Dielectric Study on the Effect of Hydrostatic Pressure on the Phase Transitions in the System of $\{(NH_4)_3H(SO_4)_2\}_{1-x}\{(ND_4)_3D(SO_4)_2\}_x$
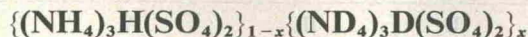
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The concentration-pressure-temperature three dimensional phase diagram of $\{(NH_4)_3H(SO_4)_2\}_{1-x}\{(ND_4)_3D(SO_4)_2\}_x$ system was studied by means of dielectric measurements in a pressure-temperature range of $p \lesssim 10$ kbar and $-100°C \lesssim T <$ room temperature. The two pressure-induced ferroelectric phases of VI and VII in the normal compound ($x=0$) are found in lower pressure region as the concentration x increases. Compounds with $x>0.90$ show the ferroelectric VI phase even at atmospheric pressure. A good correspondence between the effects of hydrostatic pressure and deuterium-substitution was established as regards the stability of the ferroelectric phases. Two pressure-induced phases (Phases VIII, IX) were newly observed in the normal-deuterated mixed crystal system.

§1. Introduction

At atmospheric pressure triammonium hydrogen disulfate $(NH_4)_3H(SO_4)_2$ has five polymorphic modifications above liquid nitrogen temperature.[1] Recently, one of the present authors (KG) found an additional phase transition at around $-210°C$.[2] Then, six phases have been known in $(NH_4)_3H(SO_4)_2$ at atmospheric pressure. They are conventionally denoted I, II, III, IV, V, and VII in the order of descending temperature. The transitions in $(NH_4)_3H(SO_4)_2$ are shown in Table I. The dielectric anomalies associated with the phase transitions in $(NH_4)_3H(SO_4)_2$ were described previously:[1,3] At atmospheric pressure, a slight break on the dielectric constant vs temperature curve is observed at the II-III and the III-IV transition temperatures. A discontinuous change in the dielectric constant accompanied with a thermal hysteresis is found at the IV-V and V-VII transitions. Besides the anomalies associated with the phase transitions, there is a broad peak of the dielectric constant along the c^*-direction at around $-25°C$ at atmospheric pressure. As hydrostatic pressure increases the broad peak becomes sharp and intense, finally it splits into two sharp λ-type maxima, and a ferroelectric phase (Phase VI) is stabilized between them. By further increase

in pressure another ferroelectric phase (Phase VII) appears in the lower temperature region. The phase transition between the two pressure-induced ferroelectric phases is of the first order. The first order nature, however, becomes more and more insignificant as pressure increases. The critical point at which the first order nature of the VI-VII transition completely disappears is estimated to be at about 11 kbar.[3]

The compound receives a marked isotope effect on the successive phase transitions. That is, the phase transitions in the deuterated compound $(NH_4)_3D(SO_4)_2$ at atmospheric pressure are quite different from those found in the normal compound; two ferroelectric phases are observed above liquid nitrogen temperature.[5] Our preliminary study on the pressure-temperature phase diagram of the deuterated compound[6] suggested that these ferroelectric phases are identical with the pressure-induced ferroelectric phases VI and VII in the normal compound. The phase transition sequence in the deuterated compound is also described in Table I. Recently, the present authors studied the phase diagram of the system $\{(NH_4)_3H(SO_4)_2\}_{1-x}\{(ND_4)_3D(SO_4)_2\}_x$.[4] The results showed that there is a marked similarity between the effects of the hydrostatic pressure and the deuterium-substitution as regards the stability of the

Table I. Phase transitions in $(NH_4)_3H(SO_4)_2$ and $(ND_4)_3D(SO_4)_2$ at atomspheric pressure. The deuterium concentration of the deuterated compound is estimated to be $x=0.97$.

$(NH_4)_3H(SO_4)_2$

Phase	I	II	III	IV	V	VII*
	trigonal	monoclinic A2/a[11)]				(Ferroelectric)
Transition temperature (°C)	140[1)]	−8[1)]	−136[1)]	−140[1)]	−210[2)]	

$(ND_4)_3D(SO_4)_2$

Phase	I	II	III	VI	III′	VII
		monoclinic A2/a[12)]		Ferroelectric		Ferroelectric
Transition temperature (°C)	122[4)]	−9[5)]	−24[5)]	−64[5)]	−92[5)]	

* Recent study of the low temperature phase diagram for normal-deuterated crystal system[2)] showed that the lowest temperature phase of $(NH_4)_3H(SO_4)_2$ is identical with the ferroelectric VII phase of $(ND_4)_3D(SO_4)_2$.

ferroelectric phases.

