Bureau of Standards, Washington, D.C.

66. Ringamoti, H. (1984) Adv. in Phys. **34**, 115.

67. Schwartz, L.H. (1976) In "Applications of mossbauer spectroscopy" (R.L. Cohen, ed.) **1**, p.37. Academic Press, New York.

68. Hiu, N.E., Vaughan, W.E., Price, A.H. and Davies, M. (1969) Dielectric properties and molecular behaviour" Van Nostrand, London.

69. Lazay, P.D. and Fleury, P.A. (1971) In "Proceedings of the second international conference on Light scattering in solids". (M. Balkanski, ed.) Flammarion, Paris.

70. Brockhouse, B.N. (1961) In "Inelastic scattering of Neutrons in Solids and liquids" IAEA, Vienna.

71. Rao, K.J., and Rao, C.N.R. (1966) J. Material Sci. 1, 238.

72. Bollin, E.M. (1970) In "Differential Thermal Analysis" (R.C. Mackenzie, ed.), 1 p.229, Academic Press, New York.

73. Parrish, W. (1968) In "X-ray and electron diffraction methods". Progress in Analytical chemistry. (H. Van Olphen and W. Parrish, eds.) 1, p.1, Plenum Press, New York.

74. Somorjai, G.A. (1968) "X-ray and electron diffraction methods" Progress in Analytical chemistry" (H. Van Olphen and W. Parrish, eds.) 1,P.101, Plenum Press, New York.

75. Vainshtein, B.K. (1981) "Modern Crystallography I-symmetry of crystals, methods of structural crystallography". Springer Series in Solid State Phys. 15, 223.

76. Iqbal, Z. (1984) In "Vibrational spectroscopy of phase transitions" (Z. Iqbal and F.J. Owens, eds.) P. 1, Academic Press, New York.

77. Bührer, W., and Iqbal, Z. (1984) In "Vibrational spectroscopy of phase transitions" (Z. Iqbal and F.J. Owens, eds.) p.271, Academic Press, New York.

78. Goodenough, J.B. (1963) "Magnetism and Chemical bonds", John Willey, New York.

79. Menyuk, N. (1970) In "Modern aspects of Solid State Chemistry" (C.N.R. Rao, ed.) Plenum, New York.

80. Mitsui, T. Nakamura, E., and Tokunaga, M. (1975) Ferroelectrics 5, 185.

81. Rao, C.N.R., and Rao, K.J. (1978) Phase Transitions in Solids, McGraw Hill, New York.

82. Wayman, C.M. (1964) Introduction to the crystallography of Martensitic Transformations" McMillan, New York.

83. Meyrick, G. and Powell, G.W. (1973). In "Ann. Rev. Material Science" (R.A. Huggins, R.W. Bube and R.W. Roberts, eds.) 3, p.377.

84. Hinger, A.B., and Troiano, A.R. (1940) Trans. AIME 140, 307.

85. Kaufmann, L. and Cohen, M. (1958) In "Progress in metal Physics" (B. Chalmers and R. King, eds.) **7**, 165.

86. Englman, R. (1972) "The John-Teller effect in molecules and crystals" John Willey, London.

87. Gehring, G.A. and Gehring, K.A. (1975) Repts. on Progr. in Phys. **38**, 1.

88. Melchur, R.L., and Scott, B.A. (1972) Phys. Rev. lett. **28**, 67.

89. Shirane, G., and Axe J.D. (1971) Phys. Rev. **B4**, 2957.

90. Peierls, R.E. (1955) "Quantum Theory of Solids" Clarendon Press, Oxford.

91. Overhauser, A.W. (1971) Phys. Rev. **83**, 3173.

92. Müller, K.A. (1981) In "Structural Phase Transitions I" (K.A. Müller and H. Thomas, eds.), p.1. Springer-Verlag, Berlin and New York.

93. Van Gool, W. (1973) In "Fast ion Transport in Solids" (W. Van Gool, ed.), North-Holland, Amsterdom.

94. Sato, H. (1970) In "Physical Chemistry: An advanced Treatise" (H. Eyring, D. Henderson and W. Jost, eds.), **10**, Academic Press, New York.

95. Suga, H., Matsno, T., and Seki, S. (1965) Bull. Chem. Soc. Jap. **38**, 1115.

96. Sawada, S. Nomura, S. Fujii, S., and Yashida, I. (1958) Phys. Rev. Lett. **1**, 320.

97. Wang, C.H., and Wright, R.B. (1973) J. Chem. Phys. **58**, 1411.

98. Stout, J.W., and Chisholm, R.C. (1962) J. Chem. Phys. **46**, 1291.

99. Granicher, H., and Müller, K.A. (1971) Mater. Res. Bull. **6**, 977.

100. Iqbal, Z. (1979) In "Magnetic Resonance of Phase transitions" (F.J. Owens, C.P. Poole and H.A. Farah, eds.) p.1, Academic Press, New York.

101. Peercy, P.S. and Fritz, I.J. (1974) Phys. Rev. Lett. **26**, 13.

102. Cowley, R.A. and Bruce, A.D. (1978) J. Phys. C: Solid State Phys. **11**, 3577.

103. Pynn. R. (1979) "Incommensurable Structures" Nature **281**, 5731.

104. McMillan, W.L. (1976) Phys. Rev. **B14**, 1416.

105. Petzelt, J. (1981) Phase Transitions **2**, 155.

106. Czanderna, A.W. Rao, C.N.R., and Hornig, J.M. (1958) Trans. Faraday Soc. **54** 1069.

107. Mitsui, T. Abe, R. Furuhata, Y. Gesi, K. Ikeda, T. Kawaka, K. Makita, Y. Nakamura, E. Nomura, S. Sawaguchi, E. Shiozaki, Y. Tatsuzaki, I., and Toyoda, K. (1969) "Numerical data and functional relationship in Science and Technology, Series III. Ferroelectric and Antiferroelectric substances" Springer-Verlag, Berlin and New York.

108. Blinc, R., and Žekš, B. (1972) Adv. Phys. **21**. 693

109. Jona, F. and Shirane, G. (1962) Ferroelectric Crystals, Pergamon Press, Oxford.

110. Shirane, G., and Takeda, A. (1952) J. Phy. Soc. Jap. **7**. 15

111. Bhide, V.G., and Multhani, M.S. (1965) Phys. Rev. **139**, 1983.

112. Perry, C.H., and Tornberg, N.E. (1969) In "Light-scattering spectra of solids" (G.B. Wright, ed.) Springer-Verlag, New York.

113. Gupta, L.C., and Vijai Raghavan, R. (1974) In "Solid State Chemistry" (C.N.R. Rao, ed.) Marcel Dekker, New York.

114. Tokunaga, M. (1966) Progr. Theor. Phys. Osaka **36**, 857.

115. Villain, J., and Aubry, S. (1969) Phys. Status Solidi **33**, 337.

116. Takagi, Y., and Sawada, S. (1968) "Materials engineering of magnetic and dielecrtic substances" Tokyo, Ohm-Sha.

117. Sachse, H. (1956) Ferroelektrika, Springer-Berlin Gottingem, Heidelberg.

118. Megaw, H.D. (1957) Ferroelectricity in crystals, Methuen &Co. Ltd., London.

119. Pulvari, C.F. (1964) "Ferroelectricity in Crystals : Progress in Solid State Chemistry" (H. Reiss, ed.) Pergamon Press, Oxford.

120. Dvořák, V. (1974) Ferroelectrics, **7**. 1

121. Pytte, E. (1970) Solid State Commu. **8**, 2101.

122. Cowley, R.A. (1963) Adv. in Phys. **12**, 421.

1233. Riste, T., Samuelsen, E.J. Otnes, K. and Feder, J. (1971) Solid State Commu. **9**, 1455.

124. Lagakos, N. and Cummins, H.Z. (1974) Phys. Rev. **B10**, 1063.

125. Lookwood, D.J., Arthur, J.W., Taylor, W. and Hosea, T.J. (1976) Solid State Commu. **20**, 703.

126. Fleury, P.A. (1976) Ann. Rev. Materials Sci. **6**, 217.

127. Cowley, R.A. Coombs, G.J., Katiyar, R.S., Ryan, J.F., and Scott, J.F. (1971) J. Phy. C-Solid State Phys. **4**, L203.

128. Schwabl, F. (1972) Phy. Rev. Lett. **28**, 500.

129. Schwabl, F. (1973) Solid State Commu. **13**, 181.

130. Töpler, J. Alefeld, B., and Heidman, A. (1977) J. Phy. C-Solid State Phys. **5**, 2711.

131. Darlington, C.N.W., and O'Connor, D.A. (1976) J. Phys. C-Solid State Phys. **9**, 3561.

132. Schutte, C.J.H. (1976) "Theory of Molecular Spectroscopy", **1**, North-Holland, Amsterdam.

133. Long, D.A. (1977) Raman Spectroscopy. McGraw Hill, New York.

134. Beattie, I.R., and Black, J.D. (1977) In "Vibrational Spectroscopy - Modern Trends" (A.J. Barnes and W.J. Orville-Thomas, eds.) Elsevier, Amsterdam.

135. Bist, H.D. Khandelwal, D.P. and Chakrapani, G. (1985) Laser and their Applications in the Indian Context. Tata McGraw Hill, New Delhi.

136. Tobin, M.C. (1971) "Laser Raman Spectroscopy" Wiley-Interscience, New York.

137. Jaffe, H.H., and Orchin, M. (1964) Theory and Application of Ultraviolet Spectroscopy. John Willey, New York.

138. Placzek (1934) Handbuch Der Radiologie **2** 205.

139. Sherwood, P.M.A. (1972) Vibrational Spectroscopy of Solids. Cambridge Univ. Press, Cambridge.

140. Smith, H. (1948) Phil. Trans.Rioy. Soc. London A**241**, 105.

141. Jain, Y.S., and Bhattacharjee, R. (1985) J. Phys. C- Solid State Phys. **18**,5299.

142. Jain, Y.S., and Bhattacharjee, R. (1986) Mol. Phys. **57**, 379.

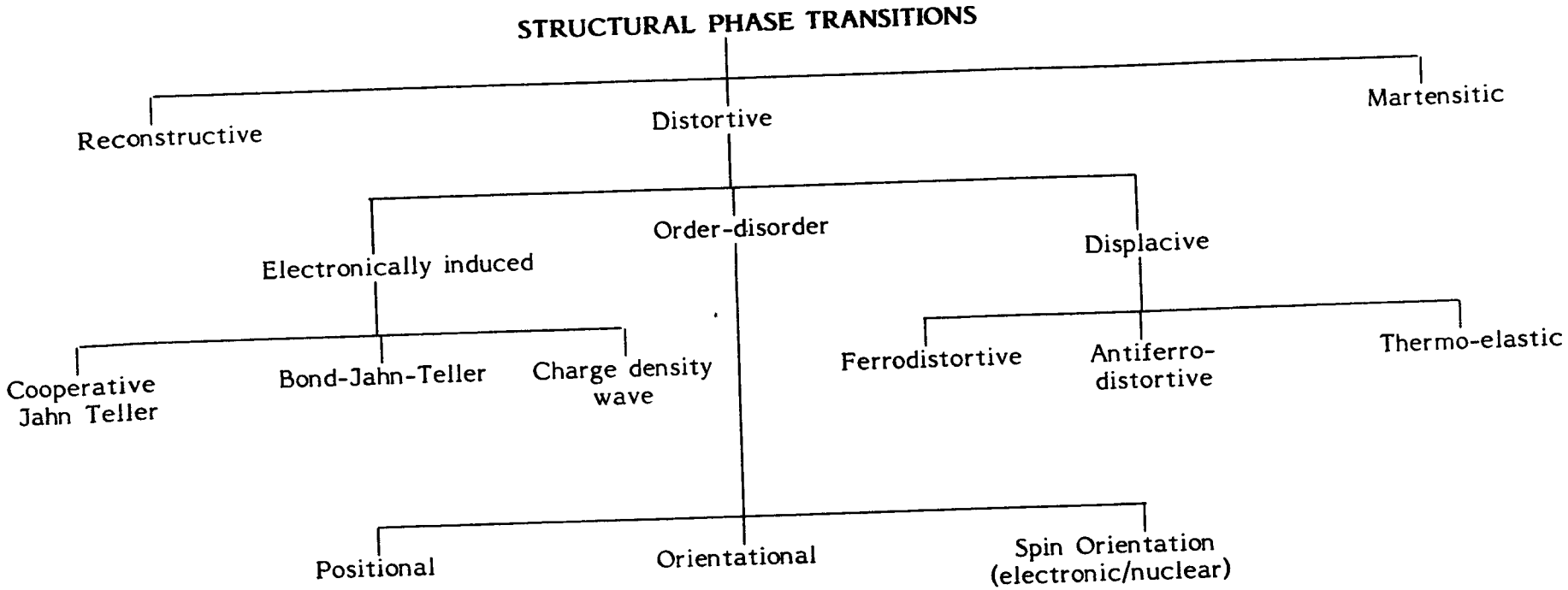
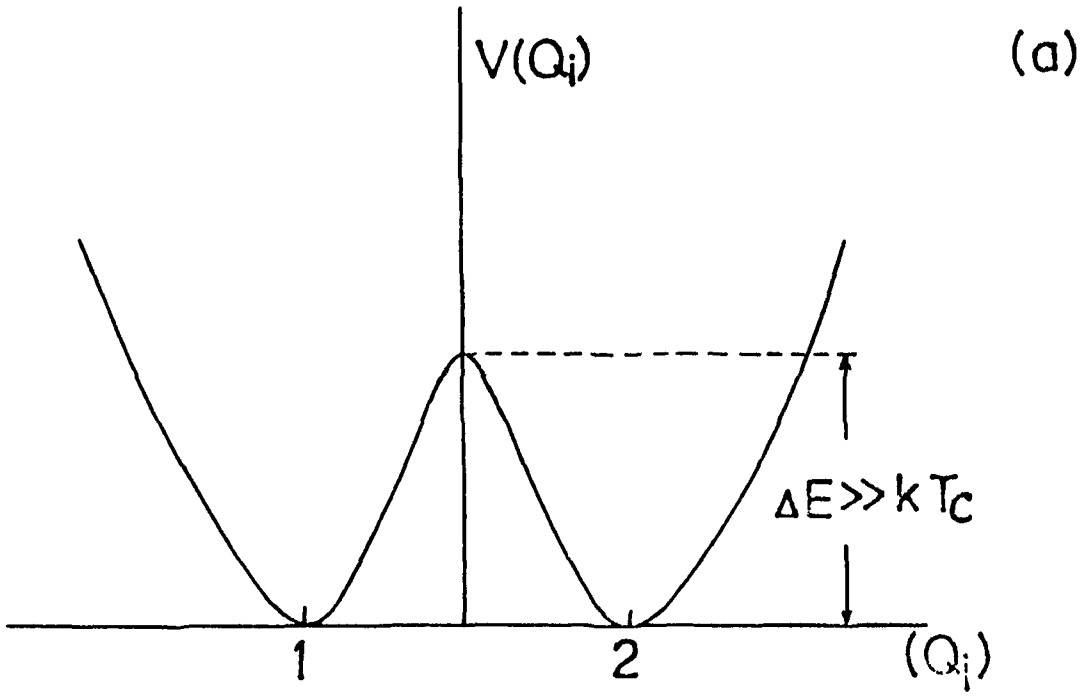


Fig. 1.1 Classification of SPTs

Fig.1.2 Single cell potentials in (a) order-disorder and (b) displacive SPTs.


V(Qi)
(a)
ΔE>>kTc
1
2
(Qi)

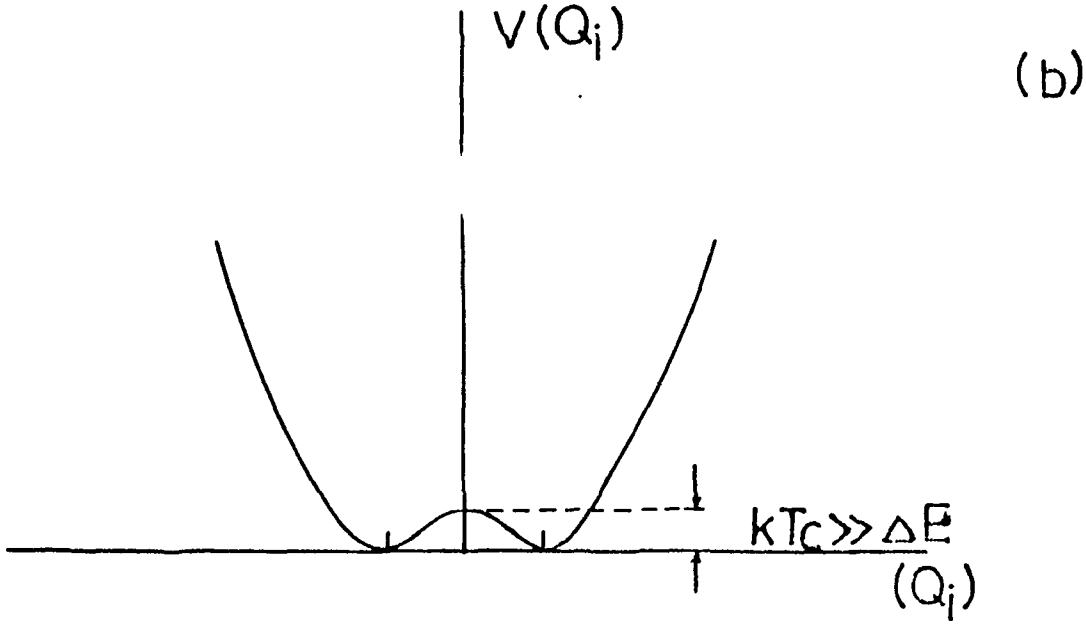
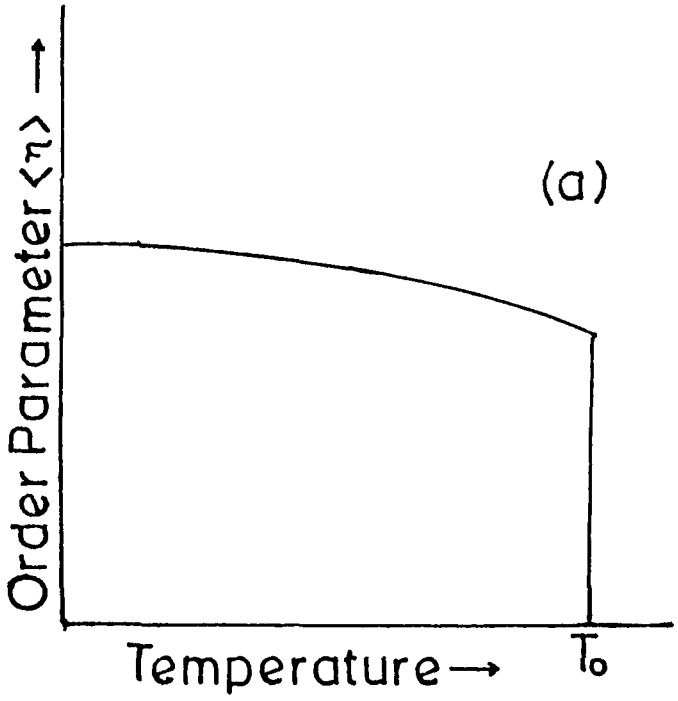
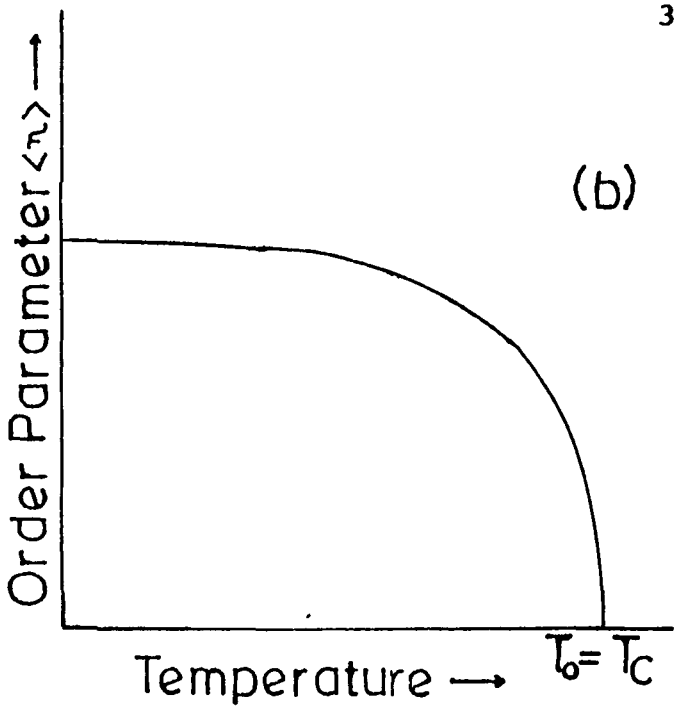
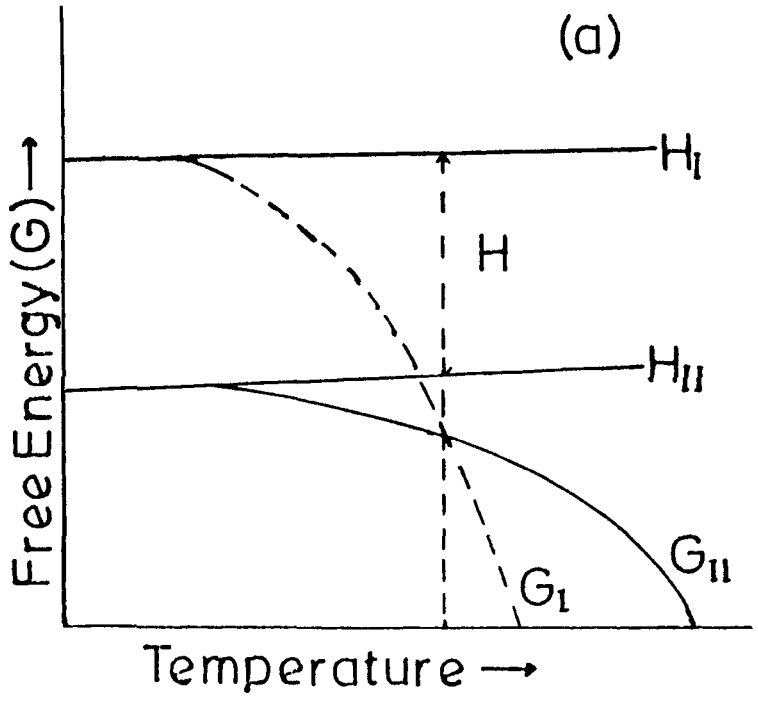

V(Qi)
(b)
kTc>>ΔE
(Qi)

Fig.1.3 Temperature behaviour of order parameter (η) near (a) first order phase transition and (b) second order phase transition.

Fig.1.4 Temperature variation of free energy(a) in a first order and (b) in a second order phase transition.


(a)
Order Parameter ⟨η⟩ →
Temperature →
T_0


(b)
Order Parameter ⟨η⟩ →
Temperature →
$T_0 = T_C$


(a)
Free Energy (G) →
H_I
H
H_{II}
G_{II}
G_I
Temperature →

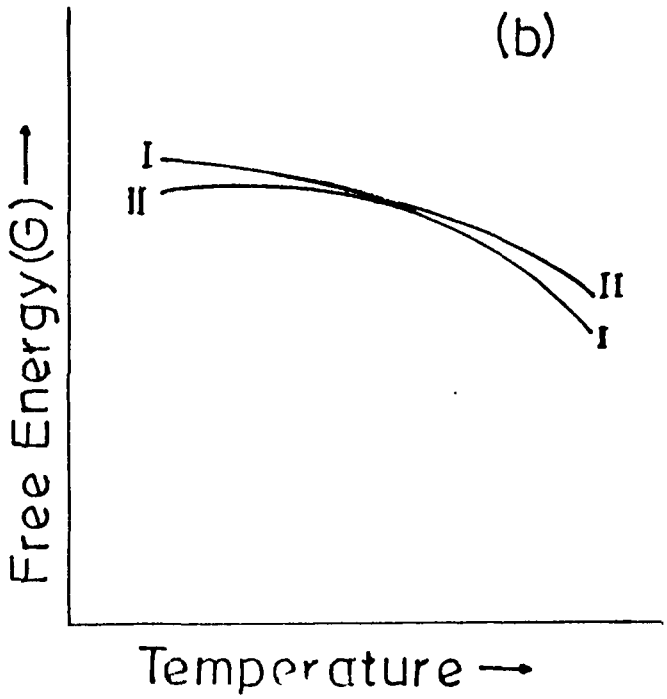

(b)
Free Energy (G) →
I
II
II
I
Temperature →

Fig.1.5(a) A uniform chain of atoms; (b) a commensurable modulation; (c) distorted chain which results when the modulation of (b) is imposed on the chain in (a); (d) an incommensurable modulation; (e) distorted chain which results when the modulation of (d) is imposed on chain in (a); (I) marks represent the original position of atoms in (a), (c) and (e).

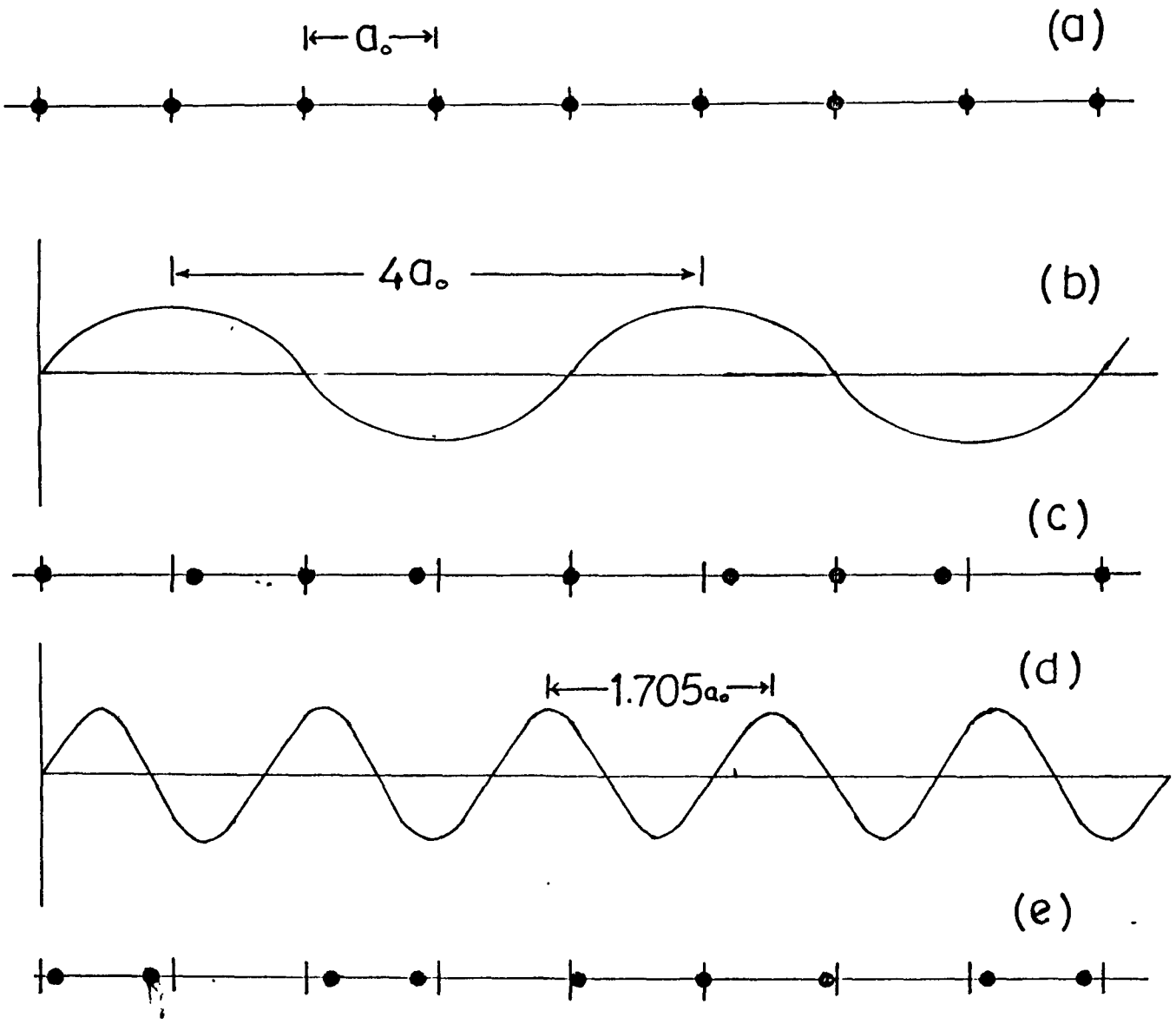
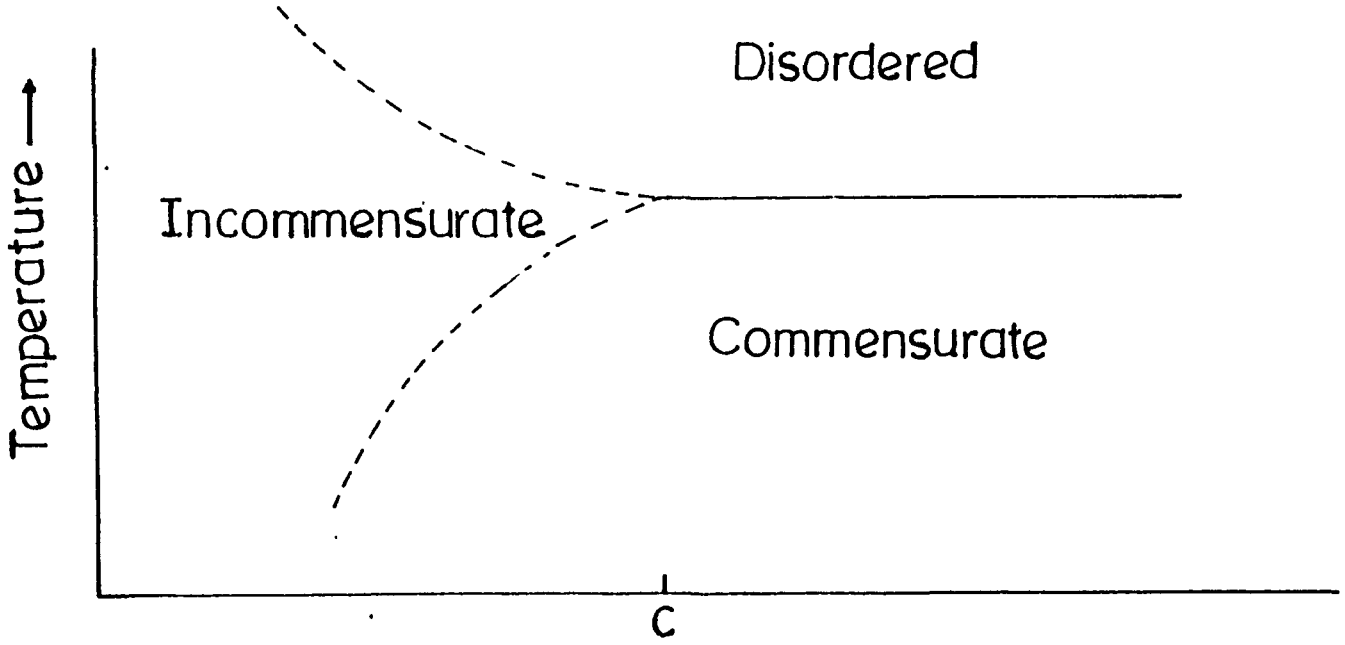

(a)
a_o
(b)
$4a_o$
(c)
(d)
$1.705a_o$
(e)

Fig.1.6 Schematic phase diagram for a system undergoing incommensurate phase transition.

