Pressure-Induced Ferroelectricity
in $(NH_4)_3H(SO_4)_2$

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Dielectric properties of single crystal $(NH_4)_3H(SO_4)_2$ were measured in a pressure and temperature region of $p \lesssim 8.5$ kbar and $-100°C \lesssim T \lesssim RT$. A broad peak of the dielectric constant along the c^*-direction which is found around $-25°C$ at 1 atm becomes sharp and intense as pressure increases, and then above 5.0 kbar a ferroelectric phase (Phase VI) appears. Further increase in pressure stabilizes another ferroelectric phase (Phase VII) in a lower temperature region. The VI-VII transition is of the first order. Temperature dependence of the spontaneous polarization was measured at various pressures. A two-sublattice model is presented to interpret the pressure and temperature dependence of the dielectric properties of $(NH_4)_3H(SO_4)_2$.

§1. Introduction

Triammonium hydrogen disulfate $(NH_4)_3$ $H(SO_4)_2$ has five polymorphic modifications at atmospheric pressure.[1] In the present paper they are denoted as Phase I, II, III, IV, and V in the order of descending temperature. The transition temperatures and the crystal systems at 1 atm are described in Table I. Ferroelectric activity has not been observed for any of the phases at 1 atm. Besides the phase transitions listed in Table I, a broad peak of the dielectric constant along the c^*-direction (perpendicular to the (001) plane of the monoclinic system at room temperature) is found at around $-25°C \sim$ $-28°C$;[1] i.e. in the region of Phase III. That is, as temperature decreases a fluctuation of electric dipoles first increases and then decreases without diverging to stabilize a ferroelectric structure. It is interesting to see the effect of external stresses or addition of impurities on the anomalous dipole fluctuation in $(NH_4)_3H(SO_4)_2$.

The hydrostatic-pressure dependence of the dielectric properties of $(NH_4)_3H(SO_4)_2$ was preliminarily reported.[2] It was shown that the broad peak of dielectric constant becomes sharp and intense as pressure increases. The maximum value of the dielectric constant tends to diverge at a critical pressure $p_0 \sim 5.1$ kbar, and a ferroelectric phase appears slightly below the critical pressure. The pressure-induced ferroelectric phase is called Phase VI. Further increase in pressure stabilizes second ferroelectric phase (Phase VII) in a lower temperature region. The pressure-temperature phase diagram of $(NH_4)_3H(SO_4)_2$ including the I–II phase boundary was published elsewhere.[3]

In the present paper the pressure and temperature dependence of the dielectric properties of single crystal $(NH_4)_3H(SO_4)_2$ is described in connection with the stabilization of ferroelectric structures at high pressures. Comparison with the dielectric properties of Rochelle salt-ammonium Rochelle salt system is given. Then, the observed results are interpreted on the basis of a two-sublattice model which is a modification of Mitsui's theory of Rochelle salt.[4] It is shown that the theory can qualitatively represent the pressure-temperature phase diagram and the variation of dielectric properties in the p-T plane.

Table I. Successive transitions in $(NH_4)_3H(SO_4)_2$ at 1 atm.

Phase	I		II		III		IV		V
Crystal system	trigonal		monoclinic		monoclinic				
Space group	$R\bar{3}m$		$A2/a$						
Transition point		140°C		$-8°C$		$-136°C$		$-140°C$	

§2. Experimental

Single crystals of $(NH_4)_3H(SO_4)_2$ were grown by slow evaporation of an aqueous solution containing 40 wt. % $(NH_4)_2SO_4$ and 24 wt. % H_2SO_4 at around 30°C.[1] The as-grown crystals were of pseudo-hexagonal plates with the dominant face of (001). After attached silver paste on the (001) surfaces as electrodes, the specimen was set in a Cu–Be high pressure bomb which had seven electrical terminal plugs. The pressure-transmitting fluid used was 1:1 mixture of *iso*- and *n*-penthane. The dielectric constant of the specimen was measured with a three terminal capacitance bridge at a constant frequency of 100 kHz as functions of temperature at various pressures up to about 8.5 kbar below room temperature. Spontaneous polarizations in the high pressures were measured with a conventional Sawyer-Tower circuit at 50 Hz. Temperature of the specimen was varied by using a liquid-nitrogen bath, and measured with a copper-constantan thermocouple which was closely set around the specimen. Pressure was measured with a manganine gauge.

§3. Results

Figures 1 and 2 indicate the temperature dependence of the dielectric constant along the c^*-direction at various hydrostatic pressures. As seen in Fig. 1, the broad peak of the dielectric constant which is found at around −25°C at 0 kbar becomes more and more conspicuous as pressure increases. The peak value of the dielectric constant is about 60 at 0 kbar, but it grows to about 1,500 at 4.90 kbar. Above about 5.0 kbar, the peak splits into two rather sharp peaks on a cooling process indicating that there is a pressure-induced phase between them. The phase is denoted as Phase VI. As temperature further decreases the dielectric constant discontinuously decreases showing that there is a phase transition to an another high pressure phase (denoted as Phase VII). On a heating process at 5.11 kbar the peak of dielectric constant at lower temperature is masked by the thermal hysteresis, and Phase VII directly transforms to Phase VI without passing through Phase III as seen in Fig. 2. Above 5.2 kbar direct transition from VI to VII takes place even on a cooling process. The VI–VII transition is of the first order accom-
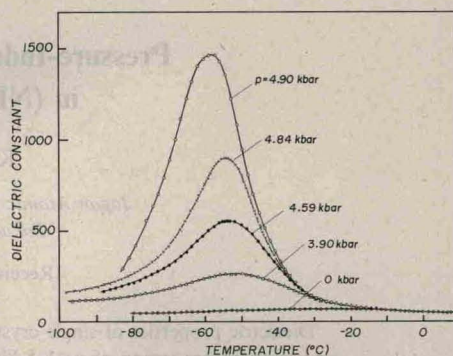

Fig. 1. Temperature dependence of the dielectric constant of $(NH_4)_3H(SO_4)_2$ along the c^*-direction at various hydrostatic pressures. Frequency: 100 kHz.
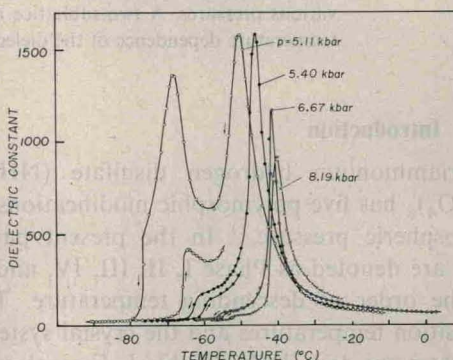

Fig. 2. Temperature dependence of the dielectric constant of $(NH_4)_3H(SO_4)_2$ along the c^*-direction at various hydrostatic pressures above 5 kbar. Frequency: 100 kHz.

panied with a discontinuous jump in the dielectric constant and with a thermal hysteresis of the transition. However, the first-order nature of the transition becomes insignificant as pressure increases. It is suggested that the thermal hysteresis of the VI–VII transition tends to zero at about 11 kbar[3] by an extrapolation.

Ferroelectric activity is found both in Phase VI and in Phase VII. Figure 3(a) and (b) respectively show the ferroelectric hysteresis loops in Phases VII and VI. Figure 4 shows the temperature dependence of the spontaneous polarization at different pressures on heating. It should be noted that above about −50°C uncertainty in the spontaneous polarization becomes large because of increase of conductivity of the specimen. At the VII–VI transition a discontinuous change in the spontaneous polarization is seen as shown by