It would be useful to complete the deuterium concentration (x)-pressure (p)-temperature (T) three dimensional phase diagram in order to understand the above peculiar isotope and pressure effects on the phase transitions in $(NH_4)_3H(SO_4)_2$. In the present study we intended to determine the x-p-T phase diagram of $\{(NH_4)_3H(SO_4)_2\}_{1-x}\{(ND_4)_3D(SO_4)_2\}_x$ system in a pressure and temperature range of $p \lesssim 10$ kbar, $-100°C \lesssim T <$ room temperature. The purposes of the study are (1) to confirm the identity relations between the pressure-induced ferroelectric VI and VII phases in the normal compound and the atmospheric pressure ferroelectric phases in the deuterated compound, (2) to detect the critical point of the ferroelectric-to-ferroelectric VI-VII phase transition (The critical point was expected to exist at a lower pressure in deuterated compound.[6)]), and (3) to search for new pressure-induced phases in the mixed crystal system. Such a study will provide a useful piece of information about the complicated phase stability in the system of $\{(NH_4)_3H(SO_4)_4\}_{1-x}\{(ND_4)_3 (SO_4)_2\}_x$.

§2. Experimental

Single crystals of $\{(NH_4)_3H(SO_4)_2\}_{1-x} \{(ND_4)_3D(SO_4)_2\}_x$ with various concentration x were prepared by slow evaporation of water-heavy water solutions. Crystals with the highest deuterium concentration $(x=0.97)$ were prepared by repeated recrystallizations from D_2O solution. The deuterium concentration in crystal was estimated from the molecular vibration spectrum intensity of ammonium ions by Raman scattering. Specimens of the pseudo-hexagonal c-plates were polished with 1,200 mesh carborundum powder. After attached with gold-foil electrodes, the specimen was set into a Cu–Be pressure vessel. The pressure-transmitting fluid used was 1 : 1 mixture of iso- and n-penthane. The details of the high pressure system used were described previously.[7,8)] The pressure and temperature were respectively measured with a manganine gauge and a copper-constantan thermocouple. The dielectric constant of the specimen was measured with a three terminal capacitance bridge at 1 kHz, or with an LCR-meter at 100 kHz and recorded on an x-y recorder. Phase transitions at high pressures were detected by anomalies in the dielectric constant.

§3. Results

In the deuterated compound (the deuterium concentration x was estimated to be 0.97), new dielectric anomalies were observed other than those which were reported previously.[3,9)] Figure 1 shows the temperature dependence of the dielectric constant ε and its reciprocal
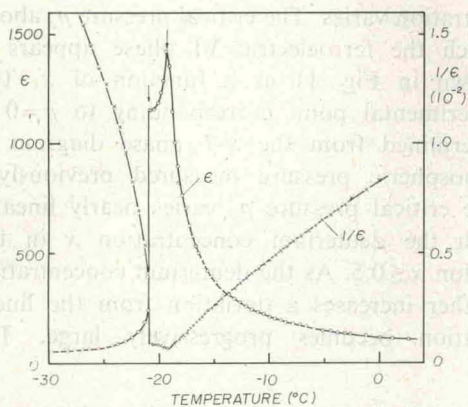
Fig. 1. Temperature dependence of the dielectric constant ε ($\bigcirc$) and its reciprocal $1/\varepsilon$ ($\times$) along the c^*-direction of $\{(NH_4)_3H(SO_4)_2\}_{0.03}\{(ND_4)_3D(SO_4)_2\}_{0.97}$ at $p=3.72$ kbar. Vertical arrows indicate the dielectric anomalies at the II-IX and IX-VI transitions. Frequency: 100 kHz.