Fig.1.7 Hysterisis loop for a ferroelectric phase transition.


Disordered
Incommensurate
Commensurate
Temperature
C

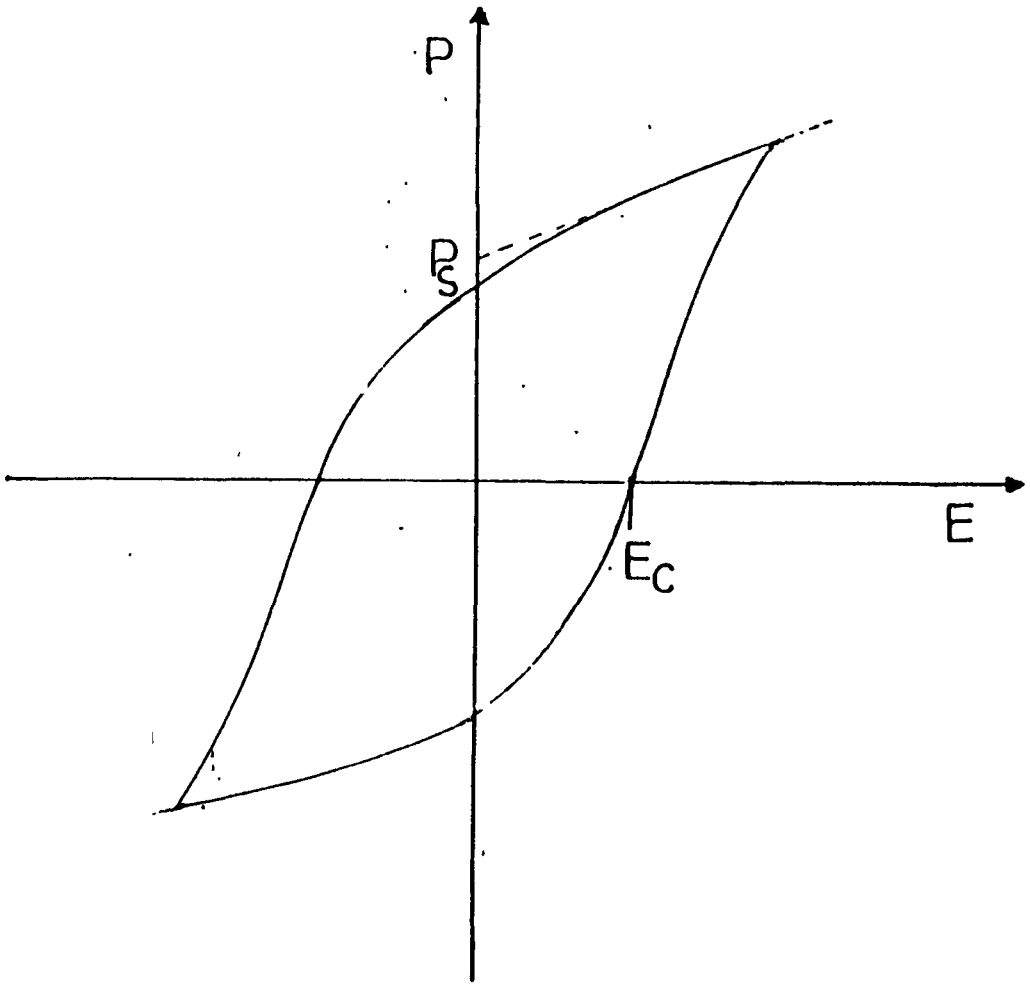
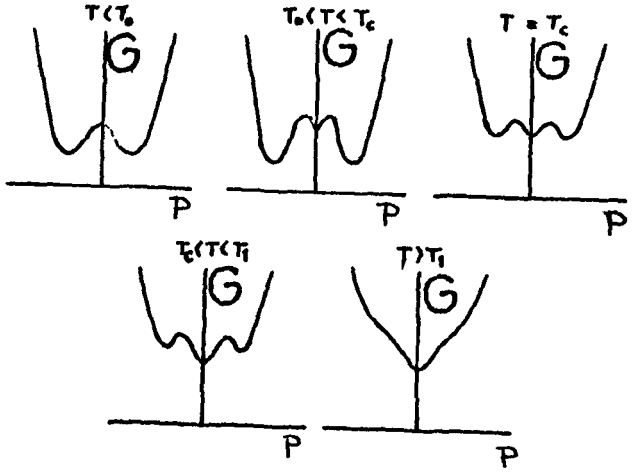

P
P_S
E
E_C

Fig.1.8a Free energy as a function of polarization at various tempeatures in case of a first order phase transition.

Fig.1.8b Free energy as a function of polarization at various temperatures in case of second order phase transition.


T<T_a
T_a<T<T_c
T = T_c
T_c<T<T_1
T>T_1
G
P

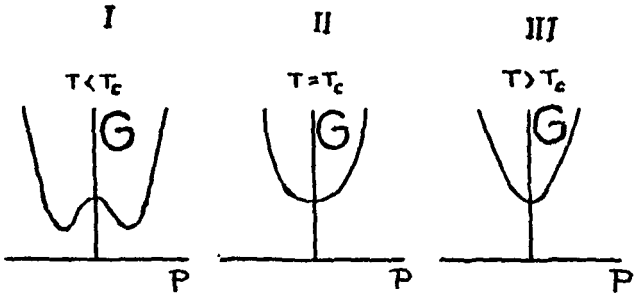
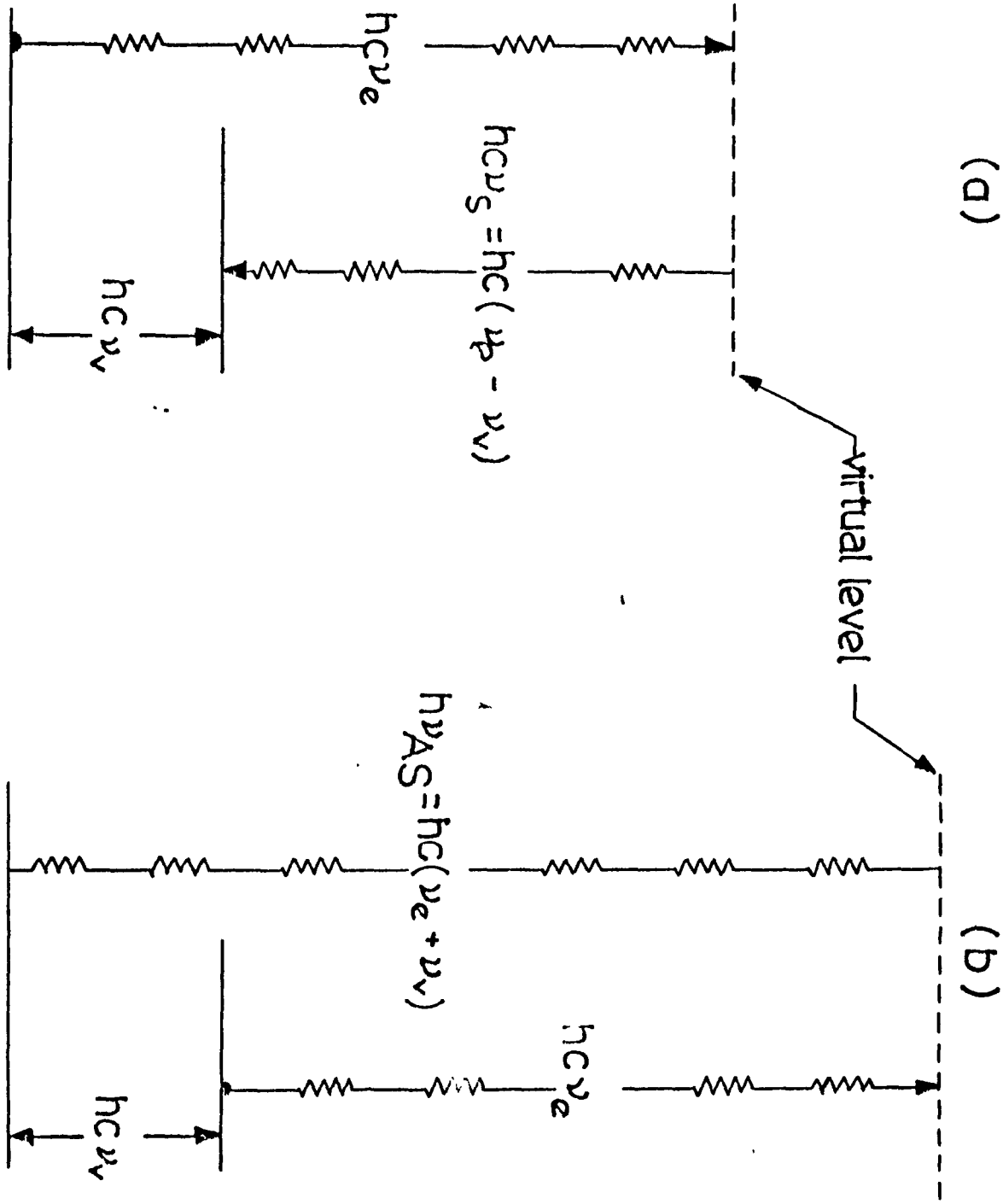

I
II
III
T<T_c
T=T_c
T>T_c
G
P

Fig.1.9 An illustration of (A) stokes and (b) anti-stokes Raman processes.


(a)
$h\nu_e$
$h\nu_S = h(\nu_e - \nu_v)$
$h\nu_v$
virtual level
(b)
$h\nu_{AS} = h(\nu_e + \nu_v)$
$h\nu_e$
$h\nu_v$

STUDIES OF STRUCTURAL PHASE TRANSITION IN AMMONIUM SULPHATE - A REVIEW

2.1 Introduction

Ammonium Sulphate(**AS**), a naturally occuring material known as **mascagnite**, is a colourless common laboratory compound having molecular weight 132.14 and specific gravity 1.759 at 300**K**[1]. It is highly soluble in water and insoluble in alcohal, acetone and ammonia; it dissociates at 508**K**. It undergoes a ferroelectric phase transition at 223**K** from para-electric(**PE**) to ferroelectric(**FE**) phase.

Cre^nshaw and Ritter[2] inferred for the first time by studying the temperature dependence of specific heat (Fig. 2.1) that **AS** undergoes a phase transition at 223**K**. It was later proved to be ferroelectric in nature[3]. Subsequently **AS** has been a subject of large number of studies which reveal its several peculiar phenomenological properties not exhibited by proper ferroelectrics such as $BaTiO_3$, KH_2PO_4, etc. The important peculiarities are the following:

(i) Low Curie-Weiss Constant: Dielectric data on **AS** reveal that its Curie-Weiss constant is as low as ≃ 20**K** (smaller by two order of magnitude in comparison) to normal ferroelectrics such as Rochelle salt (C=1700**K**), triglycine sulphate (C=3290**K**), etc.). The data also

reveal that Curie-Weiss low holds in a very narrow range of temperature above T_c. Some typical values of C reported by different groups are: 23K[4], 15.6K[5], 29K[6], 21K[7] and 11.6K[8].

(ii) Unusually large spontaneous strain: The magnitude of spontaneous strain in FE phase of AS is about 100 times higher than observed for proper ferroelectrics[5,9].

(iii) Large change in birefringence: AS also exhibit a large change ($\sim 10^{-3}$) in birefringence at T_c. This change cannot be accounted for as an electrooptic effect of spontaneous polarization; it rather finds its explanation as elastooptic effect of spontaneous strain[5].

(iv) Weak dielectric anomaly: The dielectric constants of AS have weak temperature dependence. The shape of the dielectric anomaly at T_c is also different from that observed for proper ferroelectrics[4-8].

(v) Temperature dependent spontaneous polarization: The spontaneous polarization observed in many experiments has unusual temperature dependence[10,11]. It even changes its sign at 74.5K.

For these peculiarities, the phenomenology of the phase transition in AS has not been correctly understood. Several models for the microscopic mechanism of the phase transition have been proposed. For example, O'Reilly and T̲Sang[7], associated the transition with the order-disorder of electric dipoles of distorted NH_4^+ ions, while Schlemper and Hamilton[12] associated it with the change in H-bonding. Sawada et al[13] tried to base their ideas around the displacive

type mechanism involving a soft mode having mixed character of libratory and translatory modes of the molecular ions. Jain **et al**[14] emphasised the distortion of SO_4^{2-} ion as the important change that triggers the transition. Ikeda **et al**[4] developed the phenomenological theory of phase transition in **AS** in terms of physically undefined order parameter; whose coupling with spontaneous polarization is considered to be responsible for ferroelectric behaviour. Unruh[10] suggests that the transition is not ferroelectric but ferrielectric in nature, where antiparallel NH_4^+(I) and NH_4^+(II) dipoles do not cancel each other totally in **PE** phase. Petzelt **et al**[15] proposed an oscillator - relaxator model and tried to explain the dynamic properties of **AS**.

The order-disorder model does not explain many properties such as typical temperature dependence of P_s[16], x-ray diffuse scattering[17], etc. and it has been argued at several times that the transition is not of order-disorder type[12,18]. Even the order-disorder model with many minimum potential[19] is not able to explain the transition. The displacive nature of transition has been criticized[20]. The softening of any B_{1u} mode which forms the basis of the soft mode theory[21] has not been observed in any kind of vibrational spectrum[15,20]. In this context Sawada **et al**[21] argued for settling three basic problems experimentally,

(i) whether or not the phase transition is of order-disorder type,

(ii) whether or not the NH_4^+ and SO_4^{2-} ions are distorted from regular tetrahedra and accompany permanent dipole moment, and

(iii) whether or not the spontaneous polarization of **AS** decreases with decrease in temperature.

At times it was suggested that the transition is unlikely to be entirely of the NH_4^+ ions order-disorder and displacive type[22]. Moreover P_s is well accounted for by the permanent dipole moment of the distorted NH_4^+ and SO_4^{2-} ions[23]. These facts indicate that the mechanism of phase transition in **AS** is possibly different from order-disorder/displacive type.

It is interesting to note that many compounds of A_2BO_4 type chemical composition crystallize at room temperature with D_{2h}^{16}/Pnam of **AS**. In spite of this similarity variety of different structural phase transitions have been reported in some of them. For example K_2SO_4 and **AS** exhibit distinctly different kind of transitions below 129**K** and 223**K**, respectively[24-26]. Noting that some such compounds exhibit identical dielectric properties[27] it is concluded that the phase transitions in these isomorphous compounds may have some common mechanism[28]. However, since **AS** undergoes a phase transition in the simplest possible way with no unit cell doubling and intermediate incommensurate phase, it will be interesting to further investigate the nature of its transition in detail. At the same time in order to correctly understand the micro-

scopic mechanism of the transition, it becomes necessary to review the results and interpretations of different studies on this crystal.

2.2 Crystal Structure and Unit Cell Parameters:

The crystal structure of **AS** and its mixed systems has been studied by many investigators[12,29-38]. In a comparative x-ray study of **AS** and K_2SO_4, Rb_2SO_4, it was suggested that the substitution of $8NH_4$ radicals for 8**K** atoms causes no greater distinction than the substitution of 8 Rb atoms. The space lattices of Rb_2SO_4 and **AS** are also closely comparable. Simple structure of orthorhombic lattice with four formula per unit cell was suggested for the first time by Ogg[31]. Tutton[33] showed that the classical, optical and morphological constants of **AS** belong to the alkali sulphate series.

After the discovery of ferroelectricity in **AS**, its detailed structural investigations using x-ray[35], neutron[12] and electron[34] diffraction techniques were performed. This established the crystal structure of **AS** to have D_{2h}^{16} symmetry in **PE** phase and C_{2v}^{9} in **FE** phase.

The unit cell structure depicting the atomic arrangement in the unit cell of **AS** projected on (001) plane is shown in Fig. 2.2 for both phases. The four formula unit cell contains two distinct sets of NH_4^+ions designed as NH_4^+(I) and NH_4^+(II),

which are marked by symbols I and II. For convenience of illustration different atoms (O,S,N and H) have been shown by circles in order of decreasing size, which should, however, not be confused with their atomic size.

In paraelectric phase (cf Fig.2.2a) NH_4^+ and SO_4^{2-} ions form a planner arrangement in (001) planes separated from each other by c/2 lattice distance. Atoms represented by blackened and unfilled circles are considered to be located on (001) mirror planes at c/4 and 3c/4 heights, respectively, from the base of the cell. The line-shaded circles denote pairs of O or H atoms which get interchanged with each other under mirror symmetry (σ_{ab}). In ferroelectric phase this mirror symmetry vanishes with minor changes which are apparent in Fig. 2.2b.

Recently, Hasebe[36] studied **AS** structure at different temperatures (233, 224.5, 219.5, 209, 183 and 133K) which fall on both sides of transition temperature. These results have been found to be very useful in concluding the mechanism of phase transition and its finer details. We, therefore give the useful data in Tables 2.1-2.7. These data do not differ significantly from those reported by others.

The crystal structure of **AS**-K_2SO_4 mixed system for $[(NH_4)_{1-x}Kx)]_2SO_4$; x=0.31 and 0.70 has also been investigated by x-ray diffraction[38]. It is found that mixed crystals are

isomorphous to **AS** and K_2SO_4 crystals and the SO_4^{2-} ion retains its almost tetrahedral structure. Tendency of K^+ ion going preferentially to site (II) of NH_4^+ ions is also reported.

The lattice constants of mixed crystals[37] decrease with increase in K^+ concentration in K_2SO_4-**AS** and increase with Cs^+ concentration in Cs_2SO_4-**AS**. In the Rb_2SO_4-**AS** mixed system the lattice constants **b** and **c** decrease in contrast of **a** which increases with Rb^+ concentration. The change in **b** and **c** with K^+,Rb^+ and Cs^+ concentration is more than the change in **a**. It appears that the NH_4^+ ions are packed more densely along the **a**- axis than along other two axis.

2.3 Dielectric Properties:

The dielectric properties of **AS** have been studied by a number of investigators[4-6,8,9,13,39-57]. Attempts have been made to explain the peculiar dielectric anomaly in terms of improper ferroelectric model[4], coupled oscillator model[6], oscillator-relaxator model[15] and two sublattice model[11]. Even before the discovery of ferroelectricity, the dielectric anomaly of **AS** was wellknown. For example, Courture[43] reported anomaly in dielectric constant (ε) at 25 kMc/S. Kamiyoshi[45] carried out such measurements under d.c. bias and reported that the bias causes large shift in T_c. Le Montagner[44] reported shift in T_c when the measurements were carried out in vaccum. However, the crystal is reported to exhibit normal dielectric

behaviour at microwave frequencies[8,9,42,43,44]. Hoshino **et al**[9] found that the lower limit of the frequencies at which **AS** exhibits a normal type of dielectric behaviour falls in megacycle region. The unusual shape of dielectric constant Vs temperature curve has been associated with the movement of domain walls[8]. The variation in the rate of heating/cooling also changes the sharpness of the dielectric peak.

The temperature dependence of $\varepsilon_x(T)$, $\varepsilon_y(T)$, $\varepsilon_z(T)$ measured by different groups differs significantly. According to Hoshino **et al**[9] the dielectric constant ε_z does not depend on temperature in the paraelectric phase, while observations by Kopstik **et al**[47] show a weak temperature dependence above T_c. However, Unruh[6] and Oshima and Nakamura[8] have shown that the behaviour of ε_z is governed by Curie-Weiss law in the temperature range T_c to 50°C and T_c to 10°C, respectively. Heating/cooling also changes the range in which the law is valid. The anomaly in dielectric behaviour could not be understood in terms of conventional thermodynamic approach[58] applied to proper ferroelectrics. For proper ferroelectrics, we have[59]

$$\frac{\varepsilon(+) - 1}{\varepsilon(-) - 1} = 4 \qquad (1)$$

where $\varepsilon(+)$ and $\varepsilon(-)$ are dielectric constant obtained just above and just below the T_c. While the experimental data for **AS** reveal,

$$\frac{\varepsilon(+) - 1}{\varepsilon(-) - 1} < 1 \qquad (2)$$

indicating that the spontaneous polarization is not the order parameter. Ikeda **et al**[4] on the basis of the theory of improper ferroelectrics[60], associated the dielectric anomaly with the coupling of an undefined order parameter (η) and spontaneous polarization. Kopsky[26] attempted to explain the para- and ferro-electric susceptibilities, by

(i) considering **AS** as a system of one soft (q) and several hard modes (q_i) belonging to a single non-degenerate one- dimensional representation of paraelectric symmetry, and

(ii) introducing anharmonic interactions of the form $q^3 q_i$.

Dvořák and Ishibashi[61] considered two non-equivalent sublattice polarizations, assumed to have strong coupling favouring an antiparallel alignment of dipoles and tried to account for the low Curie-Weiss constant and weak dielectric anomaly. Attempts have also been made to understand the dielectric anomaly in forms of ferrielectric structure of low temperature phase[28].

In coaxial and waveguide frequency range 0.01-10.0 and 18-26.5 GH_z, the dielectric dispersion of **AS** is reported to be of non-dispersive Debye type[53]; it has been suggested that since ε_0 is small, the slight temperature dependence of ε_ω cannot be neglected. The temperature variation of dispersion step $\varepsilon_0 - \varepsilon_\infty$ in **PE** phase follows Curie-Weiss law. No sign of analogous ferrielectric contribution to the dielectric

constant could be detected. Below To' ($T_c-T_o'=2.6K$) these experiments reveal that the relaxation frequency slows down critically to 23 GH_z. However, in the Brillouin scattering experiment, relaxation frequency is observed to fall in 150-200 GH_z range. The difference is explained by quadratic 'electrostrictive' coupling between acoustic and optical symmetry coordinates leading to a multiplication factor of 8.

The relaxation behaviour has been explained in terms of oscillator-relaxator model developed by Sawada **et al**[21] and Petzelt **et al**[15]. The temperature dependence of domain clamped ε is reported to be linear with $\frac{d\varepsilon}{dT} = 0.015/K^{-1}$. This is not in agreement with theoretical formula $\varepsilon=A[T_o^{-}-T_o]^{-\frac{1}{2}}$, where $T_o^{-}-T_o = 3K$. This difference is attributed to the temperature dependence of ε_∞.

Badr and Awad[57] have measured ε in the frequency range $100H_z$-$1MH_z$. They observed a thermal hysteresis of about 4°C and a sharp increase in ε and dielectric loss ε'. An anomalous behaviour in ε is detected around -40°C. This behaviour becomes quite pronounced for low frequency fields but disappears when the measurements are carried in the heating mode. The observed frequency dependence of ε is attributed to piezoelectric resonance. It is inferred that SO_4^{2-} ions play a major role in contributing to the anomalous behaviour of **AS**.

The experimental situation regarding the temperature

dependence of spontaneous polarization (P_s) is not conclusive. Measurements on pure[4,9,10], deuterated[48] as well K-doped[13] Rb doped[62,63] AS have been reported. According to Unruh[10], P_s changes with temperature in magnitude as well as in direction; it has maximum value 0.62 $\mu C/cm^2$ at 221.5K and decreases to -0.03 $\mu C/cm^2$ with a reversal sign at 8K. Some other experiments also suggest this behaviour[48,62,63]. However, other reports indicate temperature independent nature of P_s[4,9]. It has been reported that crystal growth influences the temperature dependence of P_s[64] and one may observed temperature dependent/independent P_s for two different samples. Attempts have been made to relate P_s to one of the B_{1u} mode[21]. The idea was, however, criticized in favour of the assumption that P_s is due to distortions of the NH_4^+ and SO_4^{2-} groups[20]. The temperature dependence is attributed to a ferrielectric structure[48] and two sub-lattice model has been tried to account for it[13]. The model is corroborated by other observations[65-67] and it has been suggested that more than one dipoles contribute to P_s.

The Coercive field (E_c) in the vicinity of transition temperature[9] increases linearly with decreasing temperature. The maximum E_c(=4KV/cm) is observed at 233K. Similar nature of E_c is reported by Matthias and Remeika[2]; the maximum Coercive field reported in their study at 231K is 2KV/cm which decreases with increasing temperature. The frequency dependence for coercive field in the frequency range 0.007-1200 Hz is also

reported[61]. E_c decreases when the frequency increases in the presence of trapezoidal electric field. The decrease in E_c has been attributed to an intrinsic bias field, which is believed to be an expression of the polarization induced ordering of certain lattice defects.

2.4 Specific Heat

Temperature dependence of specific heat (C_p) was first measured by Crenshaw and Ritter[2], and later by several investigators for pure **AS**[9,69,70], deuterated **AS**[71] as well as mixed system (**AS**-$(NH_4)_2BeF_4$)[72]. Nitta and Suenaga[69] and Shomate[70] observed a single peak of sudden change in C_p at T_c and recognise it as λ-type anomaly. However, Hoshino **et al.**[9] observed anomaly at two temperatures ~223**K** and 225.5**K**. Similar results were also obtained for deuterated **AS**[9] at 224.5 and 225**K**. The change in enthalpy and entropy at T_c have been estimated to be 930 Cal/mole and 4.2 Cal/mole. **K**, respectively. The peak at 225.5**K** is reported to shift with the rate of change of sample temperature. The temperature difference between peaks is reported to decrease when the rate of temperature variation is slowed. It is suggested that a thermal relaxation mechanism with large relaxation time should be responsible for double peaks[9]. Recently Hizashizaki and Chihara[71] reported the molar heat capacity of deuterated **AS** between 2.8 and 301**K**. The results show the transition to be of first order. However, a tail extending upto 160**K** is also observed

indicating the presence of second order effects. They estimate that

i) the heat and entropy of transition are 4270 J/mole and 20.35 J/mole K, respectively, and,

ii) the first order portion of the anomaly contributes only 40%.

2.5 DTA and TMA Measurements

In addition to the dielectric measurements Badr and Awad[57] have also studied the differential thermal analysis (DTA) and thermomechanical analysis(TMA). The DTA thermogram shows a peak at T_c indicating the first order transition. The change in TMA thermogram at the transition is associated with a rapid increase in the expansion coefficient attributed to the enhanced rotation of electric dipoles of NH_4^+ and SO_4^{2-} ions.

2.6 Electrical Conductivity

The d.c. electrical conductivity has been measured by Schmidt[73] and syamaprasad and Vallabhan[74]. The conductivity decreases with decrease in temperature but a sudden increase by an order of 4 is observed at T_c. The mechanism of conduction has been attributed to the proton tunneling and the activation energy is estimated to be 0.76eV[73]. Syamaprasad and Vallabhan[74] also reported a sudden change in electrical conductivity at 423K, which as not observed by Schmidt.

2.7 Elastic Anomaly

The transition in **AS** is accompanied by large changes in elastic properties[4,56,75,76]. Elastic constants C_{11}, C_{44} and C_{55} exhibit anomalies at T_c with maximum change ($\simeq$70%) in C_{11}[56]. The lattice strain in the ferroelectric state is 2% larger than in **PE** phase. However, the electrostrictive strain is found to be small in comparison to the total strain in the ferroelectric phase.

Attempts have been made to explain the elastic anomalies in terms of Landau type mean field theory[4,56,77] considering the higher order coupling between order parameter η and strain x. The differences in experimental and theoretical results have been attributed to the contribution to the elastic constants due to domain wall motion[4]. It is observed that the experimental results of the temperature variation of elastic constants particularly determined from Brillouin scattering (phase-comparison method) do not fit well in the expressions coming from Landau type mean field theory. In this context it is argued that Brillouin scattering data have been obtained at stress frequency of $\simeq 10^{10} H_z$; increase of the dispersion frequency of order parameter being lower than the stress frequency, the order parameter cannot follow the applied stress and the elastic constants deduced are expected to be different from their average values[77].

Relation between strain fluctuations and the elastic

constants are now investigated by molecular dynamics simulations[77-79]. Elastic softening of C_{44} has been studied through such simulations for Li_2SO_4[80-83] and experimentally observed changes at phase transition are reproduced. In view of this fact such simulations are desired to be performed for revealing the origin of elastic anomaly in **AS**.

It may be remarked that the emphasis of the investigations on elastic properties has been to reveal the details of the critical behaviour near T_c, therefore, the variation in elastic constants over a wide range of temperature has not been fully investigated.

2.8 Neutron Scattering Studies

There are several reports on neutron inelastic and elastic scattering studies of **AS**[84-88]. Three elastic peaks at 85, 200 and 335 cm^{-1} have been reported[85,87]. The first two peaks are associated with lattice translational vibrations while the last to the NH_4^+ libration. Bjorek **et al**[84] found a peak in the elastic scattering at T_c but no significant change in the inelastic scattering spectra. These observations are corroborated by other studies[85-88]. Dhalborg[87] correlated the former observation with the inference of DMR study by O'Reilly and Tsang[7] that order-disorder of NH_4^+ dipoles is responsible for the transition, while the latter observation is associated with the inference of Neutron diffraction study by Schlemper and Hamilton[12] that the H-bonds play an important

role in triggering the transition; the apparent disagreement[89] is resolved by arguing that DMR and neutron diffraction measurements reveal two different aspects of the system. The relaxation time of reorientational oscillations of NH_4^+ ions is found to be $\approx 10^{-10}$Sec. in **FE** phase and $\approx 5 \times 10^{-11}$Sec in **PE** phase. The measurements have been used to evaluate the angular correlation function for NH_4^+ ions and it is also inferred that the rotational motion of NH_4^+ group is damped[87].

2.9 Magnetic Resonance Studies

Magnetic resonance techniques have also been used to reveal the phase transition in **AS**. Mention may be made of NMR[7,18,90-100], NQR[101] and ESR[102-117]. Some related techniques viz. proton spin thermometry, proton and deutron spin lattice relaxation time measurements[7,18,37,65,100], pulsed nitrogen-proton double resonance and dipolar relaxation measulements[118,119] have also been employed. These investigations reveal:

i) Proton line width transition which occurs at -110°C has no correlation with the onset of polarization[18].

ii) discontinuous change in T_1 observed at T_c is related to the change in barrier to the rotation of NH_4^+ ion from 2.3KCal/mole in the **PE** phase to 6.1KCal/mole in **FE** phase[7]; the observation is corroborated by T_1 measurements in deuterated **AS** and two different relaxation times are attributed

to crystallographically distinct NH_4^+(I) and NH_4^+(II) ions[100].

iii) It is inferred that large amplitude oscillations of NH_4^+ions get freezed at 163K and 117K, respectively for NH_4^+(I) and NH_4^+(II) and this fact is correlated with the unusual temperature dependence of P_s[100].

iv) Line splitting observed in NMR spectra at low temperatures is believed to be due to half "frozen-in" and half "rapidly reorienting" NH_4^+ions[18]; alternatively, this is also associated with the configuration in which two-third of the NH_4^+ion are rigid and rest in motion[91].

v) NH_4^+(I) and NH_4^+(II) ions reorient at different frequencies and are coupled to each other via dipole-dipole interaction[7].

vi) NH_4^+ions do not retain their tetrahedron structure in ferroelectric phase[119].

vii) In solid solution K_2SO_4-**AS** K^+ ions are found tro be substituting for NH_4^+(I) more than NH_4^+(II)[65].

viii) The T_1 measurements in solid solutions like Rb_2SO_4-**AS**, Cs_2SO_4-**AS** reveal that the nature of transition changes from the first order to the second order with increase of the substituent (Rb^+/Cs^+)[37].

ix) The ratio of spin-lattice relaxation time of Zeeman and dipolar energy (T_{1z}/T_{1d}) is observed to be 2 in **PE** phase and 3 in **FE** phase. This is attributed to the contribution from cross-relaxation to ^{14}N which is comparable to the proton-proton relaxation in **PE** phase and negligible in **FE** phase[118].

x) The diffusion of NH_4^+ ion takes place with activation energy 18±2 KCal/mole above 300K[118].

