the transition. Then, as a_2 increases the F_1–F_2 phase boundary terminates at a gas-liquid type critical point in the a_2-t plane, and beyond the critical point two ferroelectric states can gradually transform to each other without showing an explicit transition point. In Fig. 12, the χ_F vs t curves at various a_2 values are shown in the vicinity of the gas-liquid type critical point. The critical point exists at $a_2=1.045$. It should be noted that χ_F does not show a singularity at the gas-liquid type critical point. The resultant a_2-t phase diagram is shown in Fig. 13. In the figure the position of the broad maximum of the susceptibility obtained in constant-a_2 measurements is indicated by the dotted- and-slashed curve. The inflection point of the P_F^s vs t curve is shown by the slashed curve. The phase diagram qualitatively agrees with the observed p-T diagram of $(NH_4)_3H(SO_4)_2$ shown in Fig. 6.

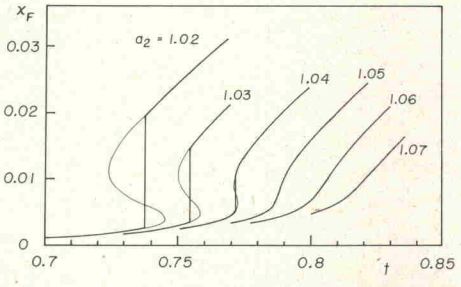

Fig. 12. Reduced temperature t dependence of the dielectric susceptibility χ_F around the gas-liquid type critical point of the F_1-F_2 transition. $a_1=0.45$, $a_3=-0.5$, $a_4=-0.2$.

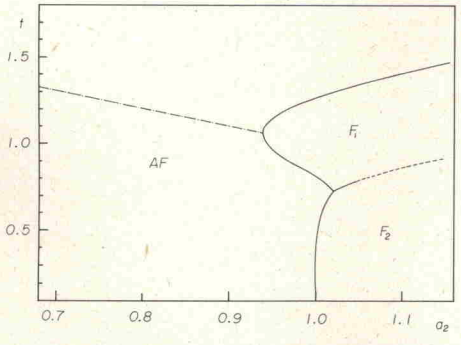

Fig. 13. Calculated a_2-t phase diagram of a two sublattice system. AF, F_1, and F_2 denote the antiferroelectric, and two ferroelectric phases, respectively. The dotted-and-slashed curve indicates the position of the maximum of the broad dielectric susceptibility peak at a_2=constant. Slashed line shows the inflection in P_F^s vs t curve at a_2=constant. $a_1=0.45$, $a_3=-0.5$, $a_4=-0.2$.

§5. Conclusive Remark

The present work reveals two pressure-induced ferroelectric phases in $(NH_4)_3H(SO_4)_2$. Dielectric measurements at high pressures showed that the broad maximum in the dielectric constant found at around -25°C at 1 atm predicts the existence of ferroelectricity at high pressures. Recently Ishibashi and Takagi[7] suggested that phase transitions in a certain group of ferroelectrics can be interpreted by multi-sublattice models such as the Mitsui model of Rochelle salt. The results of the calculation described in the preceding section show that the modified Mitsui model is also applicable to the phase transitions in $(NH_4)_3H(SO_4)_2$. There is a hope to improve quantitative agreement with the observed results by choosing proper values of parameters. However, in this work further improvement in quantitative agreement was not intended since the results will not be drastically altered in compensation for a long computation time. The existence of the II-III transition and the long-period structure in Phase III seem to request a more elaborated model than the present one. When the final crystal structures in the atmospheric-pressure phases are determined a theory should be established on the basis of the microscopic structures.

It is an interesting problem whether or not the VI-VII transition is really an isomorphous one as suggested by the simple two-sublattice model. In the present work the gas-liquid type critical point of the VI-VII transition in $(NH_4)_3H(SO_4)_2$ was not observed in the pressure region studied. Preliminary measurement of the pressure-temperature phase diagram of a deuterated compound showed that ferroelectric VI and VII Phases are stabilized even at 1 atm, and that the first order nature of the VI-VII transition completely disappears at around 8 kbar as pressure increases. Above 8 kbar any dielectric anomaly was not detected corresponding to the VI-VII transition. Unlike to the critical points of the II-III transitions in $Ca_2Pb(C_2H_5COO)_6$ and $Ca_2Sr(C_2H_5COO)_6$[8,9] a peak of dielectric constant is not observed at around 8 kbar. However the prediction of the two-sublattice model shown in Fig. 12 is in agreement with the result found in deuterated triammonium deuterium disulfate. The study

of deuterated compound would provide very useful information about the mechanism of the complicated phase transitions of $(NH_4)_3H(SO_4)_2$ since the crystal structures of Phases VI and VII can be studied at atmospheric pressure for the deuterated compound. Detailed studies on the phase transitions in deuterated compound are in progress.

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