$1/\varepsilon$ along the c^*-direction of the deuterated compound at $p=3.72$ kbar. As shown by the arrows, two anomalies are seen around the II→VI transition region. These anomalies indicate that there is an interdediate phase in a narrow temperature region between the room temperature phase of II and the ferroelectric VI phase. The intermediate phase is denoted as Phase IX. Figure 2 indicates the temperature dependence of the inverse of the dielectric constant $1/\varepsilon$ at pressures higher than 6 kbar. A clear break is seen for each curve as indicated
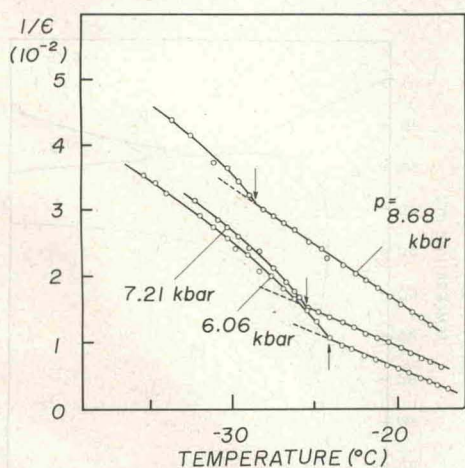
by an arrow. The dielectric anomaly corresponds to a phase transition from the room temperature phase of II to a new intermediate phase which is denoted as Phase VIII. The pressure-induced phases of VIII and IX were not noticed in our preliminary work.[6]

From the results of dielectric constant measurements, we can obtain the pressure-temperature phase diagrams for different concentration x. Figures $3 \sim 8$ show the p-T phase diagrams for compounds with $x=0$, 0.14, 0.40, 0.60, 0.79, and 0.97, respectively. The phase diagram of the normal compound shown in Fig. 3 was the one reported previously.[3] As the deuterium concentration increases the two pressure-induced ferroelectric phases VI and VII appear in lower pressure region. The intermediate phase IX can be seen in the pressure region studied for the compounds with $x \gtrsim 0.60$.

In the normal compound the II-III phase boundary was not represented by a linear relation, but it was approximated by a quadratic form of $\Theta_{II-III}=T^0_{II-III}+Kp+\gamma p^2$.[9] We estimated the parameters T^0_{II-III}, K, and γ as fimctions of x from the phase diagrams. The results are shown in Fig. 9. The II-III transition temperature T^0_{II-III} at 0 kbar and the initial pressure slope K vary with concentration x very slightly. On the other hand, the parameter

Fig. 2. Temperature dependence of the reciprocal of the dielectric constant $1/\varepsilon$ along the c^*-direction of $\{(NH_4)_3H(SO_4)_2\}_{0.03}\{(ND_4)_3D(SO_4)_2\}_{0.97}$ at different hydrostatic pressures. Vertical arrows indicate the anomalies at the VIII-VI transition. Frequency: 100 kHz.
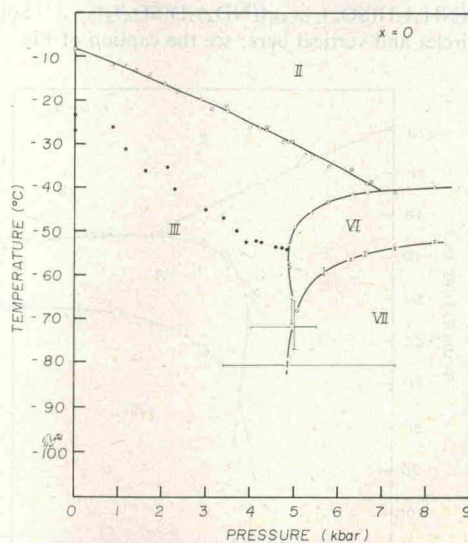

Fig. 3. Pressure-temperature phase diagram of $(NH_4)_3H(SO_4)_2$.[3] Solid circles show the position of the broad dielectric constant peak at constant-pressure runs. Short bars indicate temperature (or pressure) hysteresis of the first order transitions.

γ seems to change its sign as x varies from 0 to 0.97.