Temperature dependence of ESR spectra of VO^{2+} [103,107,108], CrO_4^{3-} [111-114], NH_3^+ [102,104,105,117], SeO_3^- [115] and Cr^{5+} [106] probes have been studied. These reveal the following:

i) At T_c the SO_4^{2-} ion get distorted and an abrupt increase in the dipole-dipole interaction energy between NH_4^+ and SO_4^{2-} dipoles occur[104,109,111].

ii) H-bonds become stronger in **FE** phase.

iii) NH_4^+(I) and NH_4^+(II) can be arranged in three different pair sites, viz. NH_4^+(I)-NH_4^+(I), NH_4^+(I)-NH_4^+(II), NH_4^+(II)-NH_4^+(II)[106], where VO^{2+} type *dopent can enter; each pair site obviously has* different temperature dependent field. The temperature dependence of ESR spectra at I-I and II-II eites are found to be quite similar to that of spontaneous polarization[108].

iv) The temperature dependence of the strength and orientation of different dipoles is different[104].

2.10 IR and Raman Studies

A wealth of papers has been reported on IR-absorption[14,20,23,90,119-114], Raman and Brillouin scattering[22,145-155]. Samples in the form of powder[134,140], microcrystalline thin films[20,132], single crystals[23,152-154] of both pure and deuterated **AS** have been investigated. Recently samples of solid solutions such as, Na_2SO_4-**AS**, etc. have also been studied.

IR/Raman spectra of these samples have been analyzed

in terms of phonon frequencies of different normal modes. Their site symmetries and correlation field splitting have been determined and the spectra have been interpreted in the framework of unit cell approximation. Apparently, these investigations are more or less complete[127,131,134,152,154], though there are minor disagreement about certain assignments. For example, the assignment for the band observed at 3310cm^{-1} in the N-H stretching region. According to Torrie **et al**[134] this band arises due to site split component of $\nu_3(NH_4^+)$mode, while Schutte and Heyns[131] associate it with $2\nu_2(NH_4^+)$. Stekhanov and Gabrichidge[130] identified it as a component of the doublet arising due to tunneling of proton along N-H.....O hydrogen bridge. Jain **et al**[20] also corroborate this assignment.

Among the external modes of **AS**, $\nu_6(NH_4^+)$ observed in the frequency range 300-360cm^{-1} has been most thoroughly investigated[127,133,134,135,141] because the mode has been suggested to be involved in the mechanism of the phase transition[7,12,87,90,91]. The temperature dependence of IR/Raman spectra has been investigated in detail. These investigations reveal:

i) The constituent ions viz. NH_4^+(I),NH_4^+(II) and SO_4^{2-} are distorted from their tetrahedral structure; distortion in SO_4^{2-} ion increases suddenly at T_c[23].

ii) NH_4^+ ions execute hindred rotational motion.

iii)Factor group splitting of different modes as predicted by factor group analysis are not observed[134], however, in some Raman work, small factor group splitting has been measured[152,154]. In a recent study[155] the observed splitting has been attributed to the hetroionic vibrational coupling between the modes of NH_4^+ and SO_4^{2-}ions. A mechanism of interionic vibrational coupling has been suggested to reveal that vibrations of the crystal consist of motion of both sets of ammonium ions rather than some vibrations due to one set and rest due to other set.

One of the objective of studying the low frequency spectra of **AS** has to detect the soft mode (if any) involved in the mechanism of phase transition. The soft mode should have B_{1u} symmetry of D_{2h} (point group of **PE** phase) and should attain A_1 symmetry of C_{2v}(symmetry of **FE** phase). Sawada **et. al**[21] argued that the soft mode should be a mixed mode of small component of translational polar symmetry and large component of librational non-polar symmetry. Unruh **et al**[156] suggested that two irreducible representations (B_{1u} and A_1) might be active in Phase Transition. Jain and Bist[20] have suggested that this should have major component as ν_3 (assymetric stretch of SO_4^{2-} and small component as $\nu_4(SO_4^{2-})$. However, no phonon soft mode has been observed in Raman[14,20], IR[134] and far IR[15,143] spectra. Petzelt **et al**[15] have argued that soft mode may not be observed due to its fast relaxing nature. Iqbal and Christoe[22] also believe that the mode should be relaxation

type. In this context, mention may be made of 'Rayleigh wing' observed in 0-50 cm^{-1} frequency range in Raman spectra[22] of yy and xy polarization. The temperature dependence of Rayleigh wing has been investigated in 290-170K range. The xy wing loses intensity in an approximately linear fashion, while the yy wing changes its profile, losing intensity and simultaneously revealing a weak intensity peak around $40cm^{-1}$ whose intensity increases slowly with decrease in temperature. The yy wing is compatible with the mode of A_1 symmetry which is the expected symmetry of the ferroelectric mode, SO_4^{2-} librations. It is possible that those wings arise from nearly free rotation of NH_4^+ ions but then some distortion from T_d symmetry is necessary to allow Raman activity. Iqbal and Christoe[22] finally state that it is not clear whether these wings could be associated with the soft mode, particularly when they change little at T_c.

2.11 Birefringences Study

The anomalies in electrooptic coefficients have been investigated by Anistratov and Martynov[5] and Strukov[157] and identified to have dielectric nature. However, the changes of birefringence $\delta(\Delta n_c)$, calculated as electrooptic effect of the spontaneous polarization is found to be two order of magnitude lower than that observed experimentally. It is, therefore, argued that the change in Δn_c arises as an elasto-optic effect of spontaneous strain which accounts

for the observed magnitude of Δn_c.

2.12 Theoretical Approaches

Several theoretical models have been proposed for the phase transition in **AS**. The order-disorder model[7] in the framework of mean field approximation has been proposed, where NH_4^+ ions are presumed to get orientationally ordered in one of the two equilibrium positions. The model however does not explain the first order nature of the transition because the necessary cooperative orientation of NH_4^+ ions is absent in the system[18]. This model has also been criticized by Hamilton and Ibers[158]. A displacive type nature involving the translation of the NH_4^+ion along the ferroelectric axis triggered by the enhanced hydrogen bonding in the **FE** phase has also been discussed[12]. However, this picture does not account for the observed spontaneous polarization[20]. Jain **et al.** using the point charge model[23] calculated the dipole-moments of individual ions arising from their distortion from T_d structure. The calculated P_s is found to be almost equal to the observed values. In view of this observation Jain **et al**[23] have proposed a model, according to which the SO_4^{2-} ion get distorted suddenly at T_c and triggers the transition. However, the further work on the model to develop a quantitative theory has not been taken up until recently[159-161]. Unruh and rüdiger[55] proposed a two-non-equivalent sublattice model, where two NH_4^+ions acts as sublattices. Some properties

of **FE** phase are explained in the framework of ferrielectric structure[28].

Both Landau type[4,28] and soft mode[21] phenomenological theories have been attempted to explain the transition. Ikeda **et al.**[4] developed a Landau type theory considering **AS** as an improper ferroelectric and expanding the free energy in terms of an order parameter η; coupling between order parameter and spontaneous polarization was introduced to account for the dielectric behaviour. Kopsky[26] considered the anharmonic interactions between soft and hard modes in order to explain dielectric susceptibilities. Soft mode theory by Sawada **et al.**[21] attributes the origin of the transition to a mixed mode of non-polar librational and polar translational modes. The model is based on the assumption that all constituent ions have perfect T_d symmetry in both phases but this assumption is not observed to be in line with the structural results[20]. Thermodynamic theories have also been attempted in the framework of two sublattice model by Dvořák and Ishibashi[61] and Onodera **et al.**[28]. These theories, however, assume that only one NH_4^+ ion is actively involved in the transition and express the free energy in terms of only one sublattice polarization; other sublattice polarization is treated as an interacting system. Recently Zinenko **et al.**[19] have examined the transition in the framework of an order-disorder model with many minimum potential. However, they found that the model does not fit

with the observed behaviour of transition in **AS**. Aizu[162] has suggested a different approach to explain the phase transition in **AS**-type system. According to this approach, there may exist a soft mode having wavelength equal to general rational number times the relevant lattice parameter.

In addition to the above mentioned studies, mention may be made of the work on domain structure[49,163], twin plane motion[164] crystal growth and nucleation[165], thermoluminscense[166] and optical constants[167]. Some of these properties are reviewed by Mejean and Calendini[168]. Apparently **AS** has been studied exhaustively. However certain aspects of its phase transition remain still unclear. For example:

i) the physical nature of order parameter, in the absence of which several theoretical studies could not be treated as the right efforts in the direction revealing the microscopic mechanism of phase transition;

ii) the involvement of different constituent ions in the microscopic mechanism of SPT about which different studies make different conclusion; studies of NH_4^+ ion dynamics reveal as if the phase transition is of second order in nature[169], while those of SO_4^{2-} ion dynamics corroborates its first order character evident from finite latent heat;

iii) origin of the peculiar temperature dependence of spontaneous polarization (P_s) is uncertain and which is attributed to the ferrielectric structure of NH_4^+(I) and NH_4^+(II) dipoles, while there are clear evidences for SO_4^{2-} ion also contributing significantly to the P_s;

At times it has been suggested that the SPT in **AS** cannot be understood entirely in terms of either the order-disorder or displacive type microscopic mechanism. But the real mechanism of transition has not been revealed. While the T_c is not affected by deuteration and the NMR linewidth remains unchanged at T_c, the H-bonds are also suggested to play a major role in triggering the transition; the way these bonds operate has not been concluded.

REFERENCES

1. Weast, R.C., and Silby, S.M. (1966-'67) "Handbook of Chemistry and Physics". 47th edition, The Chemical Rubb. Comp.

2. Crenshaw, J.L., and Ritter, J. (1932) Z. Physik. Chem. **B16**, 143.

3. Matthias, B.T., and Remeika, J.P. (1956) Phys. Rev. **103**, 262.

4. Ikeda, T. Fujibayashi, K. Nagai, T., and Kobayashi, J. (1973) Phys. Status Solidi a **16**, 279.

5. Anistratov, A.T., and Martynov, V.G. (1970) Sov. Phys. - Crystallogr. **15**, 256.

6. Unruh, H.G. (1965) Phys. Lett. **17**, 8.

7. O'Reilly, D.E., and Tsang, T. (1967) J. Chem. Phys. **46**, 1291.

8. Oshima, H., and Nakamura, E. (1966) J. Phys. Chem. Solids **27**, 481.

9. Hoshino, S. Vedam, K. Okaya, Y. and Pepinsky, R. (1958) Phys. Rev. **112**, 405.

10. Unruh, H.G. (1970) Solid State Commu. **8**, 1951.

11. Unruh, H.G., and Ayere, O. (1976) Ferroelectrics **12**, 181.

12. Schlemper, E.O., and Hamilton, W.C. (1966) J. Chem. Phys. **44**, 4498.

13. Sawada, A. Ohya, S., Ishibashi, Y. and Takagi, Y. (1975) J. Phys. Soc. Jap. **38**, 1408.

14. Jain, Y.S. Bist, H.D., and Upreti, G.C. (1973) Chem. Phys. Lett. **22**, 572.

15. Petzelt, J. Grigas, J. and Mayerová, I. (1974) Ferroelectrics **6**, 225.

16. Fujimoto, M. Dressel, L.A., and Yu, T.J. (1977) J. Phys. Chem. Solids, **38**, 97.

17. Hasebe, K., and Tanisaki, S. (1977) J. Phys. Soc. Jap. **42**, 568.

18. Miller, S.R. Blinc, R. Brenman, M., and Waugh, J.S. (1962) Phys. Rev. **126**, 528.

19. Zinenko, V.I. Blat, D. Kh., and Aleksandrov, K.S. (1980) Fiz. Tverd. Tela **22**,184.

20. Jain, Y.S. and Bist, H.D. (1974) Solid State Commu. **15**, 1229.

21. Sawada, A. Takagi, Y., and Ishibashi, Y. (1973) J. Phys. Soc. Jap. **34**, 748.

22. Iqbal, Z., and Christoe, C.W. (1976) Solid State Commu. **18**, 269.

23. Jain, Y.S., and Bist, H.D. (1974) Phys. Status Solidi **a 62**, 295.

24. Iizumi, M. Axe, J.D. Shirane, G., and Shimaika, K. (1977) Phys. Rev. **B15**, 4392.

25. Dvořák, V. and Petzelt, J. (1978) J. Phys. C- Solid State Phys. **11**, 4827.

26. Kopsky, V. (1976) Solid State Commu. **19**, 417.

27. Mitsui, T. **et al.** (1982) "Ferroelectrics and related substances" Landolt -Bomstein. New series, Group III, **106** 105, Springer-Verlag Berlin-NewYork.

28. Onodera, A. Cynshi, O., and Shiozaki, Y. (1985) J. Phys. C. -Solid State Phys. **18**, 2831.

29. Ogg, A., and Hopwood, F. L. (1916) Phil. Mag. **32**, 191, 518.

30. Taylor, W., and Boyer, T. (1927-'28) Proc. Manchester Lit. Phil. Soc. **72**, 125.

31. Ogg, A. (1928) Phil Mag. **5**, 28, 354.

32. Ogg, A. (1930) Phil. Mag. **9**, 665.

33. Tutton, A.E.H. (1930) Phil. Mag. **9** 58.

34. Udalova, V.V., and Pinskar, Z.G. (1964) Sov. Phys- Crystallgr. **8**, 433.

35. Singh, B. (1962) Doctoral Dissertation, The Pennsylvania Univ.

36. Hasebe, K. (1981) J. Phys. Soc. Jap. **50**, 1266.

37. Ohi, K. Osaka, J., and Uno, H. (1978) J. Phy. Soc. Jap. **44**, 529.

38. Siozaki, Y. Koh, S., and Sawaguchi, E. (1977) J. Phys. Soc. Jap. **43**, 721.

39. Guillien, R. (1939) Comp. Rend. **208**, 980.

40. Bayley, S.T. (1951) Trans. Faraday. Soc. **47**, 518.

41. Freymann, M. (1951) Comp. Rend. **233**, 1449.

42. Kamiyoshi, K., and Miyamoto, T. (1954) J. Chem. Phys. **22**, 756.

43. Couture- Mathieu, L. Le Montagner, S. LeBot, J., and Le Traon, A. (1956) Comp. Rend. **242**, 1804.

44. Le Motagner, S. (1957) Doctoral Dissertation Univ. of Paris.

45. Kamiyoshi, K. (1957) J. Chem. Phys. **26**, 218.

46. Kopstik, V.A. Strukov, B.A. Sklyankin, A.A., and Levina, M.E. (1960) Izv. Akad. Nauk SSSR Ser. Fiz. **24**, 1228.

47. Kopstik, V.A. Strukov, B.A. Nevodomskaya, I.K. (1960) Izv. Akad. Nauk SSSR Ser. Fiz. **24**, 1231.

48. Unruh, H.G., and Rüdiger, U. (1972) J. De Physiq, **33**, C2-77.

49. Tashev, S. (1966) Proc. Int. Meeting on Ferroelectricity, **2**, 31, Prauge.

50. Nakamura, E. Mitsui, T., and Furichi, J. (1963) J. Phys. Soc. Jap. **18**, 1477.

51. Levina, M.E., and Kolbeneva, G.I. (1972) Vestn. Mask. Univ. Khim. **13**, 211.

52. Hettich, A. (1934) Z. Physik Chem. **A168** 360.

53. Luther, G., and Unruh, H.G. (1980) Ferroelectrics **25**, 491.

54. Unruh, H.G. Sailer, E. Hussinger, H., and Ayere, O. (1978) Solid State Commu. **25**, 871.

55. Unruh, H.G., and Rüdiger, U. (1971) Proc. European Meeting on Ferroelectricity **9**, Dijon.

56. Yoshihara, A. Fujimura, T., and Kamiyoshi, K. (1976) Physica Status Solidia **39**, 369.

57. Badr, Y.A., and Awad, S. (1984) J. Phys. Chem. Solids **45**, 351.

58. Kanzig,W.(1957) "Ferroelectrics and Antiferroelectrics". Academic Press, New York.

59. Kittel,C.(1971) "Introduction to Solid State Physics", John Willey, New York.

60. Kobayashi, J. Enomoto, Y., and Sato, Y. (1972) Physica Status Solidi b **50**, 335.

61. Dvořák, V. and Ishibashi, Y. (1976) J. Phys. Soc. Jap. **41**, 548.

62. Unruh, H.G., and Ayere, O. (1975) 3rd Europ. Meeting on Ferroelectricity, Zurich.

63. Unruh, H.G. and Rüdiger, U. (1972) J. de Physique **33**, Suppl. C2-77.

64. Zaitseva, M.P., and Rozhnova, G.P. (1975) Kristallogr. **20**, 178.

65. Kashahara, M. Sasakawa, K., and Tatsuzaki, I. (1975) J. Phys. Soc. Jap. **39**, 1022.

66. Shiozaki, Y. Koh, S., and Sawaguchi, E. (1977) J. Phys. Soc. Jap. **43**, 721.

67. Shibata, N. Abe R., and Suzuki, I. (1976) J. Phys. Soc. Jap. **41**, 2011.

68. Unruh, H.G. (1965) Physik Kondensierten Materie **4**, 275.

69. Nitta, I., and Suenaga, K. (1938) J. Chem. Phys. **13**, 36.

70. Shomate, C.H. (1945) J. Phys. Chem. **6**, 1096.

71. Hizashizaki, Y., and Chihara, H. (1981) Bull. Chem. Soc. Jap. **54**, 901.

72. Smirnov, P.S. Maak, Kh., and Strukov, B.A. (1960) Sov. Phys. Crystallogr. **30**, 476.

73. Schmidt, V.H. (1963) J. Chem. Phys. **38**, 2783.

74. Syamaprasad, U., and Vallabhan, C.P.G. (1981) Solid State Commu. **38**, 555.

75. Haussuhl, S. (1965) Acta Crystallogr. **18**, 839.

76. Luspin, Y., and Hauret, G. (1972) C.R. Akad. Sci. Ser. **B274**, 995.

77. Hirotsu, S. Kunii, Y. Yamamoto, I. Miyamoto, M. and Mitsui, T. (1981) J. Phys. Soc. Jap. **50**, 3392.

78. Parrinello, M., and Rahman, A. (1980) Phys. Rev. Lett. **45**, 1196.

79. Parrinello, M., and Rahman, A. (1981) J. Appl. Phys. **52**, 7182.

80. Parrinello, M., and Rahman, A. (1982) J. Chem. Phys. **76**, 2662.

81. Klein, M.L. (1985) Ann. Rev. Phys. Chem. **36**, 525.

82. Impey, R.W. Klein, M.L., and McDonald, I.R. (1985) J. Chem. Phys. **82**, 4690.

83. Impey, R.W. Klein, M.L., and McDonald, I.R. (1985) J. Phys. C- Solid State Phys. **17**, 3941.

84. Bajorek, A. Machechina, T.A., and Parlinski, K. (1965) IAEA Symposium on Inelastic Scattering of Neutrons in Solids and Liquids **2**, 355.

85. Rush, J.J., and Taylor, T.T. (1965) IAEA Symposium On Inelastic Scattering of Neutrons in Solids and Liquids **2**, 233.

86. Leung, P.S. Taylor, T.I., and Havens, W.W.Jr. (1968) J. Chem. Phys. **48**, 4912.

87. Dahlborg, U. Larsson, K.E., and Pirkmajer, E. (1970) Physica **49**, 1.

88. Kim, H.J. (1972) J. Korean. Nucl. Soc. **4**, 306.

89. Hamilton, W.C. and Ibers, J.A. (1968) "Hydrogen bonding in Solids", p.248. Benjamin Inc. New York.

90. Blinc, R. and Levstek, I. (1960) J. Phys. Chem. Solids, **12**, 295.

91. Richards, R.E., and Schaefer, T. (1961) Trans. Faraday Soc. **57**, 210.

92. Levstek, I. (1959) Proc. Intern. Meet. Mol. Spectrosc. **3**, 1231, 4th Bologna.

93. Nordland, I. O'Reilly, E.O., and Peterson, I. (1976) J. Chem. Phys. **44**, 369.

94. Blinc, R. Miller, S.R., Brenman, M., and Waugh J.S. (1962) Collq. AMPERE **11**, 199.

95. Blinc, R. Mali, M. Osredkar, R. Prelesnik, A. Seliger, J., and Zupancic, I. (1972) Chem. Phys. Lett. **14**, 49.

96. Chiba, T. (1962) J. Chem. Phys. **36**, 1122.

97. Rabindeau, S.W., and Waldestein, P. (1965) J. Chem. Phys. **42**, 3822.

98. Kydon, D.W. Petch, H.E., and Pintar, M. (1969) J. Chem. Phys. **51**, 487.

99. Kydon, D.W. Pintar, M., and Petch, H.E. (1967) J. Chem. Phys. **47**, 1185.

100. Kydon, D.W. Petch, H.E., and Pintar, M. (1967) Phys. Lett. **25**, 360.

101. Kinspoel, R.R., Petch, H.E. and Pintar, M. (1972) J. Chem. Phys. **65**, 676.

102. Suzuki, I, and Abe, R. (1970) J. Phys. Soc. Jap. **30**, 586.

103. Pandey, S.D. and Venkateswarlu, P. (1975) J. Mag. res. **17**, 137.

104. Shibata, N. Abe, R., and Suzuki, I. (1976) J. Phys. Soc. Jap. **41**, 2011.

105. Fujimoto, M. Dressel, L.A., and Yu, T.J. (1977) J. Phys. Chem. Solids **38**, 97.

106. Manjunath, C.M. and Srinivasan, R. (1978) Phys. Status Solidi b **87**, 395.

107. Fujimoto, M., Yu, J., and Furukawa, K. (1978) J. Phys. Chem. Solids **39**, 345.

108. Kawano, M., and Furukawa, K. (1979) J. Phys. Soc. Jap. **47**, 1191.

109. Abe, R. and Shibata, N. (1977) J. Phys. Soc. Jap. **43**, 1308.

110. Barb, D., Grecu, N.M., Grecu, V.V., and Popescu, F.F. (1978) Chem. Phys. Lett. **56**, 355.

111. Bhat, S.V., Mishra, N.C. and Srinivasan, R. (1982) J. Phys. Chem. Solids, **42**, 1157.

112. Mishra, N.C. and Srinivasan, R. (1979) Proc. Nuclear Phys. and Solid State Phys. Sym. 621, Madras.

113. Mishra, N.C., and Srinivasan, R. (1980) Joint ISMAR-AMPERE Int. Conf. on Mag. reson., Delft. The Netherlands.

114. Ramnathan, K.V., and Srinivasan, R. (1978) Chem. Phys. Lett. **56**, 359.

115. Owens, F.J. (1977) Ferroelectrics **16**, 123.

116. Bailey, C.E., and Cuesta-Barro, J. (1975) J. Chem. Phys. **63**, 4120.

117. Abe, R. Shibata, N., and Dejima, K. (1978) Ferroelectrics **20**, 217.

118. Knispel, R.R. Petch. H.E., and Pintar, M.M. (1975) J. Chem. Phys. **63**, 1.

119. Hettner, G., and Simon, F. (1928) Z. Physik. Chem. **B1**, 293.

120. Pohlman, R. (1932) Phizik, **79**, 394.

121. Fock, J. (1934) Z. Phizik, **90**, 38.

122. Ananthanayanan, V. (1963) Ind. J. Pure and Appl. Phys. **1**, 58.

123. Myasnikova, T.P. (1962) Materially 4-Oi (Chetvertoi) Nouchn. Konf. Aspirantov Sb. 61.

124. Myasnikova, T.P., and Yatsenko, A.F. (1962) Sov. Phys. Solid State **4**, 475.

125. Grabriechidze, Z.A. Eremeishvili, I.P., and Dzhaparidge, I.N. (1969) Tr. Kutaio. Gos. Pedagog Instt. **32**, 289.

126. Oden, L.L. (1966) Diss. Abstra. **26**, 3654.

127. Trefler, M., and Wilkinson, G.R. (1969) Discuss. Faraday Soc. **48**, 108.

128. Guerchais, J.E. Haumesser, A., and Rohmer, R. (1965) Comp. Rend. **260**, 5571.

129. Mysnikova, T.P., and Arefev, I.M. (1964) Opt. and Spectroscop. **16**, 293.

130. Stekhanov, A.I., and Gabrichidze, Z.A. (1964) Sov. Phys. Solid State **5**, 2275.

131. Schutte, C.J.H., and Heyns, A.M. (1968) Chem. Phys. Lett. **1**, 511.

132. Schutte, C.J.H., and Heyns, A.M. (1970) J. Chem. Phys. **52**, 864.

133. Trefler, M. (1971) Can. J. Phys. **49**, 1964.

134. Torrie, B.H., Lin, C.C. Binbrek, O.S., and Anderson, A. (1972) J. Phys. Chem. Solids. **33**, 697.

135. Acharya, P.K., and Narayanan, P.S. (1973) J. Pure and Appl. Phys. **11**, 514.

136. Bazherlin, P.A. Mysansnikova, T.P., and Rakov, A.V. (1964) Sov. Phys. Solid State. **5**, 1299,.

137. Heyns, A.M. (1968) Ph. D. Dissertation Univ. of South Africa.

138. Oxton, I.A., and Falk, D.K.M. (1977) J. Mole. Structu. **37**, 69.

139. Ross, S.D. (1962) Spectro Chim. Acta. **18**, 1575.

140. Salvador, G. Sherman, W.F., and Wilkinson, G.R. (1986) J. Mole. Structu.**143**, 55.

141. Jain, Y.S., and Bist, H.D. (1974) Proc. Nuc. & Sol. Stat. Phys. Sympo. **17c**.

142. Petzelt, J. Grigas, J., and Mayerová, I. (1974) Ferroelectrics, **6**, 225.

143. Brehat, F. Wyncke, B. Fuzellier, Y. and Hadni, A. (1974) J. de Physique **35**, L-143.

144. Thrierr, J.C. (1961) Comp. Rend. **253**, 2917.

145. Da Silveria, A. (1932) Comp. Rend. **195**, 521.

146. Ananthakrishnan, R. (1937) Ind. Acad. Sci. **A5**, 76.

147. Heerdt, R., and Goubeau, J. (1948) Z. Anorg. Chem. **225**, 309.

148. Schafer, K. (1948) Z. Electro Chem. **52**, 98.

149. Blomer, F., and Moser, H. (1969) Z. Angew. Phys. **27**, 302.

150. Montero, S. Schmolz, R., and Haussual, S. (1974) J. Raman Spec. **2**, 101.

151. Iqbal, Z., and Christoe, C.W. (1976) Ferroelectrics **12**, 177.

152. Venkateswarlu, P. Bist, H.D. and Jain, Y.S. (1975) J. Raman Spectrop. **3**, 143.

153. Unruh, H.G. (1980) Ferroelectrics **25**, 507.

154. Carter, R.L. (1976) Spectrochem. Acta. **32A**, 575.

155. Kittle, S.F.A. Jayasooria, U.A., and Norrby, L.J.(1984) J.Phy. Chem. **88**, 5971.

156. Unruh, H.G., Kruger, J., and Sailer, E. (1978) Ferroelectrics **20**, 3.

157. Strukov, B.A. (1961) , **41**, Sov. Phys.-Crystallogr.

158. Hamilton, W.C., and Ibers,I.E. (1969) J. Chem. Phys. **47**, 468.

159. Bajpai, P.K. and Jain, Y.S. (1987) J. Phys. C-Solid State Phys. **20**, 387.

160. Jain, Y.S., Bajpai, P.K. Bhattacharjee, R., and Chowdhury, D. (1986) **19**, 3897.

161. Bajpai, P.K. Ram, P.N. and Jain, Y.S. (1987) J. Phy. C-Solid State Phys. **20**, 0000.

162. Aizu , K. (1973) J. Phys. Soc. Jap. **34**. 1567.

163. Strukov, B.A. and Toshev, S. (1964) Sov. Phys-Crystallogr. **9**, 426.

164. Makita, Y., Sawada, A. and Takagi, Y. (1976) J. Phys. Soc. Jap. **41**, 167.

165. Kabalkina, S.A. Vereshchagin, L.F. and Shulenin, B.M. (1962) Sov. Phys-Doklady. 7,527.

166. Bettinali, C. Ferraresso, G., and Manconi J.W. (1967) Atti. Acad. Naz. Lincei Rand., Cl. Sci. Fiz. Mat. Natur. **43**, 536.

167. Chermack, E.E.A. (1970) Diss. Abstra. Int. **B31**, 2189.

168. Casten-Mejean and Calendini Michel (1979) EMP4, Portoeoz.

TABLE 3.1 Lattice constants of **AS** at different temperatures.

