PROC. JSSF-2, KYOTO, 1980
J. PHYS. SOC. JPN. **49** (1980) SUPPL. B, pp. 182–184.

Phase Transitions and Ferroelectricity in the $(NH_4)_3H(SO_4)_2$-Type Crystals

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A review is given for the phase transitions and ferroelectricity in the $X_3H(YZ_4)_2$-type crystals. (X: NH_4, K, Rb; YZ_4; SO_4, SeO_4) In $(NH_4)_3H(SO_4)_2$ stabilization of ferroelectric VI and VII phases is discussed in the three dimensional deuterium-concentration/pressure/temperature phase space. Ferroelectricity and large isotope effect on the Curie point are found in $(NH_4)_3H(SeO_4)_2$. Deuteration of $K_3H(SO_4)_2$ and $Rb_3H(SO_4)_2$ causes new phase transitions in low temperature region.

In the present paper, phase transitions in some of $X_3H(YZ_4)_2$-type compounds are described, where X stands for a monovalent ion, e.g. NH_4, Na, K, Rb. Cs, Tl, and YZ_4 is SO_4, SeO_4 or BeF_4. These compounds are attractive because of successive phase transitions and marked isotope and pressure effects.

Phase transitions and ferroelectricity in triammonium hydrogen disulfate $(NH_4)_3H(SO_4)_2$ were widely studied by the present author and others. At room temperature, $(NH_4)_3H(SO_4)_2$ belongs to the monoclinic symmetry, but the distortion from the trigonal symmetry is very slight.[1] Ferroelastic behavior of this crystal was known long time before the terminology *ferroelasticity* was proposed.[2] The transition to the trigonal phase is found at about 140°C on heating.[1,3] Below room temperature, four phase transitions were observed by the present author at −8°C, −136°C, −140°C, and −210°C.[4,5] The phase transition sequence in $(NH_4)_3H(SO_4)_2$ at atmospheric pressure is given in Table I. In addition to the phase transitions, there is a broad peak of the dielectric constant measured along the c^*-direction at around −25°C.

When hydrostatic pressure is applied, the broad peak becomes sharp and intense.[6] The peak value of dielectric constant $\varepsilon_{\max}$ is represented by a Curie-Weiss like relation of $\varepsilon_{\max} = C^*/(p_c - p)$ as a function of pressure p, where $C^* = 3.2 \times 10^{-2}\,\mathrm{GPa}^{-1}$ and $p_c = 0.51$ GPa.[6] Slightly below the critical pressure p_c, the peak splits into two sharp maxima, and a ferroelectric phase (Phase VI) appears between them. Further increase in pressure stabilizes another ferroelectric phase of VII in the lower temperature range. The transition between the two ferroelectric phases is of the first order, but the first order nature becomes insignificant as pressure increases. The critical point of the VI-VII transition at which the first order nature of the transition disappears is estimated to be at 1.1 GPa.[3] Whether it is tricritical or of liquid-

Table I. Successive phase transitions in $(NH_4)_3H(SO_4)_2$ at atmospheric pressure. The lowest temperature phase is known to be identical with the pressure-induced ferroelectric phase of VII from the study of the phase diagram of the normal-deuterated compounds system.[5]

Phase	I	II	III	IV	V	VII
State		Ferroelastic				(Ferroelectric)
Crystal system	Trigonal	Monoclinic				
Space group	$R\bar{3}m$	$A2/a$				
T_c(°C)	140	−8	−136	−140	−210	

└Broad peak of dielectric constant around −25°C.

gas type is an interesting problem in future.

Figure 1 shows the pressure-temperature phase diagram of $(NH_4)_3H(SO_4)_2$ in a range of $p \lesssim 0.9$ GPa and room temperature $> T \gtrsim -100$°C. In the figure, a solid circle indicates the position of the broad dielectric constant peak on a constant pressure run. A similar behavior was observed by deuteration as to the stabilization of the ferroelectric VI and VII phases:[7] In deuterated crystal with the deuterium concentration more than about 90% shows the ferroelectric VI phase even at atmospheric pressure. In order to establish the phase relation between the ferroelectric phases found in high pressure region and in deuterated crystal, the pressure-temperature phase diagrams were studied for crystals with various deuterium concentrations. Then, the three dimensional deuterium concentration x/ pressure p/ temperature T phase diagram was obtained.[8] Figure 2 shows the $p-T$ phase diagram of 97% deuterated crystal as the end member of the normal-deutrated crystal system.[8] There are two pressure-induced intermediate phases, VIII and IX, between the room temperature phase of II and the ferroelectric VI phase. The structures of the intermediate phases of III, VIII, and IX are not known for the present. The II-III phase transition is characterized by a marked λ-type anomaly of the specific heat and a wide critical region although the anomaly in dielectric constant is obscure.[9] The dielectric constant variation in the transition region of II-IX-VI in deuterated crystal at high pressures somewhat resembles to that found in the paraelectric-incommensurate-ferroelectric phase transition sequence of $NaNO_2$.[10] It would be plausible that there are certain kinds of superstructures or incommensurate lattice modulations in these intermediate phases. In the deuterated crystal, the critical point of the ferroelectric-to-ferroelectric VI-VII transition seems to exist at around 0.85 GPa because of the disappearance of the thermal hysteresis. However, an appreciable dielectric constant peak is not found around the critical point.[8]