Figure 10 shows the pressure dependence of the inverse of the maximum value of the dielectric constant at the diffuse peak in Phase III for different x. The relation between $1/\varepsilon_{max}$ and pressure p is linear for each compound, that is, a Curie-Weiss like relation $1/\varepsilon_{max} = C^*(p_0 - p)$ is held. The relations between $1/\varepsilon_{max}$ against p for various deuterium concentrations x are almost parallel. Therefore the constant C^* is practically unchanged as deuterium con-

centration varies. The critical pressure p_c above which the ferroelectric VI phase appears is shown in Fig. 11 as a function of x. The experimental point corresponding to $p=0$ is determined from the x-T phase diagram at atmospheric pressure measured previously.[4] The critical pressure p_c varies nearly linearly with the deuterium concentration x in the region $x \lesssim 0.5$. As the deuterium concentration further increases a deviation from the linear relation becomes progressively large. The
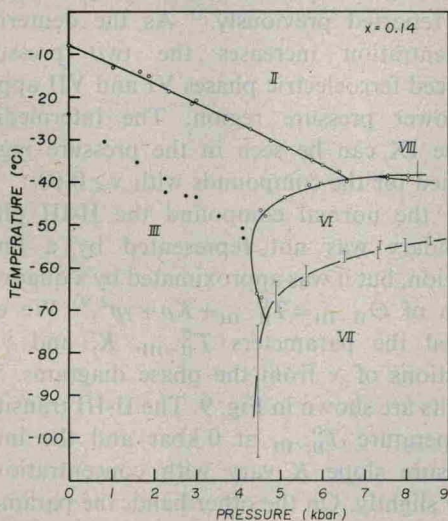

Fig. 4.   Pressure-temperature phase diagram of $\{(NH_4)_3H(SO_4)_2\}_{0.86}\{(ND_4)_3D(SO_4)_2\}_{0.14}$.   Solid circles and vertical bars: see the caption of Fig. 3.
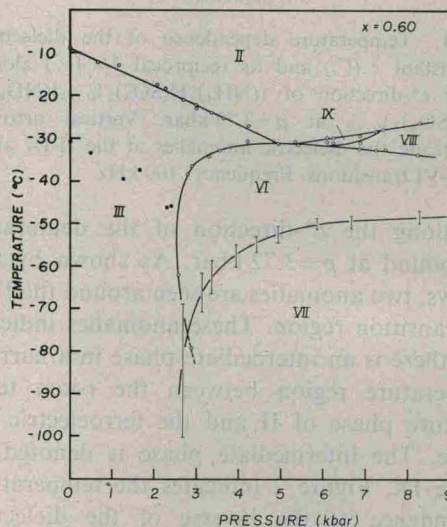

Fig. 6.   Pressure-temperature phase diagram of $\{(NH_4)_3H(SO_4)_2\}_{0.40}\{(ND_4)_3D(SO_4)_2\}_{0.60}$.   Solid circles and vertical bars: see the caption of Fig. 3.
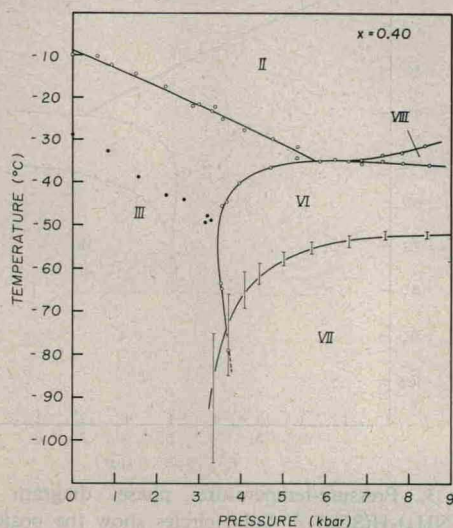
Fig. 5.   Pressure-temperature phase diagram of $\{(NH_4)_3H(SO_4)_2\}_{0.60}\{(ND_4)_3D(SO_4)_2\}_{0.40}$.   Solid circles and vertical bars: see the caption of Fig. 3.