Temp K	a (A°)	b (A°)	c (A°)
133	7.924	10.526	5.953
183	7.882	10.560	5.951
209	7.867	10.579	5.953
219.5	7.830	10.569	5.956
224.5	7.747	10.593	5.977
233	7.762	10.612	5.979

TABLE 3.2 Fractional atomic coordinates of ammonium sulphate at 219.5K

	x	y	z
S	0.2429(0)	0.4208(0)	0.25
O(1)	0.0596(2)	0.3987(2)	0.2272(6)
O(2)	0.2809(2)	0.5570(1)	0.2226(4)
O(3)	0.3343(3)	0.3487(2)	0.773(4)
O(4)	0.3020(3)	0.3798(2)	0.4754(3)
N(1)	0.6821(3)	0.3970(2)	0.2466(7)
H(1)	0.769(7)	0.324(5)	0.214(14)
H(2)	0.587(6)	0.349(4)	0.210(11)
H(3)	0.682(7)	0.485(5)	0.172(10)
H(4)	0.689(7)	0.419(5)	0.373(11)
N(2)	0.9766(3)	0.7006(2)	0.2579(8)
H(5)	1.083(7)	0.659(5)	0.250(19)
H(6)	0.994(7)	0.780(5)	0.256(20)
H(7)	0.894(7)	0.671(5)	0.149(10)
H(8)	0.942(8)	0.680(5)	0.387(11)

TABLE 3.3 Fractional atomic coordinates of ammonium sulphate at 209K

	x	y	z
S	0.2426(1)	0.4213(O)	0.25
O(1)	0.0597(2)	0.4003(2)	0.2224(4)
O(2)	0.2831(2)	0.5574(1)	0.2215(3)
O(3)	0.3361(2)	0.3477(2)	0.0793(3)
O(4)	0.2975(2)	0.3810(2)	0.4774(3)
N(1)	0.6815(2)	0.3969(2)	0.2465(5)
H(1)	0.766(6)	0.323(4)	0.203(11)
H(2)	0.590(6)	0.353(4)	0.216(11)
H(3)	0.689(7)	0.482(5)	0.165(10)
H(4)	0.692(6)	0.422(5)	0.388(10)
N(2)	0.9787(3)	0.7002(2)	0.2579(7)
H(5)	1.081(6)	0.659(4)	0.241(16)
H(6)	0.992(7)	0.784(5)	0.265(17)
H(7)	0.896(7)	0.672(5)	0.159(10)
H(8)	0.946(7)	0.672(5)	0.384(10)

TABLE 3.4 Fractional atomic coordinates of ammonium sulphate at 183

	x	y	z
S	0.2424(O)	0.4223(O)	0.25
O(1)	0.0603(1)	0.4026(1)	0.2152(3)
O(2)	0.2857(1)	0.5581(1)	0.2208(2)
O(3)	0.3389(2)	0.3464(1)	0.0853(2)
O(4)	0.2912(2)	0.3824(1)	0.4801(2)
N(1)	0.6813(1)	0.3962(1)	0.2472(3)
H(1)	0.768(4)	0.337(3)	0.205(6)
H(2)	0.584(4)	0.361(3)	0.208(6)
H(3)	0.695(4)	0.464(3)	0.158(6)
H(4)	0.679(4)	0.416(3)	0.386(6)
N(2)	0.9800(2)	0.6997(4)	0.2578(4)
H(5)	1.088(4)	0.667(3)	0.235(8)
H(6)	0.991(4)	0.779(3)	0.275(8)
H(7)	0.902(4)	0.679(3)	0.144(6)
H(8)	0.938(4)	0.676(3)	0.374(6)

TABLE 3.5 Fractional atomic coordinates of ammonium sulphate at 133

	x	y	z
S	0.2424(0)	0.4236(0)	0.25
O(1)	0.0608(1)	0.4055(1)	0.2095(2)
O(2)	0.2887(1)	0.5595(1)	0.2205(2)
O(3)	0.3407(1)	0.3460(1)	0.0894(2)
O(4)	0.2861(1)	0.3839(1)	0.4826(2)
N(1)	0.6805(1)	0.3944(1)	0.2463(3)
H(1)	0.762(3)	0.329(3)	0.205(6)
H(2)	0.578(3)	0.365(2)	0.209(5)
H(3)	0.687(4)	0.467(3)	0.164(6)
H(4)	0.693(4)	0.420(3)	0.389(6)
N(2)	0.9817(1)	0.6991(1)	0.2614(3)
H(5)	1.095(4)	0.674(3)	0.250(9)
H(6)	0.987(4)	0.783(3)	0.280(7)
H(7)	0.888(4)	0.680(3)	0.146(6)
H(8)	0.943(4)	0.673(3)	0.379(6)

TABLE 3.6 Fractional atomic coordinates of ammonium sulphate at 224.5K

	x	y	z
S	0.2455(1)	0.4195(0)	0.25
O(1)	0.0618(2)	0.3878(2)	0.25
O(2)	0.2692(3)	0.5572(1)	0.25
O(3)	0.3265(2)	0.3670(1)	0.0487(2)
O(4)	0.3265(2)	0.3670(1)	0.4513(2)
N(1)	0.6901(2)	0.4019(2)	0.2466(2)
N(2)	0.9655(3)	0.7040(2)	0.2579(3)

TABLE 3.7 Fractional atomic coordinates of ammonium sulphate at 233K

	x	y	z
S	0.2455(0)	0.4196(0)	0.25
O(1)	0.0620(2)	0.3878(2)	0.25
O(2)	0.2692(3)	0.5573(2)	0.25
O(3)	0.3267(2)	0.3670(1)	0.0486(2)
O(4)	0.3267(2)	0.3670(1)	0.4514(2)
N(1)	0.6701(3)	0.4018(2)	0.2466(4)
N(2)	0.9655(3)	0.7038(2)	0.2579(3)

Fig.2.1 Temperature dependence of specific heat in ammonium sulphate.

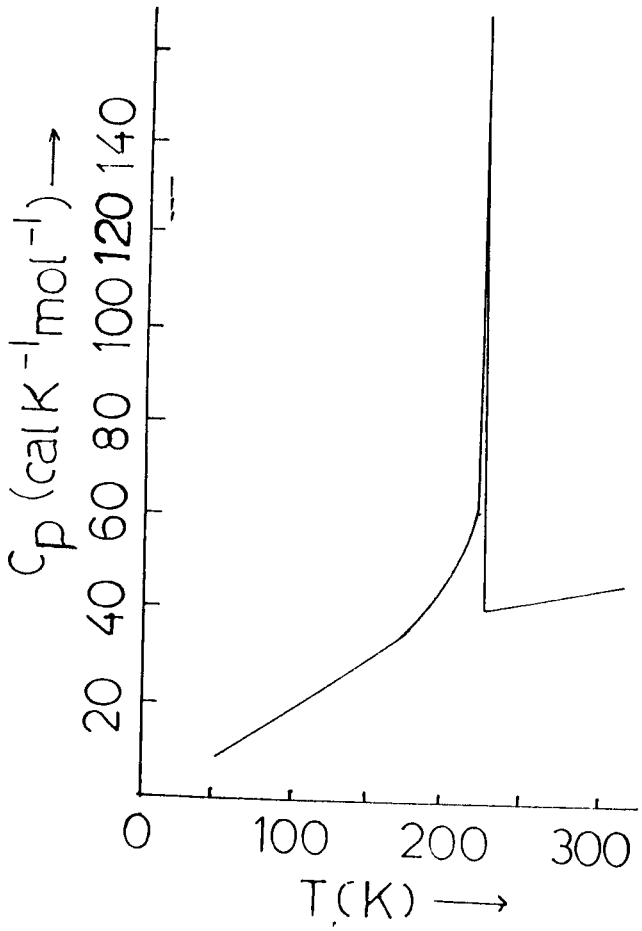
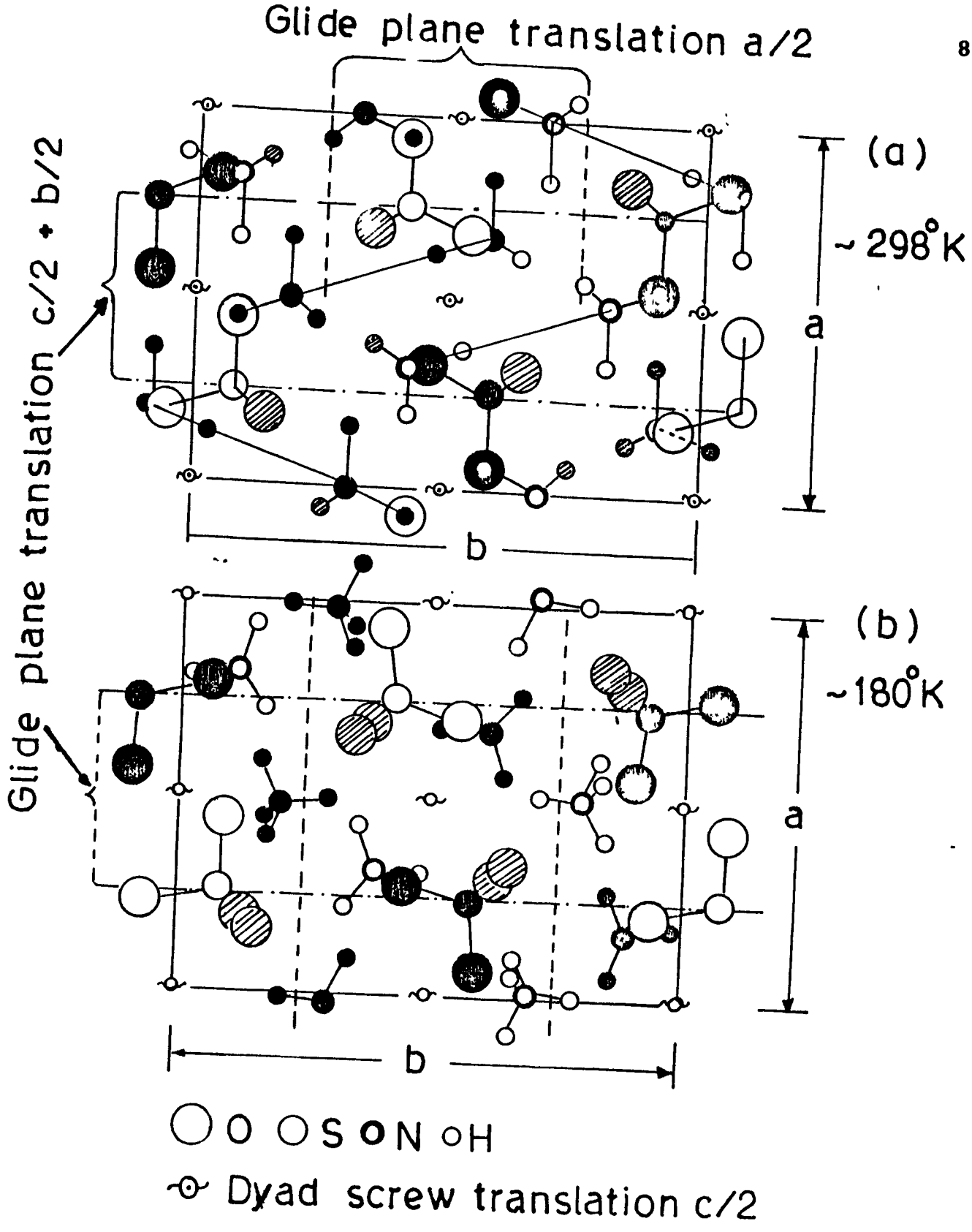

C_p (cal K^{-1} mol^{-1}) ⟶
20 40 60 80 100 120 140
0
100
200
300
T (K) ⟶

Fig.2.2 Crystal structure of $(NH_4)_2\ SO_4$ projected in (001) plane (**a**) above T_c (**b**) below T_c


Glide plane translation a/2
Glide plane translation c/2 + b/2
(a)
~298°K
a
b
(b)
~180°K
a
b
O O S N H
Dyad screw translation c/2

TEMPERATURE DEPENDENCE OF IR/RAMAN MODES OF AMMONIUM SULPHATE

3.1 Introduction

The main objective of IR/Raman studies of **AS** have been to:

i) assign the modes of vibrations as unambiguously as possible[1-4]

ii) detect the soft mode, responsible for the phase transition at 223K[5-7], and

iii) reveal the microscopic mechanism of phase transition from spectroscopic changes observed around T_c[8,9]

Although more than 25 papers (as reviewed in Chapter II) have been published from different laboratories, on the IR and Raman spectra of **AS**, study of several important aspects that can also be examined through these techniques has not been attempted. For example, crystallographically different NH_4^+ ions, viz. NH_4^+(I), and NH_4^+(II) give rise to broad bands having poor indications of any structure and therefore revealing very little information about the dynamical and structural changes (if these ions have any) at T_c. However, the situation changes if we investigate the temperature dependence of the spectra due to D-modes of partially deuterated NH_4^+ ions. In such systems the resonance coupling between nearly identical oscillators decreases significantly due to their low concentration and the D-modes appear as sharp and distinct bands belonging

to different distinguishable D-oscillators[10]. One expects to observe as many bands as the number of distinguishable internal coordinates involving D-atoms. The temperature dependence of the bands due to such modes provides an opportunity to study the changes occuring in each of such coordinates. Similarly one finds that certain investigations[11,12] indicate that the transition is of second order in contradiction with the well established fact that the transition accompanies finite heat of transition[13,14] (≃ .93K cal/mole). Spectroscopic studies can examine the structural and dynamical changes of different constituent ions with desired accuracy particularly if the spectra of the ions do not overlap. Therefore in the case of **AS** the temperature dependence of the spectra of deuterated NH_4^+ and SO_4^{2-} ions could help in resolving this kind of contradiction. The temperature dependence of the band width is capable of revealing enough informations about the relaxation processes[15], however such attempt has also not been made. In view of these observations we undertook the study of the temperature dependence of intensity, bandwidth and frequency of several theremo-sensitive modes of NH_4^+ as well as SO_4^{2-} ions, in addition to those of D-modes of partially deuterated **AS**. Our findings are reported in this chapter.

3.2 Phonons and their Symmetry

The dynamics of **AS** containing 60 atoms per unit cell can be described in terms of 180 phonon branches (177 optical

+ 3 acoustic) under the unit cell approximation. These branches arise from different normal modes of NH_4^+(I), NH_4^+(II) and SO_4^{2-}ions. These ions are known to have T_d structure in their free state. They have four fundamental modes of internal vibrations[16] viz. $\nu_1(A_1$, the totally symmetric stretching), ν_2(E, the doubly degenerate symmetric bending), $\nu_3(F_2$, the triply degenerate anti-symmetric stretching) and $\nu_4(F_2$, the triply degenerate anti-symmetric bending); A_1, E and F_2 are species of T_d point group. These modes are shown in Fig. 3.1. The external lattice modes arising from the rotational and translational degrees of freedom of F_1 and F_2 symmetry, respectively. In view of their symmetry, rotational modes are forbidden in IR as well as in Raman spectra while ν_1 and ν_2 are forbidden only in IR spectra.

The classification of 180 phonon branches for the **PE** phase (D_{2h}^{16} symmetry) and for **FE** phase (C_{2v}^{9} symmetry) can easily be worked out using standard techniques viz. Unit cell[17] and site symmetry[18,19] approaches. The results are symmarized in Tables 3.1 and 3.2, respectively.

3.3 Experimental

Ammonium sulphate of Analar grade was obtained from E.merck (Ind.) Ltd. The compound was further purified by slow evaporation of its acqueous solution in deionized double distilled water kept in a thermally insulated box with silica gel. Crystals of a few mm^3 size were collected and redissolved and the process

was repeated thrice. Fairly transparent crystals thus obtained were used for spectral investigations.

Samples of partially deuterated **AS** were obtained by dissolving the crystals of purified **AS** in mixtures of (i)90%H_2O+ 10%D_2O, (ii) 95%H_2O+5% D_2O, and (iii) 80% H_2O+20% D_2O.

IR spectra were recorded on a PE-983 spectrophotometer operated in mode-6 (resolution $1cm^{-1}$) for nujol mull placed between CsI windows. Efforts of recording the spectra in mode-7 with the highest possible resolution attainable on the instrument did not improve the quality of the observations. A standard specac low temperature cell was used to record the temperature dependence of the spectra between 110 and 300**K**. The temperature of the cell was monitored with help of a copper-constantan thermocouple fixed near the sample holder. The thermo-couple was calibrated at the temperatures of liquid N_2, melting ice and boiling water. Although the temperature was regulated to an accuracy of 1**K**, due to a possible temperature gradient along the CsI windows the level of error in the temperature measurements is estimated to be ±3**K**.

The Raman spectra were recorded on a Spex model 1403 Ramlog spectrophotometer equipped with thermoelectrically cooled (-30°C) RCAC-31034 GeAs photomultiplier tube and photon counting system. Spectra physics Argon ion laser oscillating at 514.5nm (2.00 Watt Power) was used as a source of excitation. Raman spectra of the sample were recorded for pallet made

out of finely powdered sample. The temperature dependence of the spectra was monitored using a locally fabricated low temperature cell[20] where the sample was cooled by using liquid nitrogen as coolent. The temperature was varied by simultaneously heating the sample electrically; the heating was controlled by a specac low temperature controlling unit. The temperature was monitored by using copper-constantan thermocouple fixed in the back of the pallet, to an accuracy of ±2K in the range of 100-300K.

3.4a Temperature Dependence of IR Spectra

The spectra of partially deuterated AS (at low degree of deuteration ≈ 5%) gives the well resolved structure in both N-D stretching and N-D bending region. This is shown in Figs. 3.2 and 3.3, respectively.

The N-D stretching region shows two well resolved components in the PE phase. The higher frequency component peaks at ~ 2380cm^{-1} (FWHMI=130cm^{-1}), with a shoulder at 2420cm^{-1}. The lower frequency component is observed around 2300cm^{-1} with FWHMI=190cm^{-1}. These bands do not show significant changes at T_c; some changes in the relative absorption at 2260 and 2300cm^{-1} may however be seen. In the spectra obtained at 228K the absorption intensity at 2300cm^{-1} is more than that of 2260cm^{-1}; the reverse is true at 223K. Consequently, the band appears to be centred at around 2260cm^{-1} with a shoulder at 2300cm^{-1}. On cooling the sample further, the band get resolved

into four components at around 183K. No major change in the frequency and band shape is detected on further cooling; a general increase of 10-20cm^{-1} in the frequencies of different components is observed. The band due to N-D bending (centred around 1250cm^{-1}) and that due to the N-D stretching mode (centred around 2380cm^{-1}) do not show any specific change at T_c. At temperatures far below T_c, the 2380cm^{-1} band is resolved into four sharp components, and those around 1200cm^{-1} exhibit eight components.

The ν_1 mode of SO_4^{2-} ion (Fig.3.4) falls at 979cm^{-1} at room temperature. No sudden jump in the peak position and intensity of this band is observed at any temperature above and below T_c (cf Fig.3.4). However, at T_c the band suddenly attains significant intensity and shifts to 975 ($\Delta\nu$ = 4cm^{-1}).

3.4b Temperature Dependence of Raman Spectra

The temperature dependence of the internal modes ν_1, ν_2 and ν_4 of SO_4^{2-} ion is shown in Figs. 3.5 to 3.7. In the N-H stretching region a broad and intense band is observed and its temperature dependence does not reveal any new information.

Fig. 3.8 provide the temperature dependence of frequency (ν,cm^{-1}), relative integrated intensity (I_r), Peak intensity (I_p) and half-width (FWHMI, cm^{-1}) of $\nu_1(SO_4^{2-})$. These data are plotted in Fig. 3.8. Similar results for ν_2 and ν_4 of SO_4^{2-} ion are tabulated in Tables 3.4 and 3.5, and are depicted in Figs.3.9 and 3.10, respectively.

The uncertainty in the frequencies is $\pm 1 cm^{-1}$ for the well developed sharp bands and $\pm 5 cm^{-1}$ for manually resolved and diffuse/weak bands. Similar uncertainty is estimated in FWHMI data. Errors in the I_r and I_p data lie within 2%. From the observed spectra we note that:

(i) the ν_1 mode shifts from $979 cm^{-1}$ to $975 cm^{-1}$ suddenly at T_c on cooling the sample and its peak intensity decreases sharply while I_r remains almost unchanged in the entire range of temperature monitored by us. The linewidth of this mode remains almost constant above T_c but increases at T_c; on further cooling the sample it decreases to almost the same value at 218K which then exhibits linear decrease.

(ii) The triply degenerate ν_4 band is observed in $640-600 cm^{-1}$ region with two clear peaks at 628 and $618 cm^{-1}$ at room temperature. The $I_p(628 cm^{-1})$ increases slowly as the temperature decreases. The peak at $618 cm^{-1}$ starts becoming broad and get split into two components at 618 and $614 cm^{-1}$. The $I_p(628 cm^{-1})$ increases in the same fashion as observed in PE phase on lowering the temperature. However, I_p of the rest two components decreases and at about -100°C an extra component is seen at $621 cm^{-1}$. The total integrated intensity of the band remains almost constant above and below T_c. However I_r changes suddenly at T_c

(iii) The doubly degenerate mode $\nu_2(SO_4^{2-})$ appears at $425 cm^{-1}$. I_p of the band decreases gradually on lowering the temperature. The FWHMI of the band increases with temperature, while the total integrated intensity of the band remains unchanged. Below T_c, the band splits into two components at

The NH_4^+ stretching region gives broad and diffuse band above T_c. This band shows no significant change around T_c; however, the band gets split into three components at 3235, 3117 and 3033 cm^{-1} on lowering the temperature much below than T_c.

In external mode region (below 400cm^{-1}) no significant temperature dependence was observed.

3.5 Discussion

The structural data[21] on **AS** reveal that there are six distinguishable H-atoms in **PE** and eight in **FE** phase. Therefore the vibrational spectra in the regions of N-H stretching as well as N-H bending are rich in frequencies. This results in broad and complex bands which lack in desired resolution for identifying and monitoring the behaviour of specific modes. The complexities of bands further increase due to highly anharmonic nature of H-bands interactions, responsible for several combinations and overtones of lower frequencies to appear in these regions. Unambiguous identification of the mode associated with a chosen component of the band becomes obviously difficult and the temperature dependence of such bands does not provide any conclusive evidence regarding the change in the structure and dynamics of NH_4^+ ions. However, the bands due to vibrations of D-atoms in partially deuterated ammonium ions are expected to be almost free from the above referred complexities and therefore, the temperature variation of the

bands due to N-D stretching and N-D bending is depicted in Figs.3.2 and 3.3 respectively can reveal the change in NH_4^+ ions.

The N-D stretching region is expected to show six bands components in PE and eight in FE phase. Similarly for N-D bending region one estimates 12 and 16 different oscillators to appear in the spectra of respective phases. However the number of observed band components (cf. Fig. 3.2 and 3.3) is found to be much less than these numbers except in the N-D stretching region of the low temperature spectra. Apparently, several of the oscillators that can be labelled with crystallographically distinguishable positions of D-atoms, do not have resolvable frequency difference. We observe that the N-D stretching bands do not shos significant change with change in temperature through T_c; some change in the relative absorption at 2260 and 2300 cm^{-1} may however be mentioned. In the spectra obtained at 228K, the absorption intensity at 2300 cm^{-1} is more than at 2260 cm^{-1}, while that gets reversed at 223K, consequently the band appears to be centred around 2260 cm^{-1} with a shoulder at 2300 cm^{-1}. On cooling the sample further the band gets resolved into four components around 183K. Correlation of this part of observation with the fact that large amplitude reorientational motion of $NH_4^+(I)$ get freezed at 183K[22], indicates the degree of sensitivity our data seem to have for any change in the structure and the dynamics of NH_4^+ ions. No major change in the structure frequency and band shape

is detected on further cooling the sample; a general decrease of 10-20 cm^{-1} in the frequencies of different components is observed. The band due to N-D bending (centered around 1200 cm^{-1}) and the one due to N-D stretch mode (centered around 2380 cm^{-1}) do not show any specific change at T_c; at temperature much below T_c, the 2380 cm^{-1} band gets resolved into four sharp components and those around 1200 cm^{-1} exhibit eight components.

In contrast to the minor and slow changes shown by band due to NH_4^+, $\nu_1(SO_4)$ exhibits sudden change in its frequency (shift = 4cm^{-1}) and intensity; this is evident from the comparison of the Fig. 3.2 and 3.3 with Fig. 3.4.The inference of this observation that SO_4^{2-} ion suddenly gets distorted at T_c is now a well established experimental[23] and theoretical[24,25] fact and our reinvestigation confirms it.

Schroeder and Lippincott[26] have discussed a model that relates ν_{N-H} to the distance r_{N-O} in N-H . . .O bond. Using r_{N-O}, calculated from crystal structural data[21] in Schroeder-Lippicott model, frequencies of distinguishable N-D oscillators have been calculated. The calculated and observed (given in paranthesis) ν_{N-D} frequencies are: 2459(2441), 2443(2427), 2386(2372), 2326(2355), 2278(2278), 2263(2250), 2234(2235) and 2224(2215)cm^{-1} for different ν_{N-D} within the error limits of such estimations (~30cm^{-1}) the two frequencies match closely. Evidently for any change in r_{N-D}, a corresponding change in ν_{N-D} is

expected. However, no marked change in ν_{N-D} of different oscillators is observed; it is concluded that H-bond strength at T_c is not changing significantly.

In view of our observations and their analysis it is evident that the studies of AS mainly related with the dynamics and structure of NH_4^+ ions may not exhibit sudden change at T_c and the transition may appear to have a second order behaviour, as inferred by many investigators[11,12]. On the other hand observations influenced also by the structure and dynamics of SO_4^{2-} ion would exhibit sudden change at T_c and evince first order behaviour of the transition[27-31].

A careful analysis of the temperature dependence of Raman bands shows many interesting features:

(i) the shift in $\nu_1(SO_4^{2-})$ mode is $4cm^{-1}$ which is in agreement with our IR results. Apparently the local crystal field around SO_4^{2-} ion changes suddenly at T_c;

(ii) the linewidth of $\nu_1(SO_4^{2-})$ in PE phase exhibits marginal and linear decrease on lowering the temperature to T_c. However, around T_c it first increases fast and then decreases fast; on further cooling the sample it remains almost unchanged. As such we observe a peak of width ≈5K in FWHMI vs T curve at T_c.

Out of two important possible reasons for the observation, one is the fact that the SO_4^{2-} ion attains an increased electric dipole moment at T_c causing a sudden increase in the bilinear

coupling between different modes of SO_4^{2-} ion and NH_4^+ ions. Such a bilinear coupling was invoked theoretically by Yamada et al[32] to show that the coupling shortens the life time of phonon modes and thereby increases the linewidth. However, unless the strength of dipoles again gets reduced to the value of PE phase, increased linewidth should not decrease on lowering the temperature below T_c. Apparently there is no reason for the decrease in the strength of this kind of coupling.

Secondly, in KH_2PO_4 type crystals it is suggested that the protonic motion along the O-H...O bond generates pseudospins which interact with all the phonons in the crystal and shorten their lifetime, the observation appears to have some relation with pseudo spin waves.

Other two SO_4^{2-} modes i.e. $\nu_2(E)$ and $\nu_4(F_2)$ that we have investigated, are degenerate. At T_c they exhibit sudden changes in their peak positions, split separation, integrated intensity and peak intensity. These observations clearly corroborate the inference of our IR results that SO_4^{2-} ion suddenly gets distorted at T_c. Petzelt and Dvořák[35] correlated the change in the frequency and intensity of hard modes around T_c with the order parameter. It is interesting to note that frequency of ν_1 change in such a way that its value remains constant in both PE and FE phase but a shift of 4 cm^{-1} is observed at T_c. Similar sudden changes are also observed in the frequencies of the split components of ν_2 and ν_4(cf. Figs. 3.9 and 3.10).

These observations if correlated with the theory of Petzelt and Dvořák[35] reveal that the order parameter should also change identically. The fact that order parameter in the first order phase transition indeed changes suddenly at T_c, support these observations. The fact that SO_4^{2-} ion gets suddenly distorted at T_c and the ion is the centre of the force that triggers the transition.

The lattice modes of both NH_4^+ and SO_4^{2-} ion are observed below $400cm^{-1}$ in the Raman spectra of single crystal of **AS**. However, we could not observe any distinguishable band in the spectra of Pallet; a broad and weak band was observed in this region. This may be due to the fact that libration of both NH_4^+ and SO_4^{2-} are forbidden for T_d symmetry and hence too weak to be observed since the ions are not distorted much from their tetrahedral shape. In the single crystal spectra of **AS** Iqbal and Christoe observed a temperature dependent quasi-elastic wing in some polarizations. This is not observed in pallet spectra recorded by us.

In conclusion, the temperature dependence of **IR**/Raman intensity due to internal modes of NH_4^+ and SO_4^{2-} ions and D-modes of partially deuterated **AS** reveal that NH_4^+ ions as well as H-bonding do not undergo significant changes at T_c, while the SO_4^{2-} ion undergoes a sudden change in its internal structure. Properties of the crystal depending only on NH_4^+ ions may not change suddenly at T_c, indicating as if the transi-

tion has second order behaviour. On the other hand, properties depending also on the SO_4^{2-} ion may show first order behaviour. The changes in the linewidth of SO_4^{2-} ion reveal a phonon-pseudospin coupling between the modes of SO_4^{2-} ion and NH_4^+ ion through pseudospin interaction. The observation indicates that the transition is different from order-disorder/displacive type.

REFERENCES

1. Torrie, B.H. Lin, C.C. Binbrek, O.S., and Anderson, A. (1972) J. Phys. Chem. Solids **33**, 697.

2. Schutte, C.J.H., and Heyns, A.M. (1970) J. Chem. Phys. **52**, 864.

3. Carter, R.L. (1976) Spectrochim. Acta, Part A **32**, 575.

4. Venkateswarlu, P. Bist, H.D. and Jain, Y.S. (1975) J. Raman Spectrosc. **3**, 143.

5. Petzelt, J. Grigaz, J., and Mayerovâ, J. (1974) Ferroelectrics **6**, 225.

6. Jain, Y.S. (1974) Ph. D. Dissertation I.I.T. Kanpur, India.

7. Brehat, F. Wyncke, B. Fuzellier, Y., and Hadni, A. (1974) J. de Physique **35** L-143.

8. Iqbal, Z., and Christoe, C.W. (1976) Solid State Commu. **18**, 269.

9. Jain, Y.S., and Bist, H.D. (1974) Physica Status Solidi b **62** 295.

10. Bajpai, P.K., and Jain, Y.S. (1987) J. Phys. C- Solid State Phys. **20**, 387.

11. Parsonage, N.G., and Staveley, L.A.K. (1978) In "Disorder in Crystals" Oxford Univ. Press, Oxford.

12. Dahlborg, U. Lorsson, K.E., and Pirkmaser, E. (1970) Physica **49**, 1.

13. Hoshino, S. Vedam, K. Okaya, Y., and Pepinsky, R. (1958) Phys. Rev. **112**, 405.

14. Higashigaki, Y. and Chihara, H. (1981) Bull. Chem. Soc. Jap. **54**, 901.

15. Laulicht, I., and Luknar, N. (1977) Chem. Phys. Lett. **47**, 237.

16. Herzberg, G. (1945) Infrared and Raman Spectra of polyatomic molecules; Molecular spectra and Molecular structure, Vol. 2, New York, Van Nostrand.

