STRUCTURAL PHASE TRANSITION IN IMPROPER FERROELECTRIC AMMONIUM SULPHATE

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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.

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