Fig. 7.   Pressure-temperature phase diagram of $\{(NH_4)_3H(SO_4)_2\}_{.021}\{(ND_4)_3D(SO_4)_2\}_{0.79}$.   Solid circles and vertical bars: see the caption of Fig. 3.
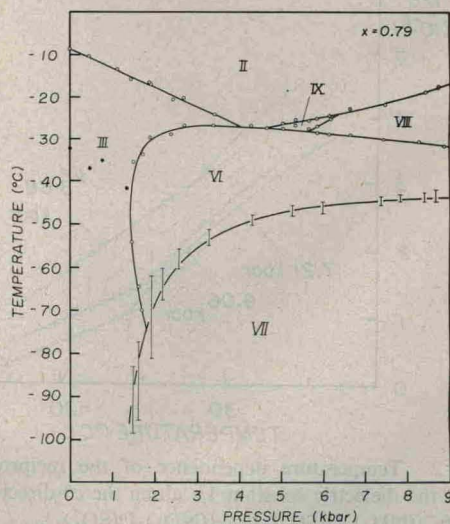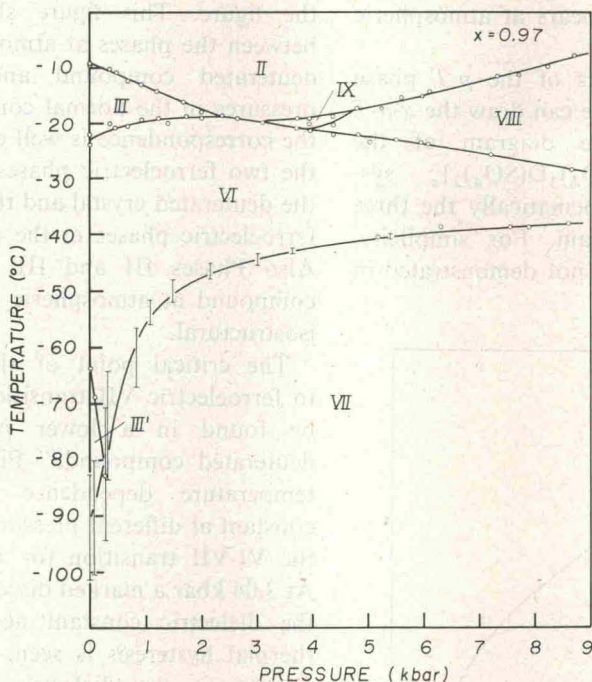
Fig. 8. Pressure-temperature phase diagram of $\{(NH_4)_3H(SO_4)_2\}_{0.03}\{(ND_4)_3D(SO_4)_2\}_{0.97}$. Vertical bars show the temperature hysteresis of first order transitions.
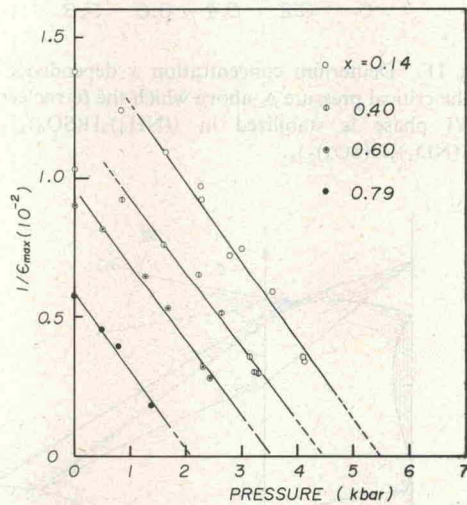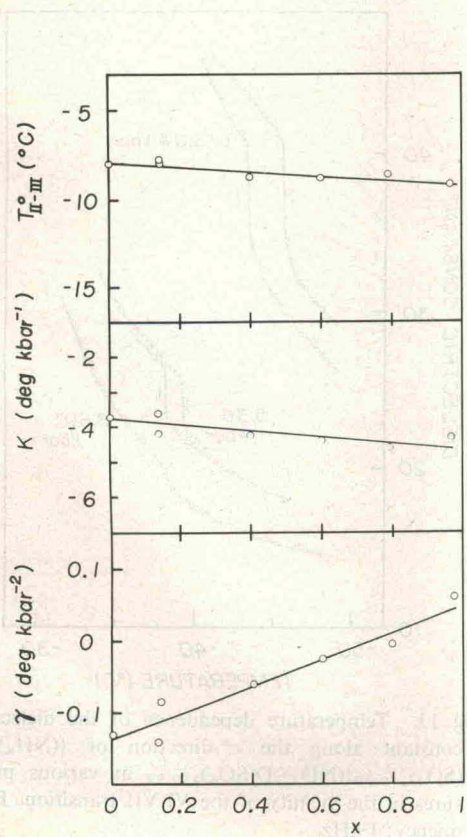

Fig. 10. Pressure dependence of the reciprocal of the maximum value $1/\varepsilon_{max}$ at the broad dielectric constant peak in Phase III for the compounds $\{(NH_4)_3H(SO_4)_2\}_{1-x}\{(ND_4)_3D(SO_4)_2\}_x$ with various x.