17. Bhagavantam, S., and Venkatarayadu, T. (1939) Proc. Ind. Acad. Sci. **A9**, 224.

18. Halford, R.S. (1946) J. Chem. Phys. **14**, 8.

19. Hornig, D.F. (1948) J. Chem. Phys. **16**, 1063.

20. Agarwal, A. (1985) Ph. D. Dissertation, I.I.T., Kanpur, India.

21. Schlemper, E.O., and Hamilton, W.C. (1966) J. Chem. Phys. **44**, 4498.

22. Kydon, D.W. Pintar, M., and Petch, H.E. (1967) J. Chem. Phys. **47**, 1185.

23. Jain, Y.S., and Bist, H.D. (1974) Solid State Commu. **15**, 1229.

24. Jain, Y.S., and Bhattacharjee, R. (1985) J. Phys. C- Solid State Phys. **18** 5299.

25. Jain, Y.S. Bajpai, P.K. Bhattacharjee, R. and Chowdhury, D. (1986) J. Phys. C- Solid State Phys. **19** 3789.

26. Schroeder, R.A., and Lippincott, E.R. (1957) J. Phys. Chem. **61** 921.

27. Jain, Y.S. Bist, H.D., and Upreti, G.C. (1973) Chem. Phys. Lett. **22**, 572.

28. Manjunath, C.V., and Srinivasan, R. (1978) Physica Status Solidi b **87**, 395.

29. Ramnathan, K.V., and Srinivasan, R. (1978) Chem. Phys. Lett. **56**, 359.

30. Badr, Y.A., and Awad, S. (1984) J. Phys. Chem. Solids **45**, 351.

31. Salvador, G. Sherman, W.F., and Wilkinson, G.R. (1986) J. Mole. Struc. **143**, 55.

32. Yamada, Y. Noda, Y. Axe, J. D., and Shirane, G. (1974) Phys. Rev. **B9**. 4429.

33. Blinc, R., and Zeks, B. (1974) In "Soft modes in ferroelectrics and Antiferroelectrics" North Holland, Amsterdam.

34. Laulicht, I. (1978) J. Phys. Chem. Solids **39**, 901.

35. Petzelt, J., and Dvořák, V. (1976) J. Phys. C- Solid State Phys.

Table 3.1a

Classification of phonons in paraelectric phase of $(NH_4)_2SO_4$ crystal
(The site symmetry approach)

Modes of AB_4 type T_d ion		Species under D_{2h}								N^x
		A_g	B_{1g}	B_{2g}	B_{3g}	A_u	B_{1u}	B_{2u}	B_{3u}	
	$\nu_1(A_1)$	1	-	-	1	-	1	1	-	4
	$\nu_2(E)$	1	1	1	1	1	1	1	1	8
	$\nu_3(F_2)$	2	1	1	2	1	2	2	1	12
	$\nu_4(F_2)$	2	1	1	2	1	2	2	1	12
Rotations	(F_1)	1	2	2	1	2	1	1	2	12
Translations	(F_2)	2	1	1	2	1	2	2	1	12
	Total [y]	9	6	6	9	6	9	9	6	60
Grand total[z]		27	18	18	27	18	27	27	18	180

N^x represents total number of phonon modes originating from particular mode of an AB_4 type tetrahedral ion in tetramolecular unit cell.

[y]Total accounting for the phonons originating from any one of the NH_4^+(I), NH_4^+(II) and SO_4^{2-}ions.

[z]Total, accounting for the phonons originating from all the three types of ions.

Table 3.1b

Classification of phonons in ferroelectric phase of $(NH_4)_2SO_4$ crystal
(A site symmetry approach)

Modes of AB_4 type T_d ion		Species under C_{2v}				N^x
		A_1	A_2	B_1	B_2	
	$\nu_1(A_1)$	1	1	1	1	4
	$\nu_2(E)$	2	2	2	2	8
	$\nu_3(F_2)$	3	3	3	3	12
	$\nu_4(F_2)$	3	3	3	3	12
Rotations	(F_1)	3	3	3	3	12
Translations	(F_2)	3	3	3	3	12
	Total[y]	15	15	15	15	60
Grand Total[z]		45	45	45	45	180

[x]N represents total number of phonon modes originating from particular mode of an AB_4 type tetrahedral ion in tetramolecular unit cell.

[y]Total account from the phonons originating from any one of the $NH_4(I)$, $NH_4(II)$ and SO_4 ions.

[z]Total accounting for the phonons originating from all the three types of ions.

Table 3.2a

Classification of phonons in paraelectric phase of $(NH_4)_2 SO_4$ (an unit cell approach*)

	D_{2h}^{16}	E	C_2^a	C_2^b	C_2^c	i	σ_{bc}	σ_{ca}	σ_{ab}	Reduced Representation								Based of representation**
										A_g	B_{1g}	B_{2g}	B_{3g}	Au	B_{1u}	B_{2u}	B_{3u}	
	A_g	1	1	1	1	1	1	1	1									
	B_{1g}	1	1	-1	-1	1	1	-1	-1									
	B_{2g}	1	-1	1	-1	1	-1	1	-1									
	B_{3g}	1	-1	-1	1	1	-1	-1	1									
	Au	1	1	1	1	-1	-1	-1	-1									
	B_{1u}	1	1	-1	-1	-1	-1	1	1									
	B_{2u}	1	-1	1	-1	-1	1	-1	-1									
	ϕ_R	0	π	π	π	π	0	0	0									
$\beta = \pm 1 + 2\cos$	ϕ_R	3	-1	-1	-1	-3	1	1	1						1	1	1	Space vector $\vec{r}$
$\beta^1 = \beta\ 2\cos$	ϕ_R	6	2	2	2	6	2	2	2	3	1	1	1					Polarizability tenser $\vec{\alpha}$
$\beta^{11} = 1 \pm 2\cos$	ϕ_R	3	-1	-1	-1	3	-1	-1	-1		1	1	1					Angular moment $\vec{L}$
	N^R	60	0	0	0	0	0	0	36									
$N^R(t) = N^R(l)$		12	0	0	0	0	0	0	12									
$\chi(N) = N^R.\beta$		180	0	0	0	0	0	0	36	27	18	18	27	18	27	27	18	Total phonon modes
$\chi(t) = N^R(t).\beta$		36	0	0	0	0	0	0	12	6	3	3	6	3	6	6	3	Translations $t^n + t^s$
$\chi(l) = N^R(l).\beta$		36	0	0	0	0	0	0	-12	3	6	6	3	7	3	3	6	Librations $l^n + l^s$
$\chi(i)$		108	0	0	0	0	0	0	36	18	9	9	18	9	18	18	9	Internal modes $\nu_i^n + \nu_i^s$

*For different notations used in this table see Ref. 16

**Superscripts n and s represent modes of NH_4^+ and SO_4^{2-} ion, respectively.

Table 3.2b

Classification of phonons in ferroelectric phase of $(NH_4)_2SO_4$ (an unit cell approach*)

C_{2v}^9	E	C_2	$\vec{\sigma}_{ac}$	σ_{bc}	Reduced Representations A_1	A_2	B_1	B_2	Bases of representations**
A_1	1	1	1	1					
A_2	1	1	-1	-1					
B_1	1	-1	1	-1					
B_2	1	-1	-1	1					
ϕ_R	0	π	0	0					
$\beta = \pm 1 + \cos\phi_R$	3	-1	1	1	1		1	1	Space vector $\vec{r}$
$\beta^1 = \beta\ 2\ \cos\phi_R$	6	2	2	2	3	1	1	1	Polarizability tensor $\tilde{\alpha}$
$\beta^{11} = 1 \pm 2\ \cos\phi_R$	3	-1	-1	1		1	1	1	Angular moment $\vec{L}$
N^R	60	0	0	0					
$N^R(t) = N^R(l)$	12	0	0	0					
$\chi(N) = N^R \beta$	180	0	0	0	45	45	45	45	Total phonon modes
$\chi(t) = N^R(t)\beta$	36	0	0	0	9	9	9	9	Translations t^n+t^s
$\chi(t) = N^R(l)\beta$	36	0	0	0	9	9	9	9	Librations l^n+l^s
$\chi(i) =$	108	0	0	0	27	27	27	27	Internal modes $\nu_i^n + \nu_i^s$

* For different notations used in this table see ref. 16

** Superscripts n and s represent modes of NH_4^+ and SO_4^{2-} ion, respectively.

Table 3.3

Frequency (ν in cm^{-1}), Relative integrated intensity (I_r), Peak intensity (I_p) and FWHMI of ν_1 mode in Raman Spectra of **AS** at different temperatures

Temperature (K)	Peak Position (cm^{-1})	Peak Intensity (I_p)	Integrated Intensity (I_r)	FWHMI (cm^{-1})
333	978.0	46.4	10.5	4.7
323	977.6	45.6	10.4	4.4
313	978.4	46.8	10.3	4.4
303	978.4	49.2	10.3	4.5
293	978.4	50.4	10.6	4.3
283	978.6	51.2	10.3	4.4
268	979.0	53.6	10.5	4.0
258	978.8	54.4	10.0	3.9
255	979.2	55.6	10.0	3.9
253	979	55.6	10.4	4.0
251	978.6	56.0	10.3	4.0
248	978.8	58.4	10.5	3.6
243	979.0	60.0	10.6	3.6
238	979.2	60.0	10.5	3.6
228	978.6	47.6	10.9	5.6
223	979.0	48.8	12.0	5.5
218	976.0	69.6	11.5	3.6
213	976.0	66.8	10.9	3.2
208	975.6	70.8	10.9	3.2
203	975.2	72.8	10.9	3.2
198	976.0	75.2	10.9	3.2
188	974.8	79.2	11.3	3.0
178	974.8	86.0	11.3	2.8

TABLE 3.4

Frequency (ν, cm^{-1}) Integrated Intensity of different components of ν_4 and Peak Intensity FWHMI of 628 cm^{-1} component in Raman Spectra of AS at different temperature.

Temperature	Peak Position(s) (cm^{-1})	Peak Intensity (Ip) of 628cm^{-1}	FWHMI (cm^{-1})	Integrated intensity
293	628, 618	22.0	5.6	3.45
273	628, 618	22.8	5.6	3.56
258	628, 618	23.0	5.4	3.48
243	628, 618	23.6	5.6	3.59
233	628, 618	24.6	5.6	3.55
228	628, 618	25.6	5.6	3.69
223	628, 618, 615	25.6	5.6	3.72
218	628, 617, 615	26.8	6	3.80
213	628, 618, 613	26.4	5.6	3.80
208	628, 618, 614	26.4	5.6	3.80
203	628, 618, 614	26.8	6	3.60
198	628, 618, 614	26.8	5.6	3.60
193	629, 618, 615	30	6.4	3.99
188	628, 618, 614	30	6	4.12
183	627, 618, 614	30	6	4.12
178	627, 618, 614	32	6	4.10
173	627, 618, 614	34	6	4.28
163	627, 617, 614	37	6	4.12
153	626, 621, 617, 614	38	6	4.02
133	626, 622, 617, 614	41	6	4.26

TABLE 3.5

Frequency (ν, unit), Peak Intensity (Ip) Integrated Intensity (I_r) and FWHMI of the components of ν_2 (SO_4^{2-}) mode in Raman Spectra of AS at different temperatures.

Temperature (K)	Peak Position (cm^{-1})	Peak Intensity (Ip)	Integrated Intensity (I_r)	FWHMI (cm^{-1})
298	456	40	9.6	3.1
283	456	40	9.6	3.0
273	455	42	9.6	3.0
263	456	42	9.6	3.1
258	455	42	9.6	3.0
253	456	42	9.6	3.0
248	456	38	9.6	2.8
243	256	38	9.6	2.8
238	456	38	10	2.8
228	456	36	12	2.8
223	458 451	27 8	12 8	2.8
218	459 453	23 13	12 10	2.8
213	460 454	18 15	9 12.8	2.8
208	462 455	18 17	8.8 12	2.7
203	462 455	18 18	8.8 12.8	2.8
198	462 456	17 15	9 13	2.7
193	464 457	20 18	8 12	2.8

Fig.3.1 Normal vibrations of a tetrahedral XY_4 molecule. The three two-fold axes (dot-dash lines) are chosen as x, y, and z axes.

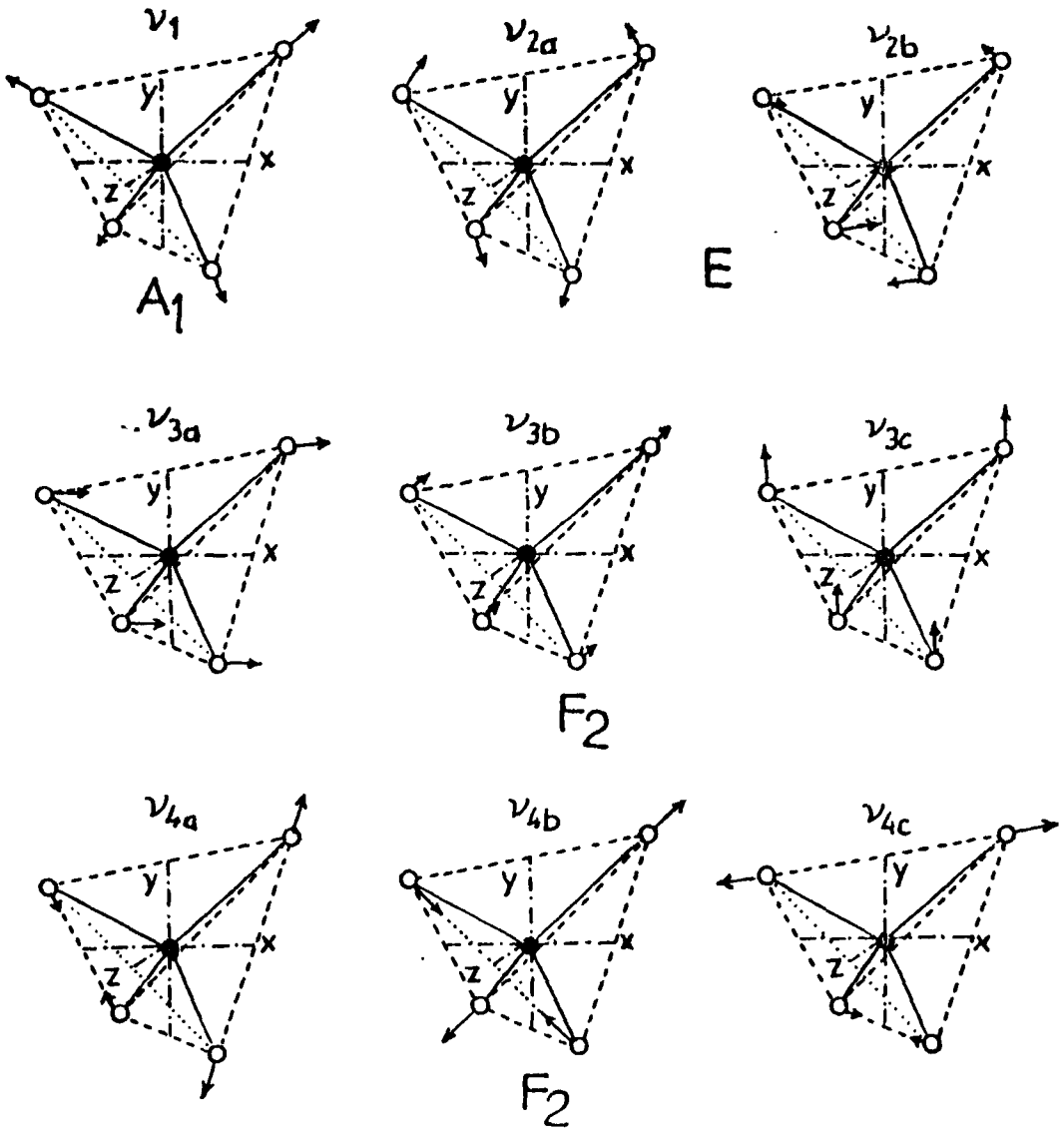

ν1
y
x
z
A1
ν2a
ν2b
E
ν3a
ν3b
ν3c
F2
ν4a
ν4b
ν4c
F2

Fig.3.2 The temperature dependence of the IR absorption of N-D stretching (2100-2500 cm^{-1}) in partially deuterated AS, preparation in 95% H_2O and 5% D_2O. The peak positions in the first band are 2300cm^{-1} and 2380cm^{-1}.

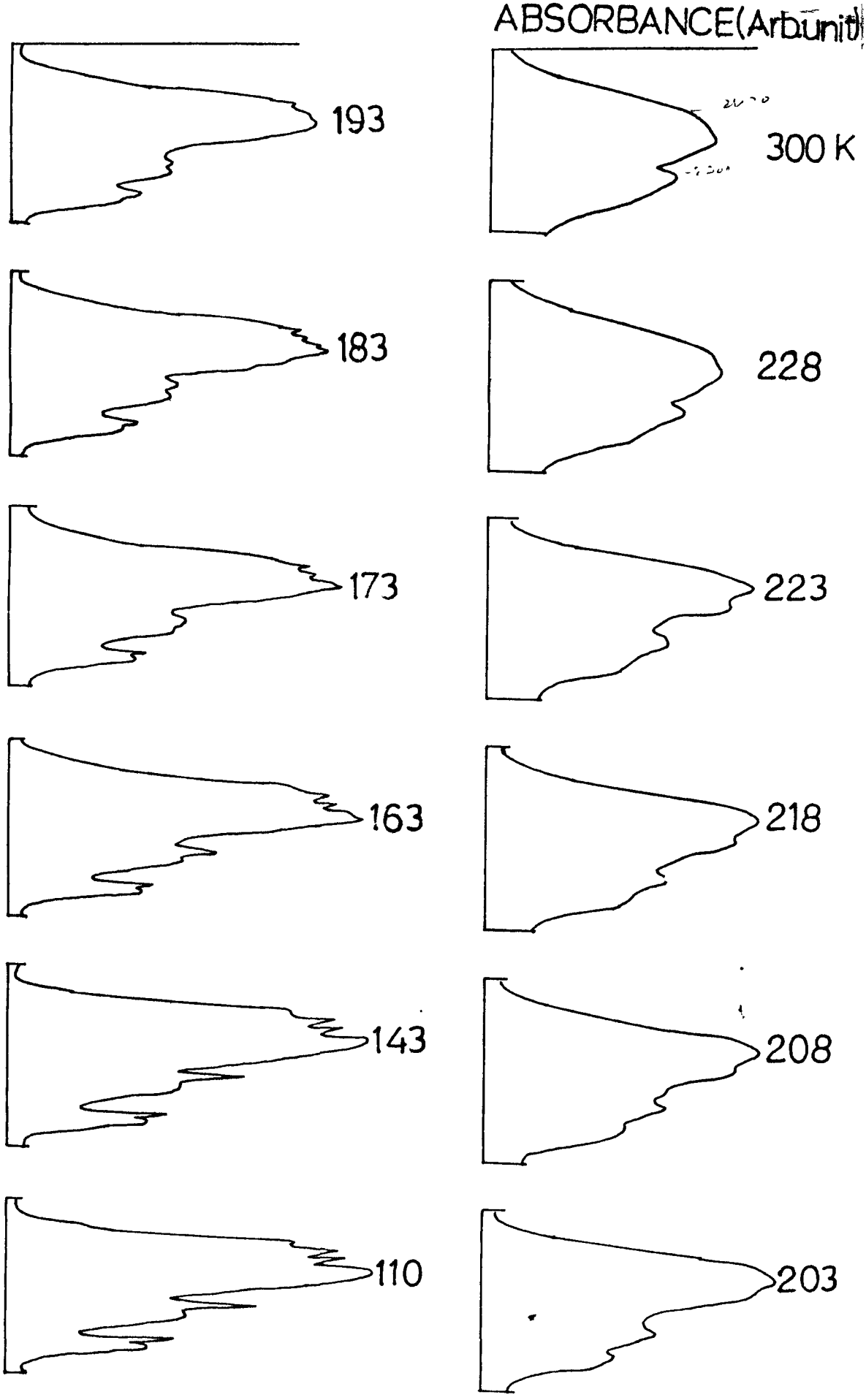

ABSORBANCE(Arb.unit)
193
300 K
183
228
173
223
163
218
143
208
110
203

Fig.3.3 The temperature dependence of the IR absorption of N-D bending (1200-1350cm^{-1}) in partially deuterated AS, prepared in 95% H_2O and 5% D_2O.

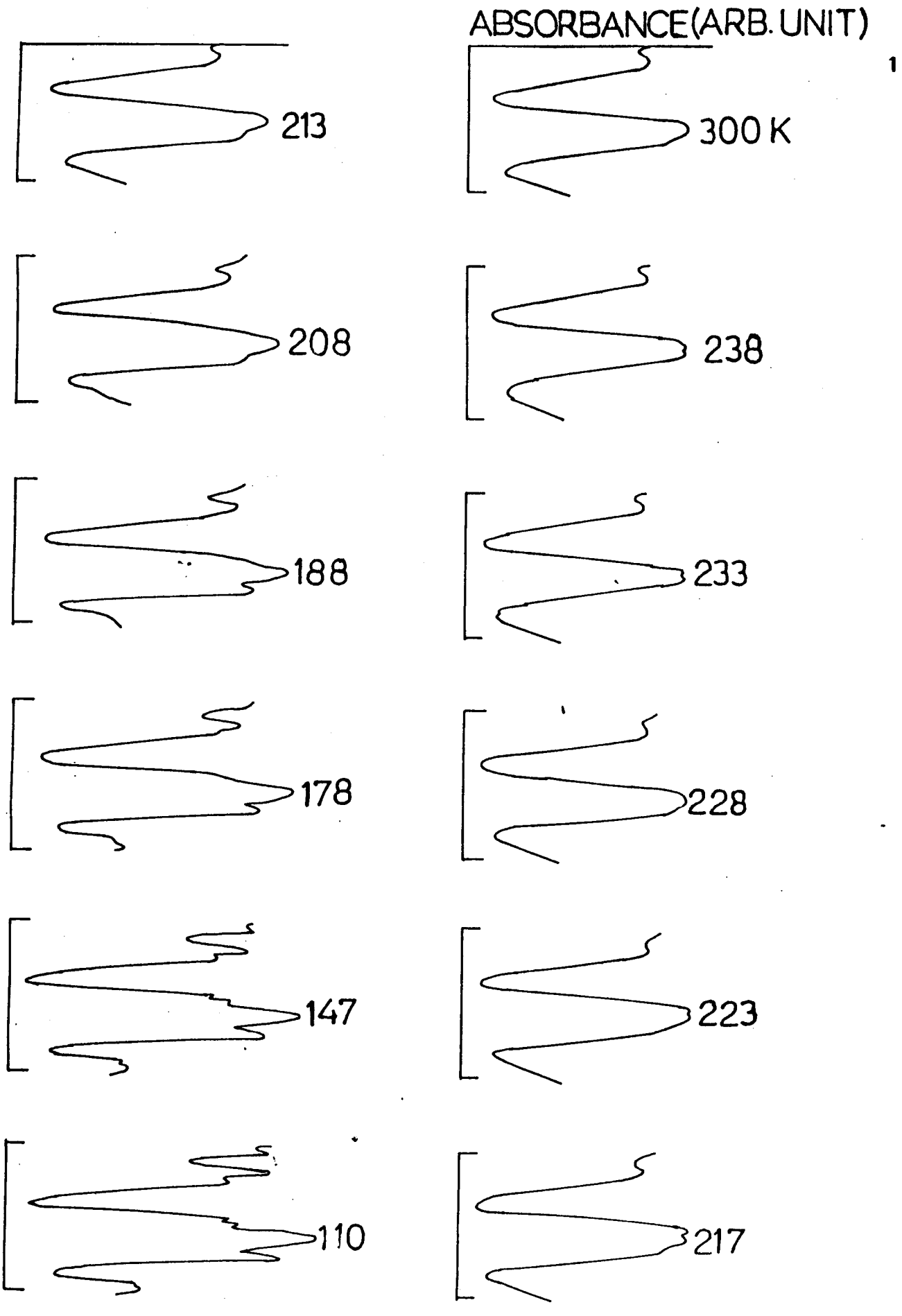

ABSORBANCE(ARB. UNIT)
213
300 K
208
238
188
233
178
228
147
223
110
217

Fig.3.4 The temperature dependence of the IR absorption of $\nu_1(SO_4^{2-})$ in partially deuterated AS. The peak positions above T_c are $972cm^{-1}$, and below T_c they are 976 cm^{-1}.

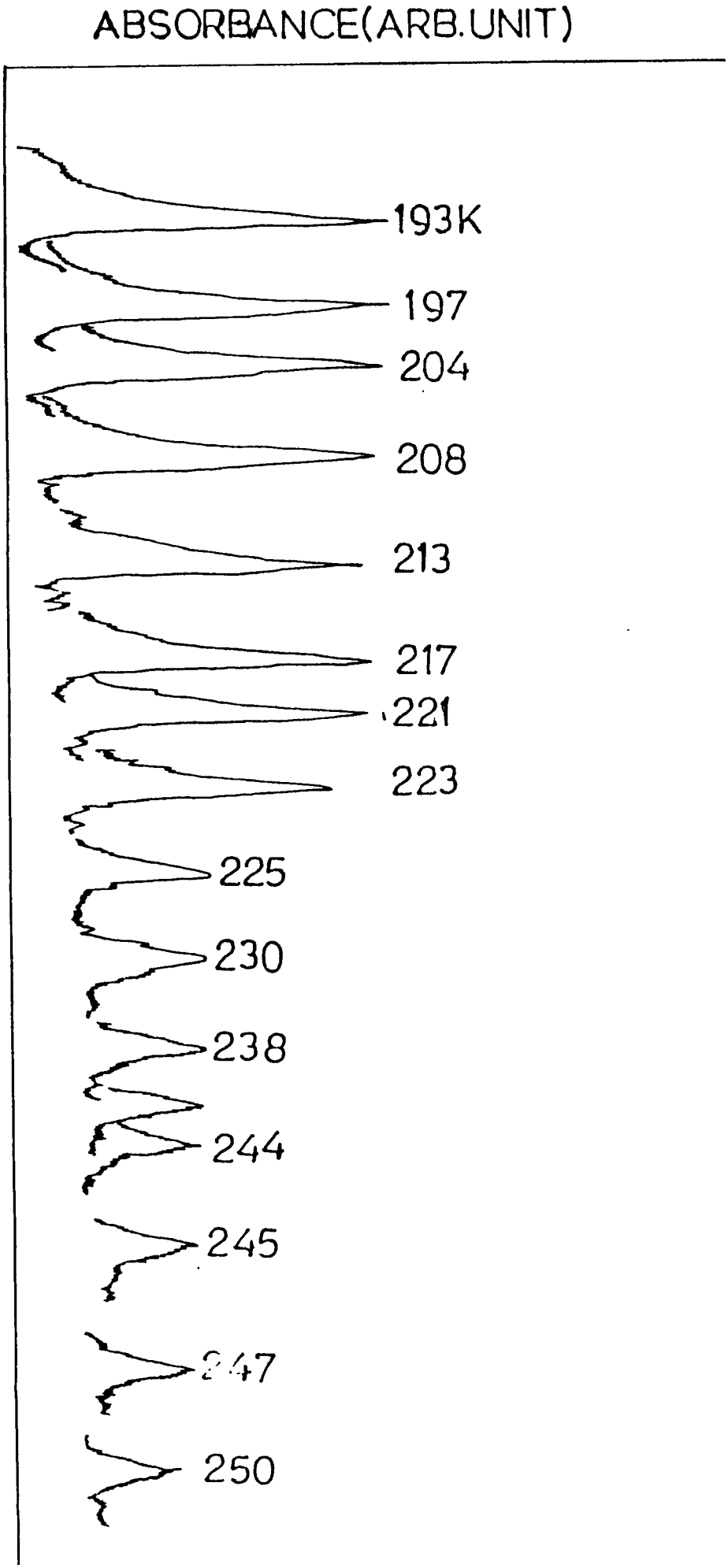

ABSORBANCE(ARB.UNIT)
193K
197
204
208
213
217
221
223
225
230
238
244
245
247
250

Fig.3.5 Temperature dependence of ν_1 mode (SO_4^{2-}) (960-990cm^{-1}) in Raman spectra.

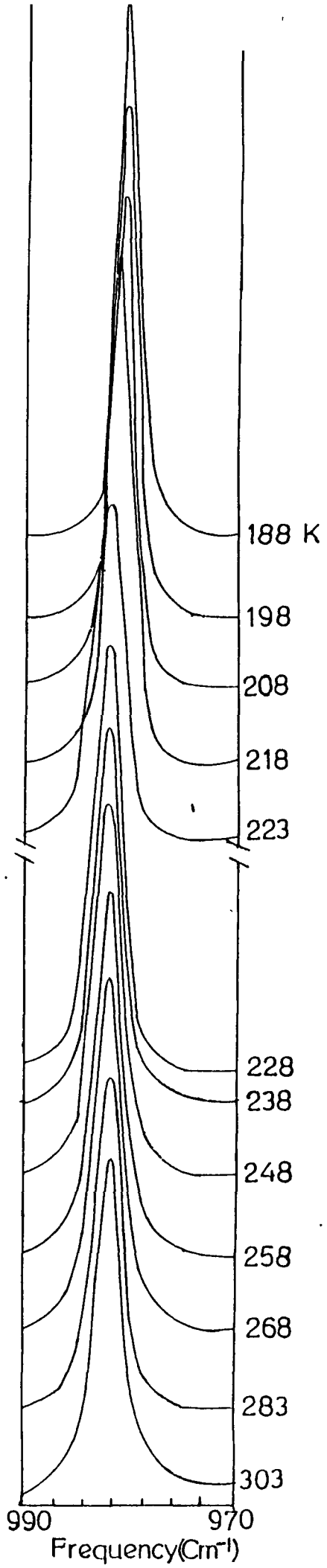

188 K
198
208
218
223
228
238
248
258
268
283
303
990
970
Frequency(Cm⁻¹)

Fig.3.6 Temperature dependence of ν_2 mode (SO_4^{2-}) (430-480cm^{-1}) in Raman spectra.

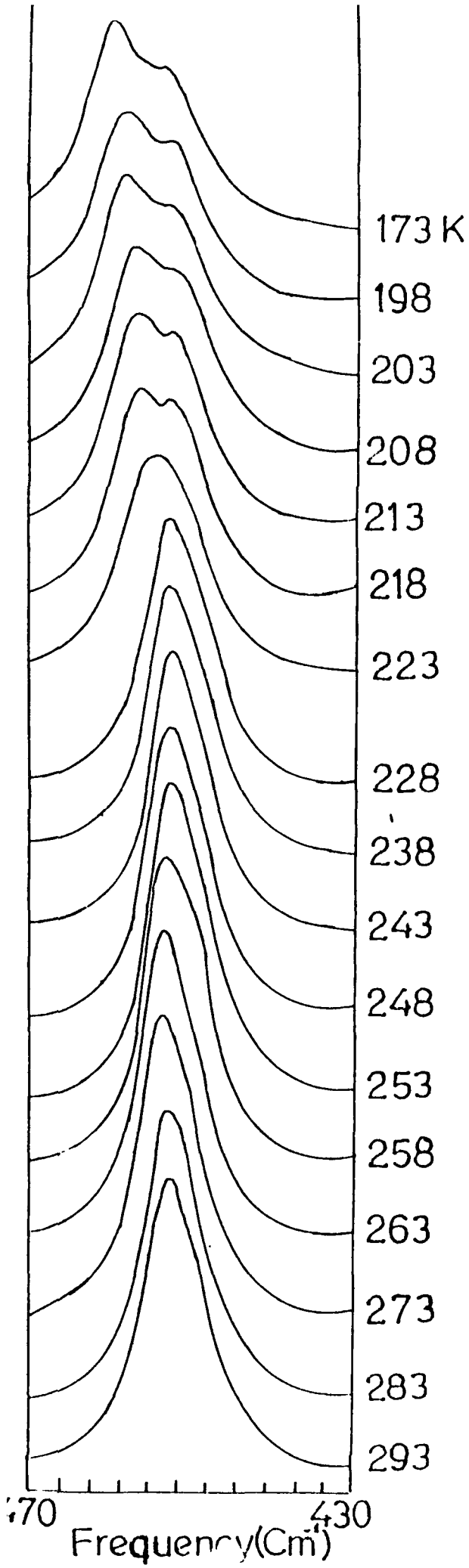

173 K
198
203
208
213
218
223
228
238
243
248
253
258
263
273
283
293
470
430
Frequency(Cm⁻¹)

Fig.3.7 Temperature dependence of υ_4 mode (SO_4^{2-}) (640-600 cm^{-1}) in Raman Spectra.