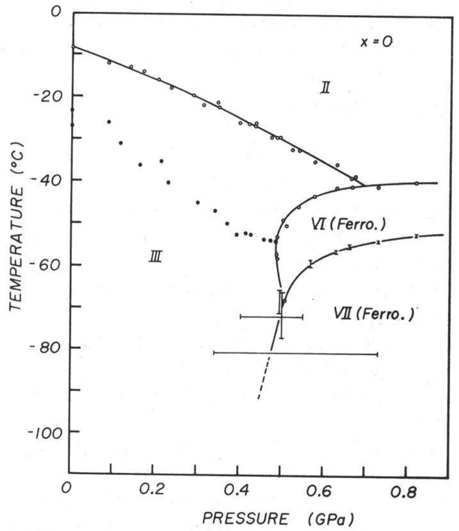

Fig. 1. Pressure-temperature phase diagram of $(NH_4)_3H(SO_4)_2$. Solid circle shows the position of the broad dielectric constant peak. Short bars indicate temperature or pressure hysteresis of first order transitions.

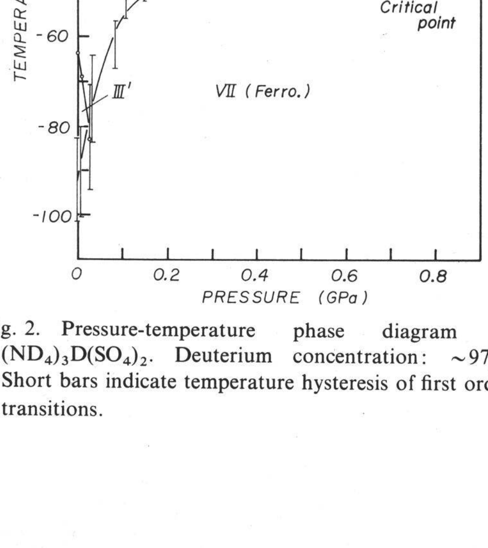

Fig. 2. Pressure-temperature phase diagram of $(ND_4)_3D(SO_4)_2$. Deuterium concentration: ~97%. Short bars indicate temperature hysteresis of first order transitions.

It was found that the phase transitions and ferroelectricity of $(NH_4)_3H(SO_4)_2$ in the pressure-temperature space can be described qualitatively from a simple two sublattice model which is a modification of Mitsui's model of Rochelle salt.[6] The calculated dielectric susceptibility and phase diagram well represent the ones observed experimentally. In the scope of the model assumed, the two ferroelectric phases, VI and VII, are isostructural, and the critical point of the phase transition between them is of the liquid-gas type.

From the above results, one may conclude that the ferroelectricity in $(NH_4)_3H(SO_4)_2$ is not fully described in a one dimensional T-space, as is done for usual ferroelectrics, but should be described in a two dimensional phase space; $p-T$ or $x-T$ space, where x stands for the concentration of deuterium. The same argument would be applied for Rochelle salt of which ferroelectricity is similar to that found in $(NH_4)_3H(SO_4)_2$.[11]

The compound $(NH_4)_3H(SeO_4)_2$ shows several phase transitions around room temperature, and becomes to be ferroelectric below -92°C.[12] The Curie temperature linearly increases with increasing pressure with a rate of 23 deg GPa^{-1}.[12] The pressure-temperature phase diagram of $(NH_4)_3H(SeO_4)_2$ is therefore simple in comparison with that of $(NH_4)_3H(SO_4)_2$. The ferroelectricity in $(NH_4)_3H(SeO_4)_2$ is enhanced by deuteration; an increase in the spontaneous polarization and raise of the Curie temperature are caused by deuteration.[13]

No phase transitions were observed in $Rb_3H(SO_4)_2$, $Rb_3H(SeO_4)_2$, and $K_3H(SO_4)_2$ below room temperature down to liquid helium temperature. The dielectric constant along the c^*-direction of these crystals monotonically increases with decreasing temperature down to liquid helium temperature. On the other hand, deuterated crystals $Rb_3D(SO_4)_2$ and $K_3D(SO_4)_2$ show phase transitions at -202°C and -189°C, respectively, which are characterized by small λ-type anomalies in dielectric constant.[14] This would be another example of marked isotope effects in the $X_3H(YZ_4)_2$-type compounds.

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