←Fig. 9. Deuterium concentration x dependence of the parameters which describe the II-III phase boundary in the p-T plane for the system $\{(NH_4)_3H(SO_4)_2\}_{1-x}\{(ND_4)_3D(SO_4)_2\}_x$: The II-III transition temperature Θ_{II-III} is represented by $\Theta_{II-III} = T^0_{II-III} + Kp + \gamma p^2$.

ferroelectric phase VI appears at atmospheric pressure for $x > 0.9$.

From the above results of the p-T phase diagrams for various x, we can draw the x-p-T three dimensional phase diagram of the $\{(NH_4)_3H(SO_4)_2\}_{1-x}\{(ND_4)_3D(SO_4)_2\}_x$ system. Figure 12 shows schematically the three dimensional phase diagram. For simplicity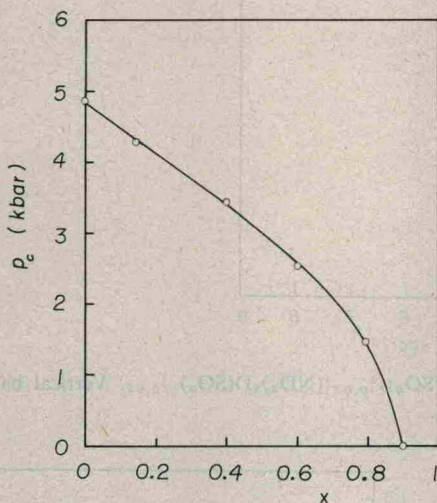, the region of Phase IX is not demonstrated in the figure. This figure shows the relation between the phases at atmospheric pressure in deuterated compound and those at high pressures in the normal compound. Especially the correspondence is well established between the two ferroelectric phases of VI and VII in the deuterated crystal and the pressure-induced ferroelectric phases in the normal compound. Also Phases III and III′ in the deuterated compound at atmospheric pressure should be isostructural.

The critical point of the ferroelectric VI to ferroelectric VII transition was expected to be found in a lower pressure region in deuterated compound.[6] Figure 13 shows the temperature dependence of the dielectric constant at different pressures in the vicinity of the VI-VII transition for $x = 0.97$ compound. At 3.04 kbar a marked discontinuous change in the dielectric constant accompanied with a thermal hysteresis is seen. The discontinuous change in the dielectric constant becomes smaller as pressure increases, and at 8.6 kbar it is hardly observable. Figure 14 indicates the pressure dependence of the square root of the

Fig. 11. Deuterium concentration x dependence of the critical pressure p_c above which the ferroelectric VI phase is stabilized in $\{(NH_4)_3H(SO_4)_2\}_{1-x}\{(ND_4)_3D(SO_4)_2\}_x$.
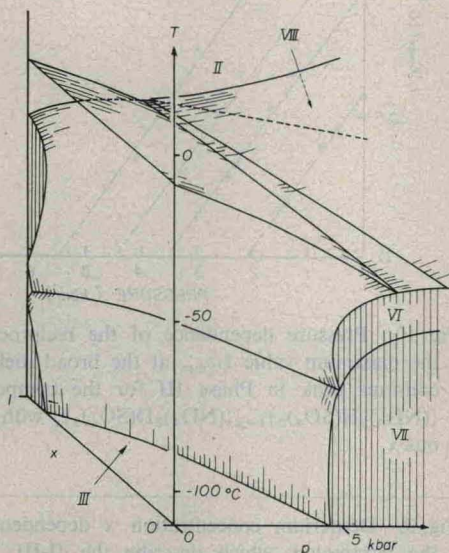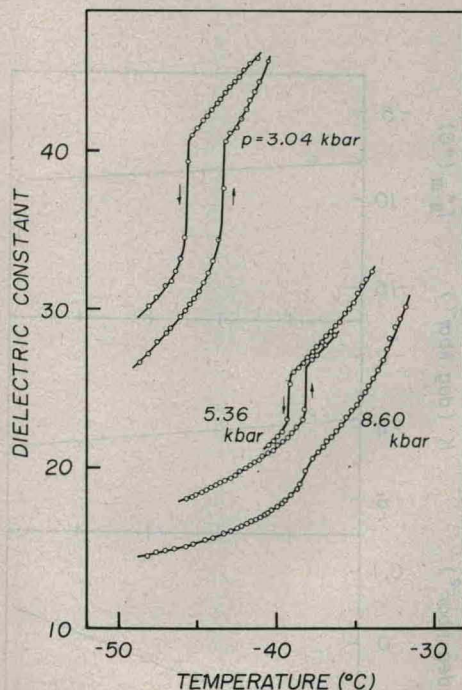