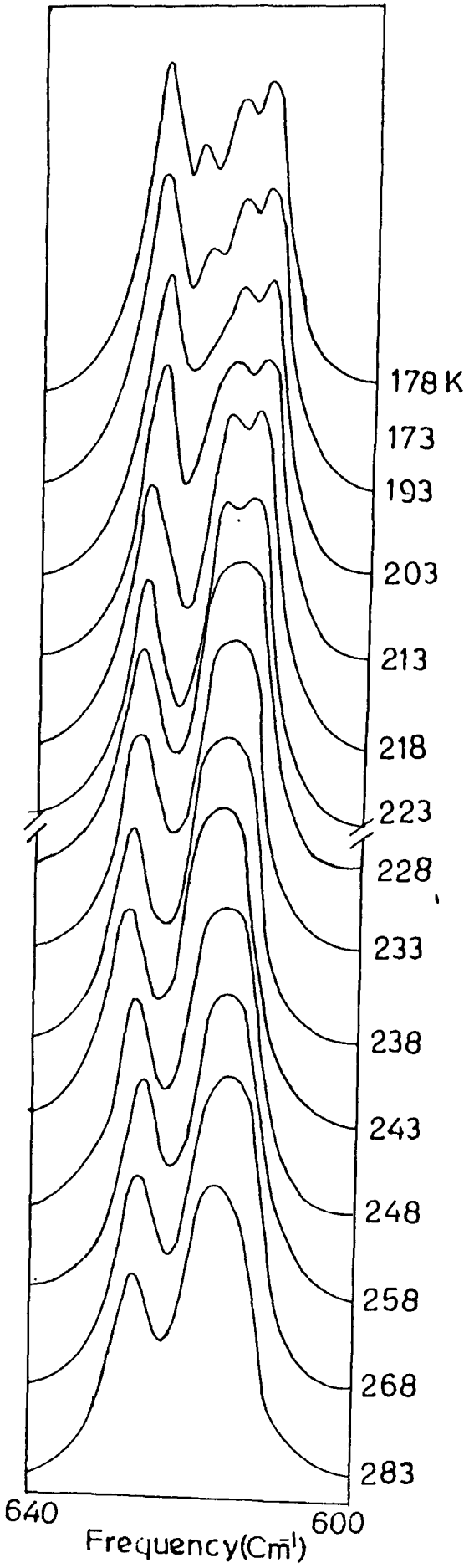

178 K
173
193
203
213
218
223
228
233
238
243
248
258
268
283
640
600
Frequency(Cm⁻¹)

Fig.3.8 Temperature dependence of (a) FWHMI, (b) Intetraged intensity, (c) Peak Intensity and (d) frequency shift of ν_1 mode of SO_4^{2-} ion in AS in Raman spectra.

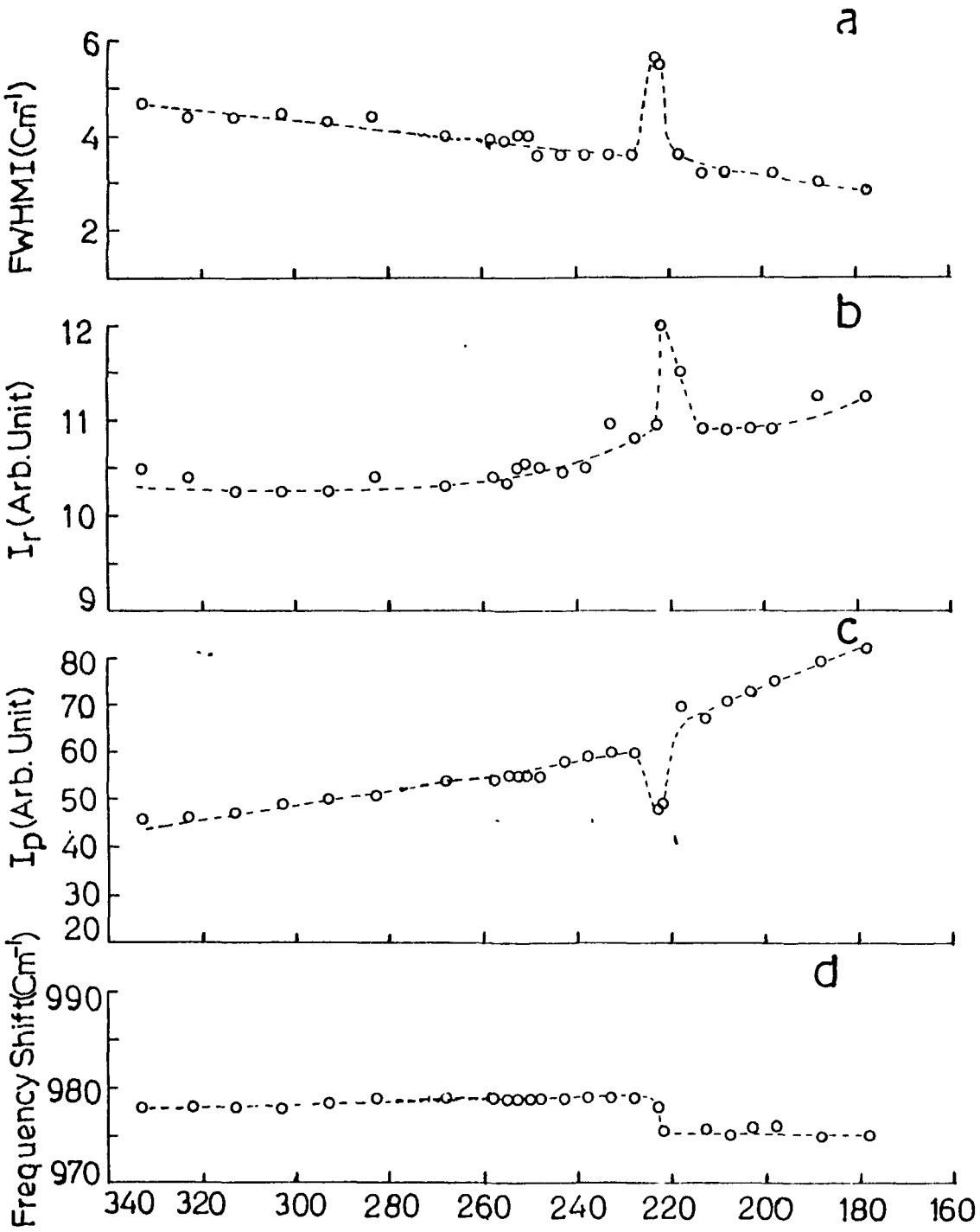

a
b
c
d
FWHMI(Cm⁻¹)
I_r (Arb. Unit)
I_p (Arb. Unit)
Frequency Shift(Cm⁻¹)
6
4
2
12
11
10
9
80
70
60
50
40
30
20
990
980
970
340 320 300 280 260 240 220 200 180 160

Fig.3.9 Temperature dependence of (a) FWHMI, (b) Integrated intensity (c) Peak Intensity and (d) Splitting of ν_2 mode of SO_4^{2-} ion in AS in Raman Spectra.

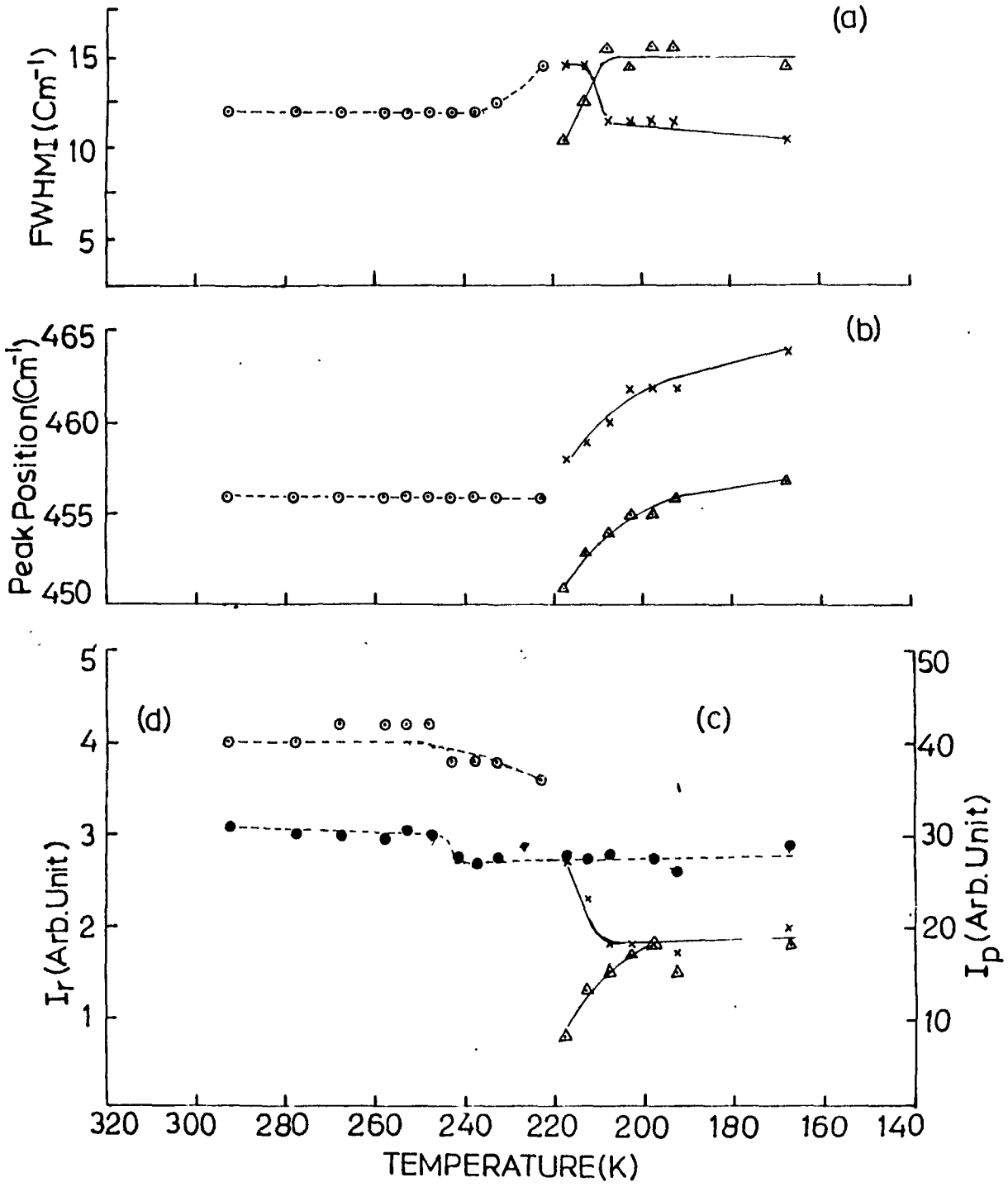
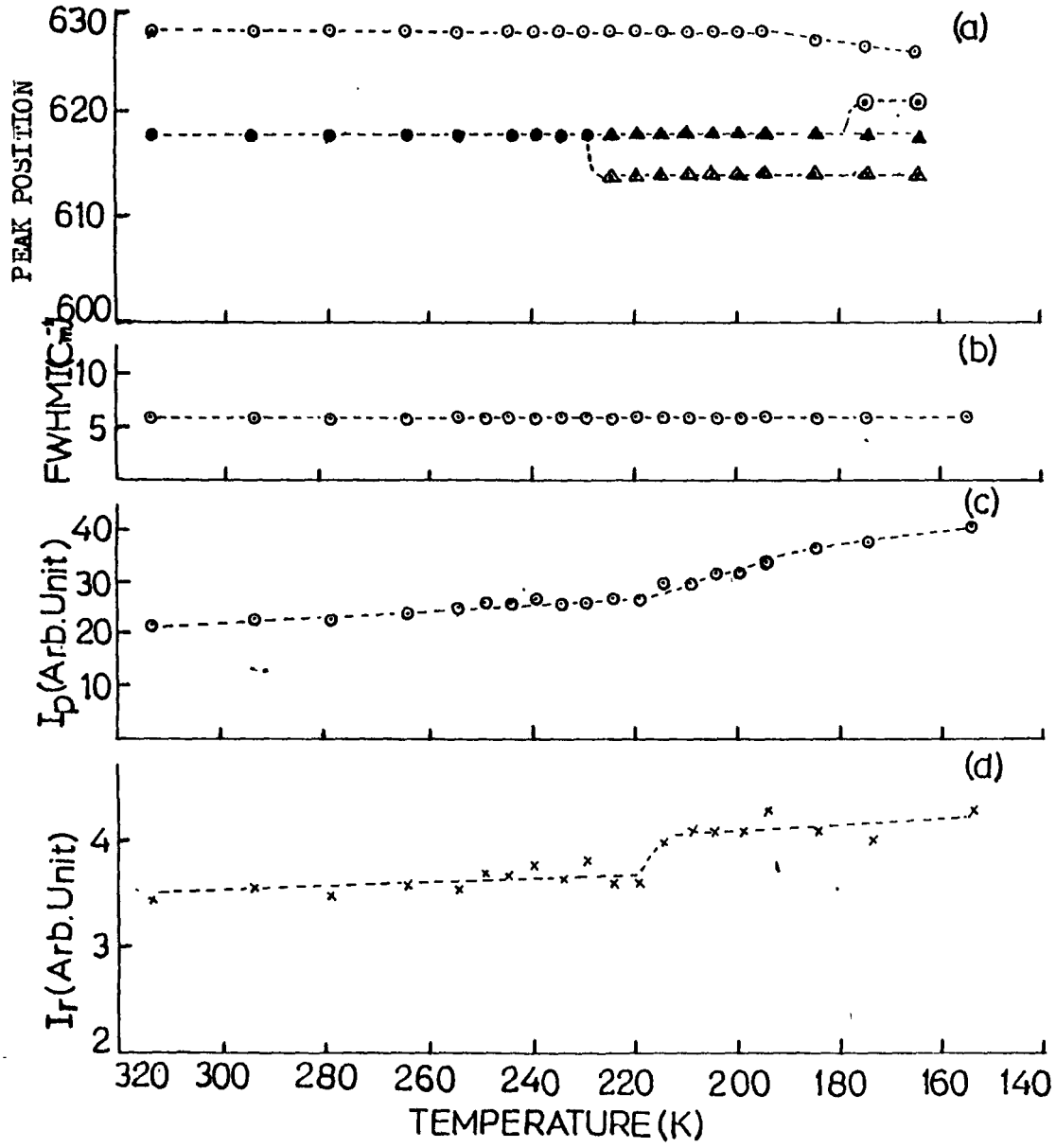

(a)
FWHMI (Cm⁻¹)
15
10
5
(b)
Peak Position (Cm⁻¹)
465
460
455
450
(d)
(c)
I_r (Arb.Unit)
I_p (Arb.Unit)
5
4
3
2
1
50
40
30
20
10
320 300 280 260 240 220 200 180 160 140
TEMPERATURE(K)

Fig 3.10 Temperature dependence of (a) peak positions of different components of $\nu_4(SO_4^{2-})$, (b) FWHMI (cm^{-1}) of 618 cm^{-1} component, (c) Peak intensity of 618 cm^{-1} component and (d) relative integrated intensity of ν_4 mode of SO_4^{2-} ion.


PEAK POSITION
630
620
610
600
(a)
FWHM(Cm⁻¹)
10
5
(b)
Ip(Arb.Unit)
40
30
20
10
(c)
Ir(Arb.Unit)
4
3
2
(d)
320 300 280 260 240 220 200 180 160 140
TEMPERATURE(K)

MICROSCOPIC MECHANISM OF PHASE TRANSITION IN AMMONIUM SULPHATE ANALYSIS OF CRYSTALLOGRAPHIC DATA

4.1 Introduction

The problem of understanding the origin of the microscopic mechanism of phase transition in AS has been attempted by several workers. According to the order-disorder type of mechanism proposed by O'Reilly and Tsang[1] the transition is due to orientational ordering of distorted NH_4^+ ions. Schlemper and Hamilton[2] associated the transition with the change in H – bonding while Sawada et al.[3] tried to develop a soft mode theory assuming that the phase transition is displacive type where a phonon of B_{1u} symmetry involving a mixed mode of translational and rotational symmetry of T_d ions plays an important role. Unruh[4] proposed that low temperature phase is Ferrielectric consisting of two oppositely polarized sublattices. Jain et al.[5-7] on the basis of their IR and Raman studies and other observations available at that time proposed a new mechanism of phase transition. Accordingly, the transition is triggered by distortion arising in the structure of the SO_4^{2-} ion; the order parameter coupled with spontaneous polarization has several components including spontaneous strain in the SO_4^{2-} ion as its major component. Although several investigations have since then corroborated this suggestion[8-11],

at times it has been suggested that a better understanding of the microscopic origin of phase transition mechanism can be obtained from detailed analysis of the structural data of the crystal kept at different temperature around T_c. Such data are now available for this crystal[12]. We, therefore, analyse these data in the present chapter and on the basis of the results of this analysis and that of IR/Raman spectra (presented in Chapter III), conclude the factual nature of the microscopic mechanism of the phase transition. The necessary crystallographic data used in the present analysis are given in Chapter II for ready reference. The conclusions of crystallographic analysis have been used to estimate the heat of transition, giving the result 4.2±0.4KJ/mole. This agrees well with the experimentally observed values[13,14] (3.89-4.27) ±0.02KJ/mole.

4.2 Analysis of Structural Data

Hasebe[12] has published crystallographic data of AS at 233, 224.5, 219.5, 209, 183 and 133K (cf. Table 2.1 to 2.6 in Chapter II). In order to make a fruitful analysis of these data, dipolar distortion ($\delta\vec{r}$) in SO_4^{2-}, NH_4^+(I) and NH_4^+(II) ions has been calculated using[6]

$$\delta\vec{r} = \sum_{r=1}^{4} (\vec{B}_i^r - \vec{A}_i) \qquad (4.1)$$

where $\vec{A}_i$ and $\vec{B}_i^r$ are the i-th components of the position vectors respectively of the A-atom and r-th B-atom of the $AB_4^{\pm n}$ tetra-

hedron. The calculated values of $\delta \vec{r}$ for all the three ions are given in Table 4.1 and are plotted in Figs. 4.1 to depict the nature of their temperature variation. A critical examination of this figure reveals the following:

i) The distortion in the SO_4^{2-} ion is less in the para-electric than in the ferroelectric phase; on cooling the crystal, it increases slowly and smoothly, except at T_c, where it suddenly increases by a factor of 2.0. The theory of distortion induced IR and Raman intensity of the forbidden modes of molecular units, developed by Jain and Bhattacharjee[15] has shown that this observation is in close agreement with what formed the basis of conclusions of Jain and Coworkers[6,7] earlier and confirmed by our detailed observations[16,17].

ii) The exact amount of the change in distortion of ammonium ions at T_c could not be estimated from the curves (Fig.4.1) because the structural data pertaining to these ions in para-electric AS at temperature near T_c are not available. However, it is clear that the changes in the distortion of NH_4^+ ions do not occur only at T_c (if they do at all) but also at other temperatures e.g. at about 183K where no phase transition is known to occur.

In addition, our observations of IR/Raman bands due to NH_4^+ ions and several other investigations conclude beyond any doubt that the structural and dynamical changes associated with NH_4^+ ions are not commensurate with the first order nature of the transition. For example,

i) NH_4^+ ions in the para-electric phase oscillate with large amplitudes which continue in the ferroelectric

phase; the NH_4^+(I) ion freezes at ~160K, while NH_4^+(II) continues moderate oscillations even upto ~90K[19].

ii) O'Rielly and Tsang[1] showed that the order-disorder phenomenon can be consistent with the first order phase transition in AS if the transition involves the cooperative reorientation of NH_4^+ ions at T_c which however does not occur according to the well discussed study of NMR data by Miller et al[19].

iii) No change in NMR linewidth takes place at T_c[20],

iv) T_c is not affected by deuteration[13] or is negligibly affected[21]

v) The intensity of the thermosensitive IR band at 3303cm^{-1} associated with NH_4^+ ions changes slowly[5].

vi) The D-modes due to distinguishable N-D oscillators do not show any sudden change in their band structure at T_c[17]

From these results though it becomes clear that the major force for triggering the transition lies in SO_4^{2-}ion. However, to get a more deep insight of the mechanism responsible for the phase transition, we calculate the magnitude of polar distortion $|\delta\vec{r}|$ and its x, y and z components using Eqn. (4.1). The temperature variation of $|\delta\vec{r}|$, $|\delta\vec{x}|$, $|\delta\vec{y}|$ and $|\delta\vec{z}|$ in passing through T_c is depicted in Fig. 4.2. A careful study of the figure reveals the following points:

i) In the range where $T > T_c$ (the PE phase) $\delta\vec{z}$ remains equal to zero (the SO_4^{2-}ion has mirror σ_{xy} site symmetry): $\delta\vec{r}$ does not change significantly while $\delta\vec{x}$ and $\delta\vec{y}$ are observed to increase and decrease, respectively. This show that the SO_4^{2-}ion in the PE phase slowly

opposite in the Table

rotates about the Z-axis (|| C-axis).

ii) At $T=T_c$, $\delta\vec{x}$ and $\delta\vec{z}$ suddenly increase, while $\delta\vec{y}$ does not change significantly. This indicates that the net dipole moment no longer remains in the xy plane. Consequently distorted NH_4^+ ions also having definite dipole moments reorient themselves under the influence of dipole-dipole interactions in order to attain the configuration of minimum free energy.

iii) In the **FE** phase ($T < T_c$) $\delta\vec{x}$ and $\delta\vec{r}$ remain almost constant while $\delta\vec{y}$ and $\delta\vec{z}$ change in such a way that as one decreases the other increases and vice-versa. This indicates that the ion in the **FE** phase slowly rotates about the x-axis (|| a-axis).

In view of our observations and their analysis it is evident that studies of **AS** mainly related to the dynamics and structure of NH_4^+ ions may not reveal sudden changes at T_c and the transition may appear to have second order behaviour as inferred by many investigators[19,22]. On the other hand observations also influenced by the structure and dynamics of SO_4^{2-}ions would reveal sudden changes at T_c and would demonstrate first order behaviour of the transition[13,23,24]. As such the analysis of the crystallographic data of Hasebe[12] confirm the observations revealed by IR/Raman study and obviously corroborate their inferences. One may also note that these observations and inferences are also corroborated by recent studies. For example, Iqbal and Christoe[25] and Hirabayashi and Abe[26] have also observed that the phase transition in **AS** in accompanied by deformation of the SO_4^{2-}ion. Badr and

Awad[8] and Abe and Shibata[26] have inferred that the SO_4^{2-} is responsible for the spontaneous polarization and it plays a vital role in the process of transition. Manjunath and Srinivasan[11] also emphasise the role of SO_4^{2-} ion. Zinenko **et al**[27] believe that the unusual behaviour of P_s in **AS** may be due to the fact that the phase transition is not associated with the ordering of NH_4^+ ions as suggested in their model but with the ordering of the SO_4^{2-} ion. We also note that:

i) Hasebe and Tanisaki[28] could not explain their X-ray diffuse scattering data in terms of order-disorder of NH_4^+ ions.

ii) Neutron diffraction data[2], which are obviously considered to be more accurate and reliable than X-ray diffraction data for determining the positions of H-atoms do not reveal order-disorder mechanism.

Evidently, the order-disorder mechanism involving NH_4^+ ions (as envisaged by Hasebe) is not supported by several investigators.

It may be mentioned that Hasebe[12] reports that the positional parameters of sulfur change slightly but those of oxygen atoms change drastically with temperature below T_c. He suggests that the configuration of the SO_4^{2-} ion below T_c can be derived from that above T_c(-40°C) by a small amount of translation followed by a rotation through a certain angle about an axis passing through sulphur. But this cannot be true in general because one cannot exclude the possibility of structural distortion of the SO_4^{2-}ion. Our calculations

(Table 4.1) evidently show that distortion in the SO_4^{2-} ion does occur. Thus Hasebe did not interpret his data correctly and consequently made an erroneous conclusion that the structure of the SO_4^{2-} ion even in the ferroelectric phase resembles the regular tetrahedron.

4.3 *Model for the microscopic mechanism*

In view of the above discussed facts, revealed from several experimental observations, we believe that the phase transition in **AS** should have the following microscopic mechanism. It may be noted that the crystal structure of **AS** with respect to the positions of NH_4^+(I), NH_4^+(II) and SO_4^{2-} ions is mainly decided by inter-ionic forces, while the structure of individual NH_4^+(I), NH_4^+(II) and SO_4^{2-} ions is decided mainly by intra-ionic forces (covalent in nature). Since the inter-ionic forces are more anharmonic than covalent forces, thermal contraction (with decreasing temperature) in the size of individual ion is less than that in the volume available for these ions in the crystal cell. Consequently, with decreasing temperature, ions experience a force that tends to squeeze and deform them. This force should obviously be resisted by the intra-ionic forces trying to retain their original shape and size. In the process, the stress on the ions increases. At T_c, this stern becomes sufficient to force the ions (and the crystal as a whole) to assume a structure and symmetry different from what they had above T_c. Guided by the fact that T_c remains

unaffected by deuteration[13,21], we infer that the main driving force for the transition is centred around the SO_4^{2-} ion; the NH_4^+ ion simply follow the change that is forced on them. The change in the strength of H bonding is also a secondary effect. As a result of increased deformation, the SO_4^{2-} ion acquires significant magnitude of electric dipole moment and this additional dipole appears between the two already existing NH_4^+ dipoles. This reduces the effective distance between the dipoles. Consequently, the distortion of the SO_4^{2-} ion is followed by its reorientation immediately to acquire the new configuration of minimum free energy; the NH_4^+ ions continue their large amplitude oscillation (through the transition point) which freezes only at temperatures as low as ~ 60K for NH_4^+(I) and ~90K for NH_4^+(II)[18].

Ferroelectricity in AS is accounted for by the permanent dipole moment of distorted ions in the crystal[6,7]. The kind of distortion that results in a permanent dipole moment comes into existence obviously when the structure of the ions becomes frozen with non-zero amplitude of IR active internal modes, ν_3 and ν_4. Rotation of the tetrahedral ion on the other hand does not lead to a structure that can have ferroelectricity unless the ion is distorted. Thus distortion is the pre-requisite of the coupling between the rotation of ions and polarization of the crystal. Further, the rotation cannot account for the change in the internal structure of the ions. It should

be noted that the rotation does not belong to the IR active F_2 species of T_d point group. Hence the freezing of tetrahedral ion, only with finite rotation, as suggested by Hasebe, about any axis cannot lead to a structure with permanent dipole moment. Consequently, even the quadrupole-dipole type weak interaction should be absent between the librating SO_4^{2-} ion (if it has T_d structure) and pseudo spins (NH_4^+ions). Obviously Hasebe's[12] observation that the SO_4^{2-} ion retains its regular tetrahedral structure and his proposed coupling between librating SO_4^{2-} ion and pseudo spins are not in line with each other. However, the fact remains that the SO_4^{2-}ion acquires increased distortion and electric dipole moment at T_c. Therefore the possibility of the said coupling can be rationalized in terms of a dipole-dipole interaction. This fact can be correlated with the sudden broadening of the linewidth of ν_1 mode in Raman spectra. But it should be remembered that this coupling comes into play only after the SO_4^{2-}ion acquires distortion. This explains how reorientation of NH_4^+ions (or their disordering as Hasebe puts it) follows as an after effect of SO_4^{2-}ion distortion. In view of these facts the importance of SO_4^{2-}ion distortion as an essential component of the order parameter is rightly emphasised; the rotation of the ion could be an additional component. This is further supported by the fact that the point charge model calculations reveal that the antiparallel NH_4^+ions at -53.5°C contribute only 0.13 $\mu C/cm^2$ to P_s against 0.4$\mu C/cm^2$ as claimed by Hasebe.

The soft mode, which fits in our model should obviously be a mixed mode of internal vibration and libration of the SO_4^{2-}ion. This falls well in agreement with the observation of Ramanathan and Srinivasan[9], Fujimoto **et al**[29], Hasebe and Tanisaki[28] and other workers[8,10]. Because of the strong interaction of the SO_4^{2-}ion with its surroundings, both components of this soft mode should be fast relaxing. Note, that Petzelt **et al**[30] and Fujimoto **et al**[29] have argued that the soft mode may not be observed if it relaxes fast. This could be the reason that the soft mode responsible for the transition in **AS** has not been observed in the far Infrared[30,31] and low frequency Raman spectra[5,31] studied upto as low as $30cm^{-1}$ phonon frequency. We also notice that the librational mode of tetrahedral ion is forbidden both in **IR** and Raman spectra. Consequently, this mode of the SO_4^{2-} ion having almost tetrahedral structure in para-electric phase of **AS** may not gain observable intensity. Even in the ferroelectric phase it may only gain low intensity. This could be another reason why the librational component of the soft mode has not been detected.

The fact that inter-ionic force is more anharmonic than intra-ionic force, as mentioned by us, should not imply that the forces governing the internal modes of the SO_4^{2-}ion are not anharmonic. In fact the internal modes of the SO_4^{2-}ion in **AS** are governed by intra-ionic potential as well as inter-

ionic potential and the anharmonic component of both these potentials influences these modes. Thus our observation regarding the nature of the soft mode is very much in line with the fact that the mode softening occurs due to anharmonicity. The frequencies of the internal modes (ν_1=976, ν_2=450, ν_3=1087 and ν_4=618cm^{-1}) of the SO_4^{2-}ion[32] in **AS** do not differ by more than a few wave numbers from those (ν_1=981, ν_2=451, ν_3=1104 and ν_4=613cm^{-1}) in its free state[33]. Therefore, it should not be difficult to believe that the internal modes of the ion retain their identity in the crystal.

