

**FERROELASTIC PHASE TRANSITION IN SOME PHENOLS-AMINES ADDUCTS
– EXPERIMENTAL AND THEORETICAL FINDINGS**

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ABSTRACT

A new type of structural phase transition has been discovered recently in a class of hydrogen-bonded organic crystals. The transition is ferroelastic, second order in nature, and associated with the spontaneous breaking of a mirror symmetry in the crystal below the transition temperature. The transition has been analysed by a phenomenological expansion of Landau free energy. We propose that the transition is induced by cooperative hydrogen bond interactions indirectly coupled through the lattice phonons. A microscopic model is formulated according to this concept.

INTRODUCTION

Crystalline solids containing phenols-amines adducts are widely used to study hydrogen bonds. Phenols-amines adducts are produced by the interaction of phenols, compound having at least one hydroxyl group, and amines, compounds having at least one amino group. The phenols and amines in the solid state are generally linked by intermolecular O–H...O, O–H...N or N–H...O types of hydrogen bonds which are among the most robust and versatile synthons in crystal engineering. Studies on the hydrogen bondings in these phenols-amines adducts can be used as models for the more complicated systems in biological systems in which hydrogen bondings play a crucial and important role. Owing to our interests in hydrogen bondings in such systems, we have investigated systematically in single crystal forms a class of phenols-amines adducts and their crystal structures were reported¹⁻⁸. Some of these single crystals of phenols-amines adducts undergo a reversible phase transition with variation in temperature. For these samples, a hydrogen atom is transferred from the phenols (which then becomes as anion) to the amines (which then becomes a cation). Hydrogen bonds are then established between the donor/amines/cation and the acceptor/phenols/anion. Interestingly, these crystals undergo a temperature-dependent structural phase transition, which is second-order ferroelastic in its nature. These are the first reported cases of structural phase transition induced by hydrogen bonding interactions.

RESULTS AND DISCUSSION

The phase transition that has been observed are classified into two categories (1) orthorhombic-to-monoclinic transition, and (2) monoclinic-to-triclinic transition. In both these categories, the phase transitions are a result of the breaking of a mirror-plane symmetry when the temperature is lowered through the critical temperature, T_c ; the lower symmetric

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phase being the low-temperature phase. The three crystal structures found to exhibit these phase transitions are quinuclidinium-2,4-dinitrophenolate (I), hexamethylenetetraminium-3,5-dinitrobenzoate-3,5-dinitrobenzoic acid monohydrate(II), and hexamethylenetetraminium 2,4-dinitrophenolate monohydrate (III). Experimentally we have solved the 3-D structures of both the high and low temperature polymorphs of (I), (II), and (III), and have also measured the temperature dependence of these unit cell parameters through their transition temperatures^{1,6,7,9}.

On the theoretical side, phenomenological expressions of Landau free energies have been formulated based on the assumption that these transitions are second order ferroelastic in nature. The temperature dependence of unit cell parameters predicted is consistent with experimental findings and functional forms of temperature dependence of shear modulus and specific heat of the bulk crystals were also derived⁹. Landau's theory, being macroscopic and phenomenological, however, cannot indicate the microscopic origin of these phase transitions. We have formulated in parallel a microscopic theory, in which the proposed main mechanism responsible for the phase transitions is the cooperative interactions of hydrogen bonds with the lattice vibrations, or phonons, of the crystal¹⁰. This findings of Landau and microscopic theories based on the experimental data were presented in this conference.

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