Fig. 12. Schematic picture of the three dimensional x-p-T phase diagram of the system $\{(NH_4)_3H(SO_4)_2\}_{1-x}\{(ND_4)_3D(SO_4)_2\}_x$. For simplicity, the region of Phase IX is not shown.

Fig. 13. Temperature dependence of the dielectric constant along the c^*-direction of $\{(NH_4)_3H(SO_4)_2\}_{0.30}\{(ND_4)_3D(SO_4)_2\}_{0.97}$ at various pressures in the vicinity of the VI-VII transition. Frequency: 1 kHz.
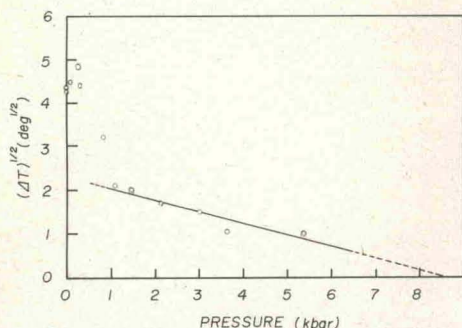
Fig. 14. Pressure dependence of the square root of the temperature hysteresis $(\Delta T)^{1/2}$ of the VI-VII transition in $\{(NH_4)_3H(SO_4)_2\}_{0.03}\{(ND_4)_3D(SO_4)_2\}_{0.97}$.

thermal hysteresis $(\Delta T)^{1/2}$ observed for $x = 0.97$ compound as a measure of the first order nature of the transition. It is seen that the first order nature of the VI-VII transition disappears at around 8.5 kbar, and above this critical pressure the transition becomes to be continuous.

§4. Conclusive Remark

From the results described in the preceding section the followings are concluded:

(1) The two ferroelectric phases in the deuterated compound at atmospheric pressure correspond to the pressure-induced ferroelectric phases VI and VII in the normal compound, respectively.

(2) The two intermediate phases VIII and IX are newly found in high pressure region in the normal-deuterated compound system.

(3) In the deuterated compound with $x = 0.97$ the critical point of the ferroelectric-to-ferroelectric VI-VII phase transition exists at a relatively low pressure around 8.5 kbar.

As to the stabilization of the ferroelectric phases of VI and VII, the effects of the deuterium-substitution and pressure application are analogous, namely, both the deuterium-substitution and the pressure application enhance the ferroelectricity. On the other hand, the II-III transition temperature varies very slightly by the deuterium-subsitution, but it is depressed by the pressure-application with a moderate rate. For the present, the nature of

the II-III transition is not understood since the crystal structure of Phase III has not been known as yet. Although the dielectric anomaly associating the II-III transition is insignificant, there is a conspicuous specific heat anomaly with a wide critical region.[10] Probably a certain kind of super-lattice structure would exist in Phase III. The dielectric anomalies at the II-IX-VI transitions shown in Fig. 1 resemble those found for the paraelectric-incommensurate-ferroelectric phase transitions in $NaNO_2$.[7] So that an incommensurate long period structure may be expected in Phase XI by the analogy with the case of $NaNO_2$.

In the present study the nature of the critical point of the VI-VII transition is not clarified: Whether the critical point is tricritical or gas-liquid type? In order to solve the problem it is necessary to determine the transition parameter of the VI-VII transition. Since the ferroelectric VI and VII phases can be seen at atmospheric pressure in the deuterated compound, the transition parameter will be easily determined from the crystal structure analysis on the deuterated compound. The mechanism of the complicated phase transitions and the unique pressure and isotope effects observed in $(NH_4)_3H(SO_4)_2$ are the problem to be solved in future.

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