In order to examine how the mechanism of transition in **AS** proposed in this report is different from displacive / order-disorder type, we consider the transition as an operator, which forces some set(s) of atom(s)/molecule(s) to change their position(s)/posture/internal structure through freezing of their translational/rotational/internal modes with non-zero amplitude. In this framework the displacive type transition is the result of freezing of translatory modes (for example, the transition in $BaTiO_3$) while the order-disorder type may arise due to freezing of translatory/rotatory modes of the unit (e.g. transition in KH_2PO_4, NH_4Cl, etc.). However, a transition resulting from the freezing of internal modes of the unit cannot be fitted into the class of displacive/order disorder type; such a transition should obviously be named differently. Perhaps it could be known as **molecular distortion**

type since this leads to some distortion in the structure of molecular unit(s) rather than causing a change in their position and/or posture. Normally, a transition arise due to freezing of a mixed mode having different amplitude of translatory/rotary/internal modes. However, the nature of the mode with maximum amplitude may be chosen to decide whether the transition is of displacive/order-disorder/molecular distortion type. It may be remarked that the distortional type transition may only occur in crystals having molecular unit(s). If we examined the transition in **AS** in the framework of this kind of classification, it may easily be seen to be the **molecular distortion type.**

Ikeda **et al**[23] developed a theory of phase transition in **AS** through which they try to account for the temperature variation of dielectric constant, spontaneous polarization, elastic compliance, etc. They introduced an order parameter (η) of undefined physical nature and its coupling with its spontaneous polarization ($P_s=P_3$) and stress(X) in the free energy formulation, expressed by

$$G= \tfrac{1}{2}\beta (T-T_\eta)\eta^2+\tfrac{1}{4}\gamma\eta^4+\tfrac{1}{6}\delta\eta^6+f\eta P_3+\ldots \qquad 4.2$$

Many terms of G formulated by Ikeda **et al**[23] are not reproduced here as they are unimportant for our discussion. Notations β, T_η, δ, etc. have their usual meaning; f is the measure of coupling between η and P_3. Ikeda **et al** conclude that temperature

variations of relative order parameter satisfies

$$(T-T_o)/(T_c-T_o)+Py^2+Qy^4+n(1-FJ+g_3y^2F^2) = 0 \qquad (4.3)$$

where y is the relative order parameter defined as

$$y = \eta(T)/\eta(T_c) = \frac{\text{Spontaneous } \eta \text{ at } T < T_c}{\text{Spontaneous } \eta \text{ at } T = T_c}$$

$$F = (1+dy^2+ey^4)/(1+g_3y^2)$$

$$J = 1+3dy^2+5ey^4$$

They evaluated the values of all relevant parameters e.g. T_o=216.5, P=-4.33, Q=3.12, n=0.39, d=-0.06, e=0.01, etc. from a variety of experimental results such as temperature variation of dielectric constants, polarizability, elastic compliances, etc. and used these values in eqn.(4.3) to obtain the y against T curve reproduced in Fig.4.3. In this figure we also mark the temperature variation of relative distortion of the SO_4^{2-} (Δ_{rel}) deduced from structural data and distortion induced IR absorbance (I) of ν_1 of SO_4^{2-}, using the relation[15]

$$I = K|\vec{\delta r}|^2 \quad (K \text{ is constant})$$

$$\Delta_{rel} = \frac{(|\vec{\delta^- r}(T)| - |\vec{\delta^+ r}(T_c)|)}{(|\vec{\delta^- r}(T_c)| - |\vec{\delta^+ r}(T_c)|)} \qquad (4.4)$$

where positive and negative signs respectively signify the values of distortion $|\vec{\delta r}|$, above and below T_c at the temperature given in parentheses. It is interesting to note that within the error limits the two curves match closely. This not only supports the basic points of the theory of Ikeda **et al**, but also corroborates our conclusion that SO_4^{2-} ion

distortion is the basic component of the order parameter. In addition, it identifies the physical nature of the order parameter which was not spelled out by Ikeda **et al** and hence clarifies the physical details of the microscopic mechanism of **PT**. For example, the applied electric field (E) induces lattice polarization mainly by disturbing the electron charge density, orientation of permanent dipoles and the inter-ionic separation such as r (SO_4^{2-}-NH_4^+). However, E does not affect the inter-atomic separation in the structure of the ions such as SO_4^{2-}, NH_4^+, etc. unless its strength is as high as crystal fields. This implies that ordinary E and its conjugate parameter P (the electric polarization) can hardly affect the magnitude of $\delta\vec{r}$ (SO_4^{2-}), the order paameter. In view of this, we can easily understand the weak coupling between $\delta\vec{r}$ (SO_4^{2-}) and P_3(as considered by Ikeda **et al**) and also the fact that T_c is not affected by applied electric field[13].

The heat of transition (ΔH_T) is the energy involved in the first order change in the system. In view of the above discussion, we recognize the change in the polar distortion of the SO_4^{2-} ion as the major first order change in the crystal at T_c and use this for evaluating ΔH_T. This change can be understood in terms of the freezing of the ν_3 and ν_4 polar modes of the ion with finite amplitude. Minor first order changes that need to be accounted for by other degrees of freedom of the crystal are possible due to their coupling with the SO_4^2 ion distortion. However such changes are only

expected to account for a minor share of ΔH_T. Note that the change in electric dipole moment associated with ν_3 is an order of magnitude higher than that associated with the ν_4 mode; the former mode should result in stronger long range dynamical interaction between different SO_4^{2-} ions in the crystal. Such an interaction is vital for the cooperative motion responsible for the first order transition. ν_3 should therefore be the favoured mode of motion for bringing about the distortion in the SO_4^{2-}ion and triggering the transition; low level mixing of the ν_4 mode is possible but should not be given much importance in estimating ΔH_T. In view of these arguments ΔH_T can be evaluated to a good approximation from

$$\Delta H_T = \tfrac{1}{2} k_f [(|\delta^{-}\vec{r}\ (T_c)|^2 - |\delta^{+}\vec{r}\ (T_c)|)^2] \qquad (4.5)$$

where k_f is the force constant that governs the asymmetric stretching mode (ν_3) of the SO_4^{2-}ion and $|\delta^{+}\vec{r}\ (T_c)|$ and $|\delta^{-}\vec{r}(T_c)|$ are the magnitudes of the polar distortion just above and just below T_c. Taking k_f=9.07 mdyn $\mathring{A}^{-1}$ [33], $|\delta^{+}\vec{r}\ (T_c)|$ = 0.022(2) and $|\delta^{-}\vec{r}\ (T_c)|$ = 0.044(2), ΔH_T is found to be 4.2±0.4kJ mol^{-1}. This value agrees well with the values 3.89kJ mol^{-1} [13] and 4.27±0.02kJ mol^{-1} [14] calculated from the specific heat data within the error limits involved in the theoretical estimation and in the experimental results. This agreement not only corroborates the assertion that the change in the polar distortion of the SO_4^{2-}ion is the major first order change that occurs

at T_c but also supports our argument that the distortion arises mainly due to the freezing of the ν_3 stretching mode rather than that of the ν_4 mode with finite amplitude. This also supports the molecular distortion type (MD-type) model for the phase transition in AS.

In conclusion, the temperature dependence of distortion of ions in AS calculated from x-ray crystallographic data reveals that the triggering force for the transition lies in the SO_4^{2-}ion; changes in the structure of NH_4^+ions ocur as follow up process. The change in the strength of H-bonding is also a secondary effect. The soft mode of the transition is the mixed mode of internal vibrations and libration of the SO_4^{2-}ion. All these conclusions are found to be consistent with the theory of this transition developed by Ikeda **et al** which explains reasonably well the several experimental observations. The order parameter of the transition is the distortion of the SO_4^{2-}ion. The temperature variation of the polar distortion of the SO_4^{2-}ion and its components reveals that the SO_4^{2-}ion rotates about the Z-axis in the PE phase and about the X-axis in the FE phase. A quantitative account of the observed latent heat has been given. The calculated value 4.2±0.4kJ mol^{-1} agrees well with the experimental values 3.89 and 4.27±0.02kJ mol^{-1}. All these inferences strongly support the model of the microscopic mechanism of the PT to be of **molecular distortion type (MD-type)**. Accordingly, the MD-type transition leads

to a change mainly in the structure and symmetry of molecular unit rather than in their location and orientation and it can only occur in crystals having one or more than one kind of molecular unit.

REFERENCES

1. O'Reilly, D.E., and Tsang, T. (1967) J. Chem. Phys. **46**, 1291.

2. Schlemper, E.O., and Hamilton, W.C. (1966) J. Chem. Phys. **44**, 4498.

3. Sawada, A. Takagi, Y., and Ishibashi, Y. (1973) J. Phys. Soc. Jap. **34**, 748.

4. Unruh, H.G. Sailer, E. Hussinger, H., and Ayere, O. (1978) Solid State Commu. **25**, 871.

5. Jain, Y.S. (1974) Ph.D. Dissertation I.I.T. Kanpur, India.

6. Jain, Y.S., and Bist, H.D. (1974) Physica Status Solidi b **62**, 295.

7. Jain, Y.S., and Bist, H.D. (1974) Solid State Commu. **15**, 1229.

8. Jain, Y.S. Bist, H.D., and Upreti, G.C. (1973) Chem. Phys. Lett. **22**, 572.

9. Ramnathan, K.V., and Srinivasan, R. (1978) Chem. Phys. Lett. **56**, 359.

10. Narayana, M., and Kevan, L. (1981) Physica Status Solidi a **68**, 703.

11. Manjunath, C.V., and Srinivasan, R. (1978) Physica Status Solidi b **87**, 395.

12. Hasebe, K. (1981) J. Phys. Soc. Jap. **50**, 1266.

13. Hoshino, S. Vedam, K. Okaya, Y., and Pepinsky, R. (1958) Phys. Rev. **112**, 405.

14. Higashigaki, Y., and Chihara, H. (1981) Bull. Chem. Soc. Jap. **54**, 901.

15. Jain, Y.S., and Bhattacharjee R. (1985) J. Phys. C- Solid State Phys. **18**, 5299.

16. Jain, Y.S. Bajpai, P.K. Bhattacharjee, R. and Chowdhury, D. (1986) J. Phys. C- Solid State Phys. **19**, 3789.

17. Bajpai, P.K., and Jain, Y.S. (1987) J. Phys. C- Solid State Phys. **20**, 387.

18. Kydon, D.W. Pintar, M., and Petch, H.E. (1967) J. Chem. Phys. **47**, 1185.

19. Miller, S.R. Blinc, R. Brenmgn M., and Waugh, J.S. (1962) Phys. Rev. **126**, 528.

20. Blinc, R.,and Levstek, I. (1960) J. Phys. Chem. Solids **12**, 295.

21. Unruh, H.G., and Rüdiger, U. (1972) J. de Physique **33**, C2-77.

22. Parsonage, N.G., and Staveley, L.A.K. (1978) "Disorders in Crystals" p.350 Oxford Univ. Press. London.

23. Ikeda, T. Fujibayashi, K. Nagai, T., and Kobayashi, J. (1973) Physica Status Solidi a **16**, 279.

24. Brehat, F. Wyncke, B. Fuzellier, Y., and Hadni, A. (1974) J. de Physique **35** L-143.

25. Iqbal, Z., and Christoe, C.W. (1976) Solid State Commu. **18**, 269.

26. Abe, R., and Shibata, N. (1977) J. Phys. Soc. Jap. **43**, 1308.

27. Zinenko, V.I. Blat, D. Zh., and Aleksandrov. K.S. (1980) Sov. Phys. Solid State **22**, 106.

28. Hasebe, K., and Tanisaki, S. (1977) J. Phys. Soc. Jap. **42**, 568.

29. Fujimoto, M. Dressel, L.A. and Yu, T.J. (1977) J. Phy. Chem. Solids. **38**, 97.

30. Petzelt, J. Grigas, J., and Mayerová, I. (1974) Ferroelectrics **6**, 225.

31. Barb D, Grecu N.M., Grecu, V.V., and Popescu, F.F. (1978) Chem. Phys. Lett. **56**, 355.

32. Venkateswarlu, P. Bist, H.D. and Jain, Y.S. (1975) J. Raman Spectrosc. **3**, 143.

33. Herzberg, G. (1945) "Molecular Spectra and Molecular Structure", II, p.167. Van Nostrand, New York.

TABLE 4.1

Temperature dependence of distortion in NH_4^+(I), NH_4^+(II) and SO_4^{2-}ions and their x, y, z components in AS

Temperature (K)	ion	$\delta\vec{x}$	$\delta\vec{y}$	$\delta\vec{z}$	$\delta\vec{r}$
	NH_4^+(I)				
219.5		0.0109	0.1162	0.1036	0.1561
209		-0.0865	0.0804	0.0833	0.1446
183		-0.0063	0.0718	0.1892	0.2025
133		0.0158	-0.0357	0.1083	0.1152
	NH_4^+(II)				
219.5		-0.0517	0.1310	-0.0619	0.1599
209		0.0220	0.1460	-0.1036	0.1804
183		0.0070	-0.0232	0.0190	0.0310
133		0.1094	-0.1432	-0.0560	0.1886
	SO_4^{2-}				
219.5		-0.0407	-0.0106	-0.0149	0.0446
209		-0.0472	-0.0127	-0.0036	0.0490
183		-0.0512	-0.0032	-0.0083	0.0520
133		-0.0530	-0.0052	-0.0119	0.0546
224		-0.0201	-0.0074	0	0.0215
233		-0.0155	-0.0106	0	0.0188

Fig.4.1 Plot of temperature dependence of the distortion in NH_4^+(I) (O), NH_4^+ (II) (ø) and SO_4^{2-}(●) ions.

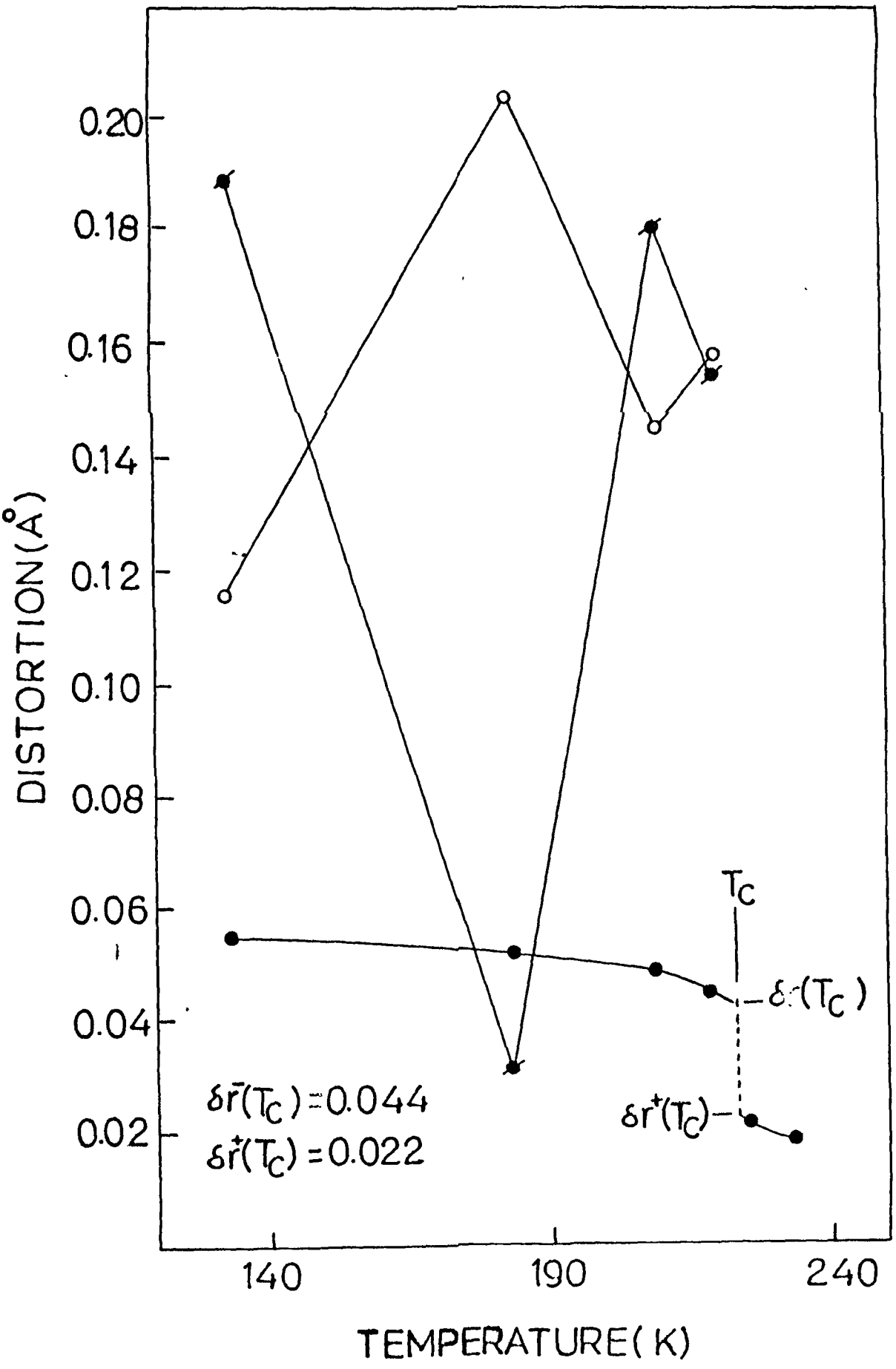

0.20
0.18
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
DISTORTION(Å)
140
190
240
TEMPERATURE(K)
T_C
$\delta\bar{r}(T_C)$
$\delta r^+(T_C)$
$\delta\bar{r}(T_C) = 0.044$
$\delta\bar{r}^+(T_C) = 0.022$

Fig.4.2 The temperature dependence of the SO_4^{2-} ion distortion $\delta\vec{r}$ and its components ($\delta\vec{x}$, $\delta\vec{y}$, $\delta\vec{z}$) calculated from the data of Hasebe.

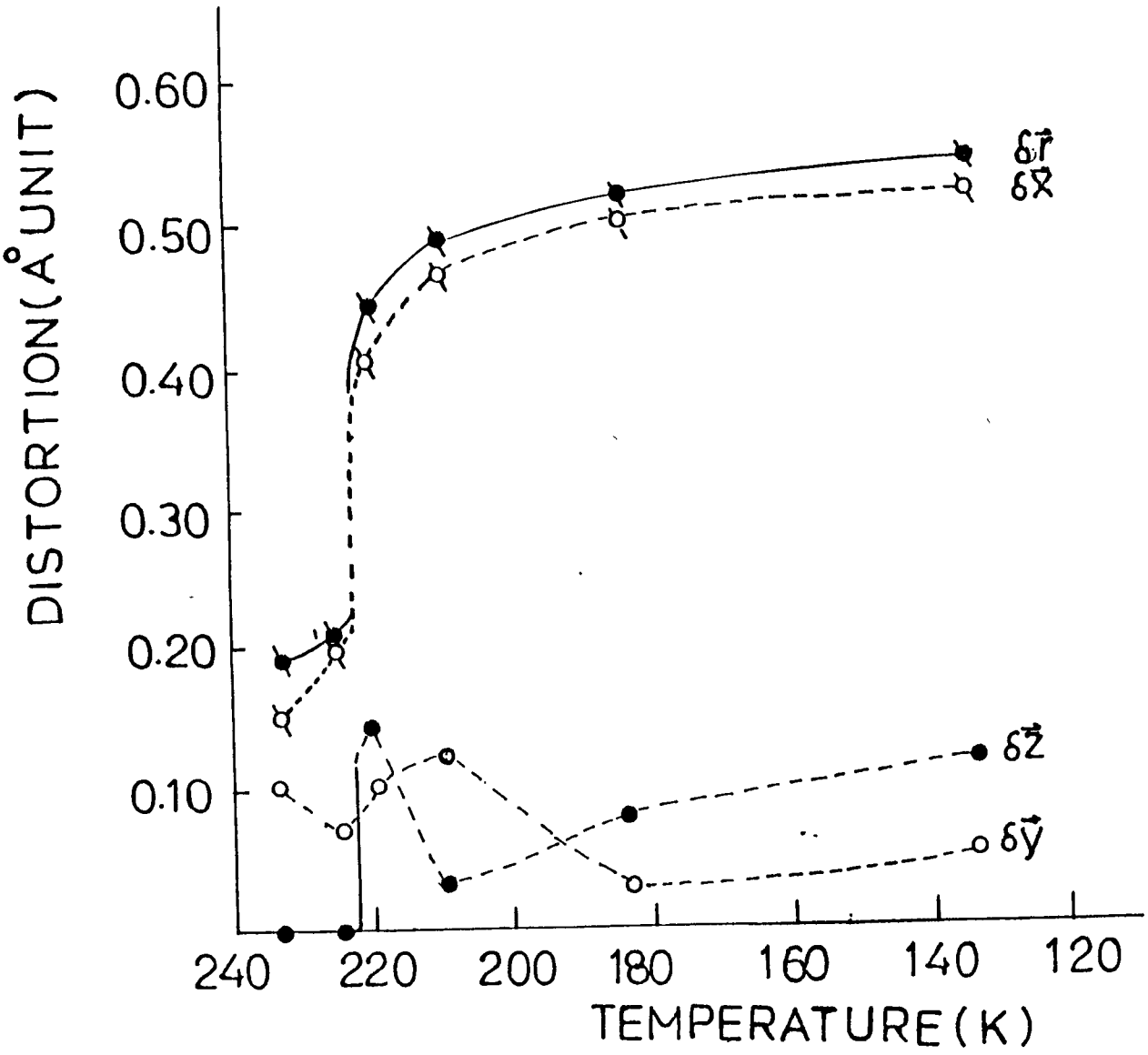
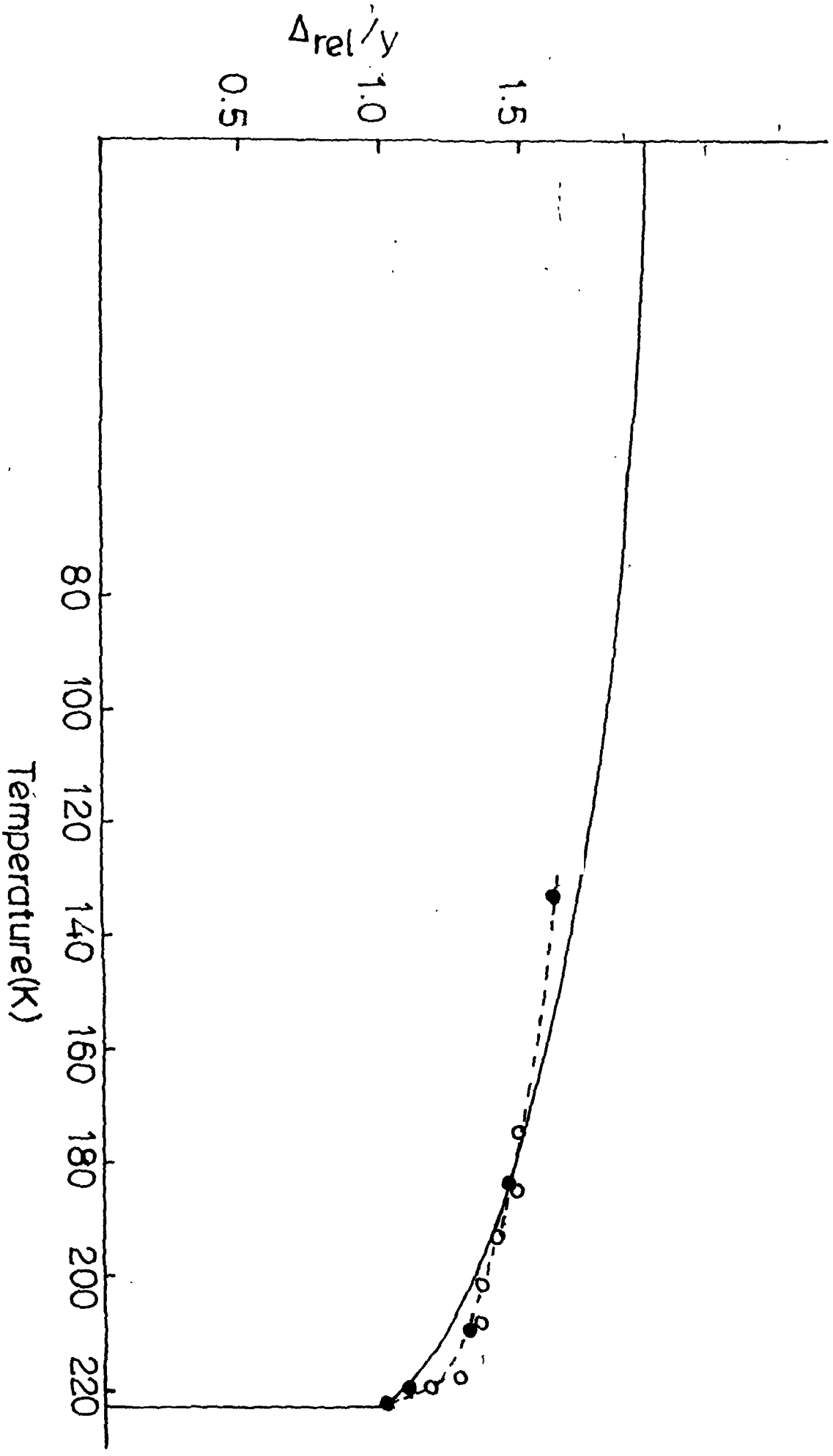

DISTORTION(Å UNIT)
0.60
0.50
0.40
0.30
0.20
0.10
δr
δx
δz
δy
240
220
200
180
160
140
120
TEMPERATURE(K)

Fig.4.3 Comparison of the tempeature dependence of the order parameter (y) used in the thermodynamic theory of transition by Ikeda **et al** (1973) and the experimental values of relative disotrtion in the SO_4^{2-} ion deduced from crystal structural data (●) and also from IR absorption intensity (O) of the distortion induced transition associated with the ν_1 mode of the ion.


Δ_{rel}/y
0.5
1.0
1.5
80
100
120
140
160
180
200
220
Temperature(K)

CHAPTER - V

PHENOMENOLOGICAL THEORY OF PHASE TRANSITION IN IMPROPER FERROELECTRIC AMMONIUM SULPHATE

5.1 Introduction

Several theoretical approaches have been developed to understand the microscopic mechanism of phase transition in **AS** (as reviewed in chapter II) based on (i) order-disorder of distorted NH_4^+ions[1], (ii) change in H-bond strength[2], (iii) displacive type mechanism involving a mixed mode of translatory and rotatory modes of NH_4^+ions[3], (iv) ferrielectric structure[4], (v) two sublattices of NH_4^+(I) and NH_4^+(II) and some other considerations[6,7]. However, none of these models as argued in the preceding chapters consistently account for the experimentally observed peculiar properties of the crystal. In chapter IV, we have concluded the molecular distortion type microscopic mechanism for the phase transition in **AS** based on our IR/Raman studies and analysis of crystallographic data as well as several other observations. Thus the physical nature of the order parameter has unambiguously been identified for the first time. In **this** chapter we use this mechanism as a base to develop the Landau type meanfield theory for the phase transition in **AS**, by introducing a linear coupling between the order parameter (SO_4^{2-}ion distortion) with spontaneous polarization. The theory is used to account for the temperature dependence of dielectric constants. The temperature dependence

of spontaneous polarization and its possible origin is also discussed.

5.2 Theoretical Formulation

The phenomenological theory of improper ferroelectrics is based on the coupling between the order parameter and the spontaneous polarization[8-15]. The spontaneous polarization and the z-component of SO_4^{2-} ion distortion in AS have the same symmetry, therefore, the lowest order interaction term in the expansion of free energy will be linear in both η and P_s. We further note that

i) AS is an improper ferroelectric where T_c does not change by electric field biasing[16], and

ii) the order parameter below T_c changes very slowly with temperature[17], while the changes in P_s may be significant. According to Unruh[4] P_s assumes maximum value 0.62 $\mu C/cm^2$ at 221.5K and goes to -0.03 $\mu C/cm^2$ at 8K through zero magnitude at 74.5K.

Both these observations reveal that the coupling between η and P_s is weak. It may be mentioned here that Ikeda et al[15] have also discussed the phenomenological theory of the transition in AS, however, in their formation they did not spell out the physical nature of the order parameter and in addition to the linear coupling between η and P_s they also included the terms of higher order coupling in their free energy expansion. The inclusion of higher order coupling may not be justified particularly when lowest order coupling is itself weak. One

also observes that by including higher order coupling, the calculated x and y components of dielectric constant exhibit discontinuity at T_c[15], whereas no such behaviour is found experimentally. We, therefore believe that the higher order coupling if at all is negligibly small, and the linear coupling term should be sufficient to understand the phenomenology of the transition in **AS**. Thus the free energy (G) of the system can be expressed as

$$G = \tfrac{1}{2}\alpha\eta^2 + \tfrac{1}{4}\gamma\eta^4 + \tfrac{1}{6}\delta\eta^6 + f\eta P_z + \tfrac{1}{2}\chi_{xx}^{-1} P_x^2 + \tfrac{1}{2}\chi_{yy}^{-1} P_y^2 + \tfrac{1}{2}\chi_{zz}^{-1} P_z^2 \qquad (5.1)$$

where $\alpha = \beta (T - T_\eta)$ and the terms, $\frac{1}{2}\chi_{ii}^{-1} P_i^2$ $(i = x,y,z)$ give the dielectric response of the system in an external applied field. Here f gives the strength of the coupling between order parameter (η) and the spontaneous polarization (P_z). As the total polarization results from the dipoles associated with SO_4^{2-}ion as well as NH_4^+(I) and NH_4^+(II) ions, the energy of the coupling $f\eta P_z$, may be given by

$$f\eta P_z = f_1\eta P_z^S + f_2\,\eta\, P_z^{n_1} + f_3\,\eta\, P_z^{n_2} \qquad (5.2)$$

where P_z^S, $P_z^{n_1}$ and $P_z^{n_2}$ are the polarization due to SO_4^{2-}, NH_4^+(I) and NH_4^+(II), respectively. In writing the Eqn. (5.2), we have considered the fact that the dielectric behaviour can equally be affected by changes in the structure and dynamics of NH_4^+ions although the transition is triggered by the SO_4^{2-}ion distortion. However, since the SO_4^{2-}ion distortion remains

fairly constant and P_z changes significantly with temperature, (discussed later in sec. 5.3) it is reasonable to argue that the temperature dependence of P_z is mainly due to the continuous reorientation of NH_4^+ dipoles and the coupling between order parameter and NH_4^+ dipoles is weak. Obviously the coupling between η and P_z is largely governed by $f_1 \eta P_z^s$.

Using G (Eqn. 5.1) in the equilibrium condition $\frac{\partial G}{\partial \eta} = 0$ we get

$$\alpha\eta + \gamma\eta^3 + \delta\eta^5 + f\ P_z = 0 \qquad (5.3)$$

In this expression the higher terms in η may be neglected to deduce the dielectric response for paraelectric phase

$$\eta = -(f/\alpha)P_z \qquad (5.4)$$

where P_z is the polarization produced in the lattice by subjecting the crystal to electric field E_z. Relation for dielectric constants may be obtained by using $\varepsilon_i = 1 + P_i/\varepsilon_o E_i$ alongwith the Eqn. (5.4) and $\frac{\partial G}{\partial P_i} = E_i$, E_i being the applied electric field, the result is

$$\varepsilon_x^P = 1 + \frac{1}{\varepsilon_o \chi_{xx}^{-1}} \qquad (5.5)$$

$$\varepsilon_y^P = 1 + \frac{1}{\varepsilon_o \chi_{yy}^{-1}} \qquad (5.6)$$

$$\varepsilon_z^P = \varepsilon_z^o + \frac{C}{T - T_o} \qquad (5.7)$$

where $\epsilon_z^o = 1 + (1/\epsilon_o)\ \chi_{zz}$, with curie constant $C = (f^2/\beta)\ \chi_{zz}/\epsilon_o$ $\cdot\chi_{zz}/\epsilon_o$. Here $T_o = T_c + (f^2/\beta)\ \chi_{zz}$, is the temperature where ϵ_z tends to infinity.

For ferroelectric phase in the absence of electric field and stress, we have

$$\left.\frac{\partial G}{\partial \eta}\right|_{\substack{\eta=\eta_s \\ P=P_s}} = 0; \quad \left.\frac{\partial G}{\partial P}\right|_{\substack{P=P_s \\ \eta=\eta_s}} = 0 \tag{5.8}$$

where η_s and P_s are the spontaneous value of order parameter and polarization, respectively. Using Eqn. (5.1) and (5.8), we get

$$\alpha\eta_s + \gamma\eta_s^3 + \delta\eta_s^5 + fP_s = 0 \tag{5.9}$$

$$\frac{P_s}{\chi_{zz}} + f\eta_s = 0 \tag{5.10}$$

In the presence of external applied field, the value of η_s and P_s will change and the new equilibrium will be obtained for

$$\eta = \eta_s' = \eta_s + \Delta\eta \tag{5.11}$$
$$P = P_s' = P_s + \Delta P$$

Using relation $\left.\frac{\partial G}{\partial \eta}\right|_{\substack{\eta=\eta_s' \\ P=P_s'}} = 0$ and $\left.\frac{\partial G}{\partial P_i}\right|_{\substack{\eta=\eta_s \\ P=P_s}} = E_i$, we can express E_i in terms of P_i to have

$$\epsilon_x^f = 1 + \chi_{xx}/\epsilon_o \tag{5.12}$$

$$\epsilon_y^f = 1 + \chi_{yy}/\epsilon_o \tag{5.13}$$

$$\varepsilon_z^f = 1 + \frac{\chi_{zz}}{\varepsilon_o}\left[\overline{1 + \frac{f^2\chi_{zz}}{a - f^2\chi_{zz}}}\right] \tag{5.14}$$

where $a = \alpha + 3\gamma\eta_s^2 + 5\delta\eta_s^4$ (5.15)

To investigate the temperature dependence of η and the dielectric constants we introduce a parameter y, the relative distortion of SO_4^{2-} ion defined by

$$y = \eta(T) \;/\; \eta(T_c) \tag{5.16}$$

where η (T) represents the value of order parameter at a given temperature T and $\eta(T_c)$ is that at T_c. Out of three (x,y and z) components of the dielectric constant, the expression for only z-component has explicit temperature dependence through $\alpha = \beta(T-T_\eta)$. Expression (5.14) may now be rewritten as

$$\varepsilon_z^f = 1 + \frac{\chi_{zz}}{\varepsilon_{oo}}\left[\overline{1 + \frac{A}{Py^2/2 + Qy^4}}\right] \tag{5.17}$$

$$P = \gamma\eta_c^2 \;/\beta\;(T_c - T_o) \tag{5.18}$$

$$Q = \delta\eta_c^4 \;/\beta\;(T_c - T_o) \tag{5.19}$$

and

$$A = \varepsilon_o\, \chi_{zz} f^2/4\,\beta\,(T_c - T_o) \tag{5.20}$$

Using Eqns. (5.16), (5.18), (5.19) and (5.20), the equilibrium condition $\left.\frac{\partial G}{\partial \eta}\right|_{\substack{\eta = \eta_s \\ P = P_s}} = 0$ can be rearranged to

$$t + Py^2 + Qy^4 = 0 \tag{5.21}$$

where

$$t = T - T_O / T_c - T_o, \tag{5.22}$$

Clearly Eqn. (5.21) provides temperature dependence of relative order parameter y.

5.3 Results and Discussion

The SO_4^{2-} ion distortion that we have concluded to be the order parameter is shown in chapter IV. In brief it represents the change in S-O bond lengths and O-S-O bond angles from the values compatible to tetrahedral structure. In other words it is the measure of the departure from the non-polar tetrahedral structure to a polar structure. In the present case the polar structure of SO_4^{2-} ion has C_s symmetry in paraelectric phase which changes to C_1 in ferroelectric phase. It has been shown that changes in S-O bond lengths as a result of freezing of symmetric ν_3(S-O stretch) polar mode present a reasonably accurate account of the observed heat of transition, revealing that the structural change responsible for the transition mainly involves the change in interatomic separation between S and O atoms of the SO_4^{2-} ion. In Figure 5.1 we plot the temperature variation of relative distortion of SO_4^{2-} ion. (Δ_{rel}) deduced from structural data using the relation

$$\Delta_{rel} = \frac{(|\delta\vec{r}^{-}(T)| - |\delta\vec{r}^{+}(T_c)|)}{(|\delta\vec{r}^{-}(T_c)| - |\delta\vec{r}^{+}(T_c)|)} \qquad (5.23)$$

where positive and negative sign signify the values of distortion $|\delta\vec{r}|$ above and below T_c at the temperature given in parentheses, respectively. $|\delta\vec{r}|$ is defined in chapter IV.

It may be mentioned that even in paraelectric phase SO_4^{2-} has finite distortion and therefore in order to evaluate the relative distortion as an exact

synonym of the relative order paremeters y (Eqn. 5.16), we substract $|\delta\vec{r}^{+}(T_c)|$ from $|\delta\vec{r}^{-}(T)|$ in Eqn. 5.23. Here $|\delta\vec{r}^{+}(T_c)|$ serves as a threshold distortion at which the transition commences.

It is found that the temperature variation of experimentally observed Δr_{rel} agrees well with Eqn.(5.22) and for P= -5.46 and Q = 4.46 and this fixes the values of these parameters for the use in Eqn. (5.17) to evaluate the tempeature variation of ϵ_z^f. If the polarizability of the ions does not change when the system goes from **PE** to **FE** phase, one may use ϵ_o/χ_{zz} and $A = C(\epsilon_o/\chi_{zz}/4(T_c-T_o)$ obtained by matching the paralectric experimental values with Eqn. (5.7) in the evaluation of z-components of dielectric constant in ferroelectric phase (eqn. 5.17). However, the theoretical results so evaluated do not agree with experimental values (see Fig.5.2). It appears that the above stated condition about the polarizability of the ions is not valid for **AS**. It should be noted that the microscopic mechanism of transition in **AS** envisages change in the structure and symmetry of microscopic units i.e. SO_4^{2-}, NH_4^{+}(I) and NH_4^{+}(II) and these ions acquire different magnitude of dipole moments below T_c. The magnitude also changes with change in temperature. Consequently **AS**, as a system of electric dipoles, which are the microscopic bases of dielectric properties to a larger extent, is different in ferroelectric phase than in paraelectric phase. Obviously ϵ_o/χ_{zz} and A to be used in

Eqn. (5.17) for evaluating ε_z^f are expected to differ from those value obtained from the agreement between experimentally measured ε_z^P and Eqn. (5.7). Moreover, the increased SO_4^{2-} ion electric dipole is located between the two NH_4^+ dipoles. The strength of the coupling of SO_4^{2-} ion distortion with other dipoles and thereby with macroscopic polarization P_z also increases.

In the light of the above discussion, we consider a set of changed values of A and ε_o/χ_{zz} to account for the observed temperature dependence of ε_z^f below T_c. The best agreement between the calculated results and the experimentally observed values (cf. Fig. 5.2) is obtained for A = .53 and ε_o/χ_{zz}= .206

The ferroelectric transition is the result of long range cooperation between molecular units. If there is no change in the polarisabilities of ions and the strength of the dipole moment associated with them, permitivity is expected to revert to its paraelectric value below T_c. However, in the present system there is a marked change in the dipole moments associated with the ions and this should obviously change the coupling between η and P_s. With the values of A = .53 and ε_o/χ_{zz} = .206 obtained as the best fit accounting for the observed temperature variation of ε_z^f (Eqn. 5.17) the coupling constant f is found to be 2.4 times that of the paraelectric value.

It may be mentioned that the measured dielectric constants reported in the literature[15,16,19-23] have some disagreement

as pointed out by Anistratov and Martinov.[23] However the latest data of Ikeda **et al**[15] agree with most of the results reported previously. We have therefore considered these data to be most reliable for our discussion. It may be mentioned that according to Eqn. (5.12), (5.13) ϵ_x and ϵ_y are expected to remain constant with temperature. This is consistent with experimental observations (Fig. 5.2). Minor differences can easily be understood in terms of minute microscopic changes that occur in the system. These changes are not supposed to be accounted for in such a phenomenological theory.

At this point some comment about the temperature dependence of spontaneous polarisations P_s would be in order. In the present theoretical framework P_s is related to the order parameter η_s through constant f and dielectric susceptibility χ_{zz} (Eqn. 5.10). As χ_{zz} is fairly constant below T_c, the spontaneous polarization is expected to exhibit the temperature dependence similar to η_s (see Fig. 5.1). This result seems to be in line with the experimental findings of temperature independent P_s by Hoshino **et al**[16] and Ikeda **et al**.[15] However, it may be mentioned that the experimental situation regarding the temperature dependence of P_s is not conclusive. Measurements by other reveal that : (i) P_s changes with temperature smoothly in magnitude as well as direction,[18] and (ii) the growth conditions of the crystal greatly influence the results[24] and one can observe P_s depending on temperature for one crystal and

temperature independent for the other. We make the following observations in this context.

i) All the ions in the crystal (i.e. SO_4^{2-}, NH_4^+(I) and NH_4^+(II) contributes to P_s[25] and we can have

$$P_s = n\,[p^s \cos(p^s, z) + p^n \cos(p^n, z) + p^n \cos(p^n, z)] \quad (5.24)$$

Here n is the number density of dipoles of SO_4^{2-}(p^s), NH_4^+(I)(p^n) and NH_4^+(II) (p^n), clearly, continuous orientation of the dipoles with the change in temperature will introduce temperature dependent change in P_s through cosine factors in Eqn.(5.24) even if the magnitude of different dipoles remain temperature invariant. The fact that all the three dipoles continuously reorient with temperature has already been concluded on the basis of the analysis of crystallographic data and NMR data.

ii) In the present approach we introduce the interaction of the order parameter η with the spontaneous polarization due to individual ions including NH_4^+ions through Eqn.(5.2). In principle this interaction should reveal the nature of P_s with change in temperature. However, the interaction coefficient f_1,f_2 and f_3 characterize weak coupling between η and P_s and the orientations of the dipoles are governed by relatively stronger dipole-dipole interactions. Consequently the continuous reorientation of dipoles and hence the temperature dependence of P_s cannot be strictly connected with the temperature dependence of the order parameter η_s.

iii) We also see the Eqn. (5.10) is derived from the stability conditions using the free energy expansion,

Eqn.(5.1). In strict sence this expansion is valid near T_c only. Obviously change in a physical property of the crystal at temperature away from T_c cannot be traced accurately in the framework of the phenomenological theory like this. This should be particularly true when the order-parameter interact only weakly with polarization.

In conclusion, the linear coupling between order parameter and polarization is sufficient to explain the ferroelectric transition in **AS** and its dielectric behaviour. The SO_4^{2-} ion distortion acts as the order parameter. The analysis clearly confirms the molecular distortion type (MD-type) mechanism in this system. A qualitative explanation of the temperature dependence of the spontaneous polarization and a clear picture of its microscopic origin is presented.

REFERENCES

1. O'Reilly, D.E., and Tsang, T. (1967) J. Chem. Phys. **46**, 529.

2. Schlemper, E.O., and Hamilton, W.C. (1966) J. Chem. Phys. **44**, 4498.

3. Sawada, A. Takagi, Y., and Ishibashi, Y. (1973) J. Phys. Soc. Jap. **34**, 748.

4. Unruh, H.G., and Rudiger, U. (1972) J. de. Physique **33** C2-77.

5. Sawada, A. Ohya, S. Ishibashi, Y., and Takagi, Y. (1975) J. Phys. Soc. Jap. **38**, 1408.

6. Petzelt, J. Grigas, J., and Mayerova, I. (1974) Ferroelectrics **6**, 225.

7. Iqbal, Z., and Christoe, C.W. (1976) Solid State Commu. **18**, 269.

8. Levanyuk, A.P., and Sannikov, D.G. (1968) Exp. Theor. Fiz. **55**, 256.

9. Levanyuk, A. P., and Sannikov, D.G. (1970) Fiz. Tverd. Tele. **12**, 2997.

10. Dvořák, V. (1970) J. Phys. Soc. Jap, **28**, Suppl. 252.

11. Dvořák, V. (1971) Physica Status Solidi b **45**, 147.

12. Dvořák, V. (1974) Ferroelectrics **7**, 1.

13. Ovorkale, V. and Petzelt, J. (1971) Phys. Lett. **35A**, 209.

14. Kobayashi, J. Enomoto, Y., and Sato, Y. (1972) Physica Status Solidi b **50**, 335.

15. Ikeda, T. Fujibayashi, K., Nagai J., and Kobayashi, J. (1973) Physica Status Solidi a **16**, 1979.

16. Hoshino, S. Vedam, K. Okaya, Y. and Pepinsky, R. (1958) Phys. Rev. **112**, 405.

17. Bajpai, P.K. and Jain, Y.S. (1987) J. Phys. C- Solid State Phys. **20**, 3789.

18. Unruh, H.G. (1970) Solid State Commu. **8**, 1951.

19. Kamiyoshi, K., and Miyamoto, T. (1954) J. Chem. Phys. **22**, 756.

20. Koptsik, V.N. Strukov, B.A. Sklyankin A.A., and Levina, M.E. (1960) Izv Akad. Nauk SSSR, Ser. Viz. **24**, 1228.

21. Oshima, H., and Nakamura, E. (1966) J. Phys. Chem., Solids, **27**, 481.

22. Unruh, H.G. (1956) Phys. tell. **17**, 8.

23. Anistratov, A.T., and Martynov, V.G. (1970) Sov. Phys. Crystallography 15, 256.

24. Zaitseva, M.P. and Rozhnova, G.P. (1975) Kristallogr. 20, 178.

25. Jain, Y.S., and Bist, H.D. (1974) Physica Status Solidi b. 62, 295

Fig.5.1 Temperature variation of the typical order parameter for the first order phase transition (- - -) and the relative distortion of SO_4^{2-} ion recognised as the order parameter for ammonium sulfate (circles). These points match with Eqn(5.21) for P= -5.46 and Q = 4.46 (cross points).

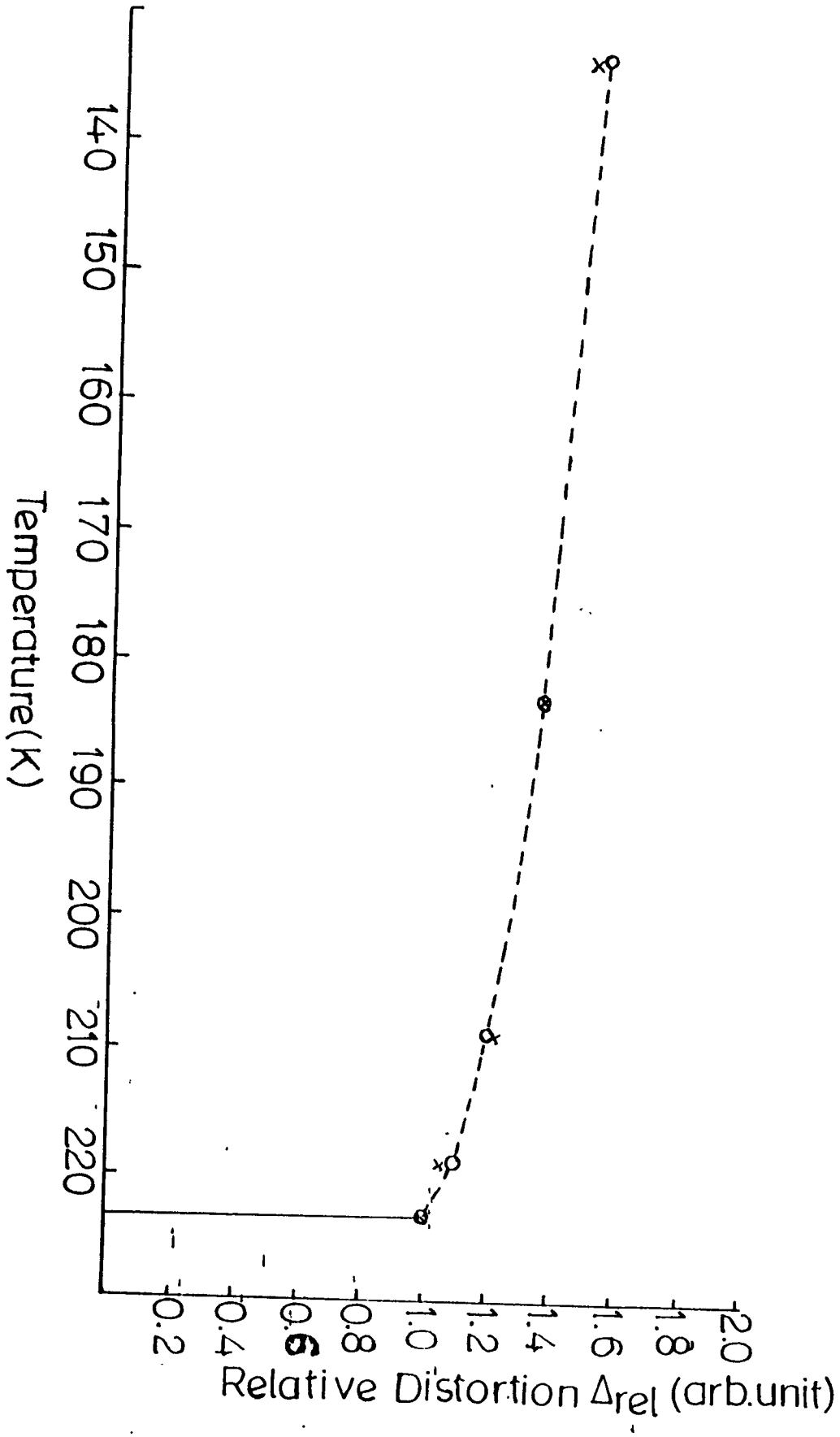
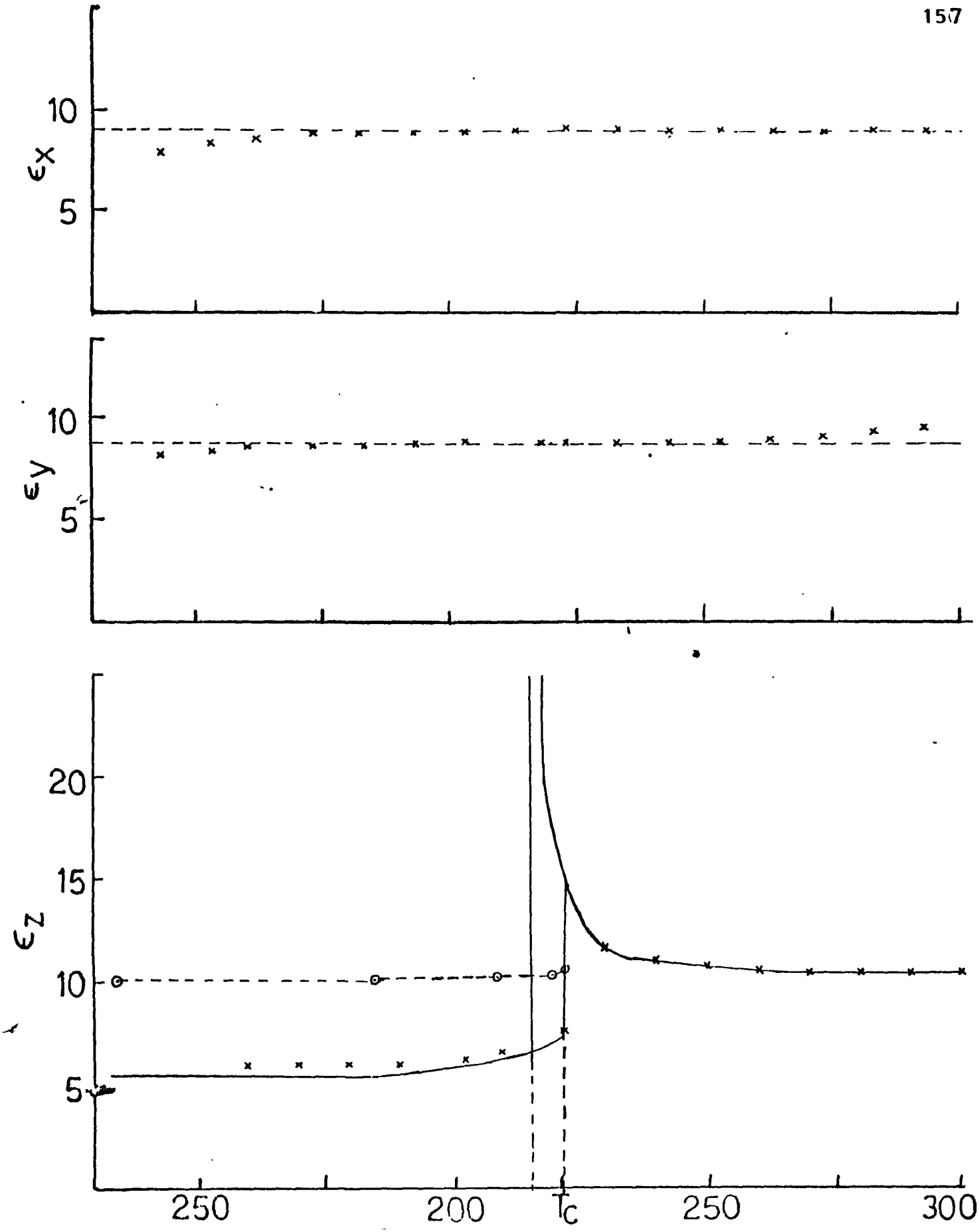

Temperature(K)
140
150
160
170
180
190
200
210
220
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
Relative Distortion Δ_{rel} (arb.unit)

Fig.5.2 Comparison of the temperature dependence of the dielectric constants ϵ_x, ϵ_y and ϵ_z present theory (-) and experimental values (X) (Ikeda **et al** 1973); for ϵ_z in paraelectric phase two results match for $\epsilon_o \chi_{zz}$= 0.11 and A =.097; however for these values ϵ_z in ferroelectric phase calculated from Eqn.(5.17) (circles) does not match with experimental values. The agreement is obtained for $\epsilon_o \chi_{zz}$ = .206 and A = .53.


10
ϵ_x
5
10
ϵ_y
5
20
15
ϵ_z
10
5
250
200
T_c
250
300

CHAPTER - VI

SUMMARY AND CONCLUSIONS

The present investigation was undertaken with a view to understand the correct microscopic mechanism of phase transition in **ammonium sulphate**, which in many respects represents a class of crystals such as $(NH_4)_2\ Cd(SO_4)_3$, $(NH_4)_2\ BeF_4$, etc.[1] exhibiting structural phase transition with peculiar phenomenological properties. We were motivated to undertake this work in view of the fact revealed for the first time from the study by Jain and Bist[2,3] that SO_4^{2-} ion gets distorted at T_c and the microscopic mechanism of the transition should be centred around this change, indicating towards a new type of phenomenological behaviour. Since after the work of Jain and coworkers[3] several experimental observations corroborated their inferences[4-9]. However, there have been some reports[10-12] not only giving the NH_4^+ ions an importance for having major role in the mechanism of phase transition but also questioning its first order nature well evident from the finite latent heat involved in the transition[13]. These reports confused the understanding of the phase transition and we felt a need to critically examine the results of various investigations and the suggestion of Jain and coworkers[3] to settle the issue of apparent contradiction and to reveal the factual mechanism of structural phase transition.

In view of the fact that IR and Raman spectroscopic studies can reveal the structural and dynamical changes in the crystal around T_c, the temperature dependence of several modes of NH_4^+ and SO_4^{2-} ions as well as those due to D-modes of partially deuterated NH_4^+ ion (at low degree of deuteration) have been investigated. The study of D-modes is of particular interest since these modes can provide information about the change around individual H-atoms. At times, it was suggested that structural data if available at different temperatures near T_c can help in revealing the physical changes at T_c, and the required data have recently been published by Hasebe[14] for this crystal. Therefore, the analysis of his crystal structural data was also undertaken.

From the IR and Raman studies, it is inferred that changes in NH_4^+ ions as well as those in H-bonding at T_c are minor and gradual. On the other hand similar study of SO_4^{2-} modes reveal that the SO_4^{2-} ion undergoes a significant and sudden change. The change in linewidth of ν_1 (SO_4^{2-}) modes in Raman spectra indicates the presence of phonon-pseudospin coupling. The sudden change in the intensities, split separation/frequency shift in SO_4^{2-} modes are found to be consistent with the theory of Dvořák and Petzelt[15] revealing that order parameter should change the way these quantities change with temperature. Analysis of IR/Raman spectra also reveals that the transition is triggered by SO_4^{2-} ion distortion and the changes in NH_4^+ ions are its after-effect.

It is found that the properties of the crystal depending only on NH_4^+ions may not change suddenly at T_c, indicating that the transition has second order behaviour. On the other hand, properties depending also on the SO_4^{2-}ion may show first order behaviour. Perhaps this is the reason that several investigators[10,11] studying the properties depending on the NH_4^+ions only mistook the transition to be of second order, even when the transition is known to have non-zero heat of transition.

The temperature dependence of molecular distortion in SO_4^{2-}, NH_4^+(I) and NH_4^+(II), calculated from x-ray crystallographic data reveals that the SO_4^{2-}ion distortion changes slowly and smoothly, except at T_c, where it suddenly increases by a factor of 2.0. This is found to be consistent with our experimental study of IR Raman spectra. The changes in the distortion of NH_4^+ions (if at all occur) are gradual. Moreover, the temperature variation of the polar distortion of the SO_4^{2-}ion and its components reveals that SO_4^{2-}ion rotates about z-axis in the paraelectric phase and about x-axis in the ferroelectric phase. The analysis confirms the spectroscopic conclusion that SO_4^{2-}ion distortion is the order parameter of the transition. It is concluded that the type of transition occuring in ammonium sulphate is different from the well known displacive/order-disorder type. A new microscopic mechanism for the phase transition proposed to be known as molecular distortion type (MD-type) has been concluded. MD-type transition can only take place in crystals having one or more than one kind of molecular

units. It leads to a change mainly in the structure and symmetry of such units, rather than in their location and orientation and it is expected to arise mainly from ν_3 polar mode of SO_4^{2-}ion. The model has been used to estimate the heat of transition, giving the result 4.2+0.4kJ/mole; this agrees well with the experimentally observed values (3.89-4.27)±0.02kJ/mole[13,16]. The physical nature of the order parameter has been clearly understood for the first time. The relative distortion in SO_4^{2-}ion calculated through crystallographic data as well as **IR** absorbance using the theory of the intensity of forbidden modes matches closely with the theoretical temperature dependence of the order parameter[17].

A phenomenological theory of the phase transition in improper ferroelectric Ammonium sulphate has been discussed, on the basis of molecular distortion type microscopic mechanism. The distortion in SO_4^{2-}ion is considered as the order parameter and its coupling with the spontaneous polarization in the free energy expression is included to account for the ferroelectric behaviour. In previous theories[17,18] of this phase transition where an unidentified quantity was considered as the order parameter, higher order coupling is taken in free energy expression. In our approach, it is concluded that the higher order coupling is negligibly small and the linear coupling term should be sufficient to understand the phenomenology of the phase transition in **AS**

The theory has been used to account for the dielectric behaviour in both paraelectric and ferroelectric phases. The temperature dependence of $\varepsilon_x, \varepsilon_y$ and ε_z (components of dielectric constants) deduced from our theory matches quite closely with the experimental results. The temperature dependence of the order parameter has also been calculated and it matches very well with the SO_4^{2-} ion distortion and obviously confirms our conclusion that SO_4^{2-} ion distortion acts as the order parameter. A qualitative explanation of the temperature dependence of the spontaneous polarization and a clear picture of its microscopic origin is presented.

In conclusion, the thesis summarizes the uptodate knowledge about the phase transition in ammonium sulphate and concludes the factual nature of the microscopic mechanism of the phase transition in this crystal. The peculiar nature of this phase transition has been shown to originate from a new mode of microscopic mechanism i.e. molecular distortion type not known earlier. The basic difference of this mechanism from the well known order-disorder and displacive type has been spelled out.

It should be noted that many compounds such as $(NH_4)_2 Cd(SO_4)_3$, $(NH_4)_2 BeF_4$ etc. exhibit ferroelectric transition similar to that of **AS**. These properties are entirely different than those of proper ferroelectrics. It may therefore be argued that the phase transition in these materials might also be

similar to that of $(NH_4)_2\ SO_4$ and the MD-type microscopic mechanism of phase transition might successfully be applied to understand the phenomenal behaviour of structural phase transition in these compounds also.

REFERENCES

1. Onodera, A. Cynshi, O., and Shiozaki, Y. (1985) J. Phys. C- Solid State Phys. **18**, 2831.

2. Jain, Y.S., and Bist, H.D. (1974) Solid State Commu. **15** 1229.

3. Jain, Y.S., and Bist, H.D. (1974) Physica Status Solidi a**62** 295.

4. Jain, Y.S., Bist, H.D. Upreti, G.C. (1973) Chem. Phys. Lett. **22**, 572.

5. Ramnathan, K.V., and Srinivasan, R. (1978) Chem. Phys. Lett. **56**, 359.

6. Narayana, M., and Srinivasan, R. (1978) Physica Status Solidi b**68**, 703.

7. Manjunath, C.V., and Srinivasan, R. (1978) Physica Status Solidi, b**87**, 395.

8. Hirabayashi, K., and Abe, R. (1980) J. Phys. Soc. Jap. **48**, 520.

9. Barb, D. Greecu, N.M., Green, V-V. and Popescu, F.F. (1978) Chem. Phys. Lett. **56**, 355.

10. Dalhborg, U. Larsson, K.E., and Pirkmajer, E. (1970) Physica **49**, 1.

11. Parsonaje, N.G., and Staveley, L.A.K. (1978) In "Disorder in Crystals" Oxford University Press, Oxford.

12. Miller, S.R. Blinc, R. Brenman, M. and Waugh, J.S. (1962) Phys. Rev. **126**, 528.

13. Hoshino, S. Vedam, K. Okay, Y., and Pepinsky, R. (1958) Phys. Rev. **112**, 405.

14. Hasebe, K. (1981) J. Phys. Soc. Jap. **50**, 1266.

15. Dvořák, V. and Petzelt, J. (1978) J. Phys. C- Solid State Phys. **11**, 4827.

16. Higashagaki, Y., and Chihara, H. (1981) Bull. Chem. Soc. Jap. **54**, 901.

17. Ikeda, T. Feyibayashi, K. Nagai, T., and Kobayashi, J. (1973) Physica Status Solidi a**16**, 279.

LIST OF RESEARCH PAPERS

1. Structural Phase transition in Ammonium Sulphate: Role of deuterated NH_4^+ ions and heat of transition.

   P.K. Bajpai and Y.S. Jain : J. Phys. C-Solid State Physics 20 (1987) 3989.

2. Phase transition and temperature dependence of the molecular distortion of ions in Ammonium Sulphate.

   Y.S. Jain, P.K. Bajpai, R. Bhattacharjee and D. Chowdhury. J. Phys. C-Solid State Phys. **19** (1986) 387.

3. Phenomenological theory of phase transition in improper ferroelectric Ammonium Sulphate:

   P.K. Bajpai, P.N. Ram, and Y.S. Jain. J. Phys. C-Solid State Phys. **20** (1987) 0000.

4. A phenomenological theory of phase transition in improper ferroelectric Ammonium Sulphate.

   P.K. Bajpai, Y.S. Jain and P.N. Ram. Solid State Phys. Phys. Symposium (1987) Pantnagar.

5. On the temperature dependence of the linewidth of SO_4^{2-} modes in the Raman Spectra of $(NH_4)_2SO_4$

   P.K. Bajpai, Y.S. Jain, P.K. Khulbe and H.D. Bist. (Under preparation)

6. Effect of crystal field on the vibrational modes of molecular units.

   P.K. Bajpai, Y.S. Jain and R. Bhattacharjee. (Under preparation).