

## Pressure-Temperature Phase Diagram of Ferroelectric Ammonium Bisulfate $\text{NH}_4\text{HSO}_4$

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The pressure-temperature phase diagram of ferroelectric  $\text{NH}_4\text{HSO}_4$  was studied by means of dielectric and differential thermal analysis (DTA) measurements in a pressure and temperature region of  $p \lesssim 8 \times 10^3 \text{ kg cm}^{-2}$ ,  $-120^\circ\text{C} \lesssim T \lesssim 200^\circ\text{C}$ . The high pressure phase found by Bridgman above about  $1 \times 10^3 \text{ kg cm}^{-2}$  at room temperature is proven not to be identical with the low temperature non-ferroelectric phase (Phase III) at 1 atm. The liquidus line was newly determined by DTA. A new high pressure phase (Phase VI) was found above  $4 \times 10^3 \text{ kg cm}^{-2}$  just below the melting point. A change in the order of the transition at the upper Curie point was found at about  $0.6 \times 10^3 \text{ kg cm}^{-2}$ .

### §1. Introduction

Ammonium bisulfate  $\text{NH}_4\text{HSO}_4$  shows two phase transitions at 1 atm; Phase I  $\xrightarrow{-3^\circ\text{C}}$  Phase II  $\xrightarrow{-119^\circ\text{C}}$  Phase III. Ferroelectric activity of Phase II was first reported by Pepinsky *et al.*<sup>1)</sup> Although Pepinsky *et al.*<sup>1)</sup> showed a polar symmetry  $P1$ , ferroelectric activity of Phase III has not been observed so far. Before the discovery of the ferroelectricity Bridgman<sup>2)</sup> studied the pressure-temperature phase diagram of  $\text{NH}_4\text{HSO}_4$  above room temperature up to about  $10^4 \text{ kg cm}^{-2}$ . Bridgman found that three phases are stabilized at high pressures, and denoted them as Phases II, III, and IV. In the present paper, however, Bridgman's Phases II, III, and IV are called Phases IV, V, and VII, respectively, in order to avoid confusion to the conventional abbreviation adopted for the atmospheric pressure phases. At room temperature the I-IV transition takes place at about  $10^3 \text{ kg cm}^{-2}$ <sup>2)</sup> and the transition pressure increases with increasing temperature. An interesting point is that the I-IV phase boundary given by Bridgman extrapolates itself to  $-119^\circ\text{C}$  at 1 atm; i.e. just to the II-III transition point. Then, it is a question whether the high pressure phase of IV is identical with the low temperature non-ferroelectric phase of III.

The effect of hydrostatic pressure on the two Curie points of  $\text{NH}_4\text{HSO}_4$  was measured by Polandov *et al.*<sup>3)</sup> in a limited pressure range of  $p \lesssim 1.2 \times 10^3 \text{ kg cm}^{-2}$ . They observed that

both the upper and the lower Curie points increase with increasing pressure. The II-III phase boundary given by Polandov *et al.* is nearly at the extrapolation of the I-IV phase boundary given by Bridgman. However, Polandov *et al.* did not discuss the relation between Phase III and Phase IV. A powder X-ray diffraction study by Bradley *et al.*<sup>4)</sup> showed that the high pressure phase IV belongs to the orthorhombic symmetry which is different from the triclinic space group  $P1$  of Phase III determined by Pepinsky *et al.*<sup>1)</sup>

Recently Aizu<sup>5)</sup> developed a group theoretical interpretation of the successive phase transitions in  $\text{NH}_4\text{HSO}_4$ . He concluded that the paraelectric room temperature structure of  $B2_1/a$  is ferroelastic and can be deduced from a prototype structure of  $Pm\bar{m}n$ . The prototype structure can not be realized at 1 atm up to the melting point. Aizu supposed that the prototype phase might be stabilized at high pressures as in the case of  $\text{LiH}_3(\text{SeO}_3)_2$ .<sup>6)</sup> Since Bridgman<sup>2)</sup> did not measure the liquidus line, it remains to be a problem whether or not the prototype phase really exists just below the melting point at high pressures.

According to Polandov *et al.*<sup>3)</sup> the maximum dielectric constant at the upper Curie point markedly decreases with increasing pressure. Similar depression of the maximum dielectric constant was found in ferroelectric triglycine selenate (TGSe).<sup>7)</sup> The present authors interpreted the phenomenon in TGSe as a result of a change in the order of the transition at

high pressures. The change in the order of the ferroelectric transition is also expected for the upper Curie point of  $\text{NH}_4\text{HSO}_4$ .

In the present work, we intended to complete the phase diagram of  $\text{NH}_4\text{HSO}_4$  in an extended pressure-temperature range of  $p \lesssim 8 \times 10^3 \text{ kg cm}^{-2}$ ,  $-120^\circ\text{C} \lesssim T \lesssim 200^\circ\text{C}$ . The purposes are to confirm (1) whether the high pressure phase IV found by Bridgman is identical with the low temperature non-ferroelectric phase III, (2) whether the prototype phase exists just below the melting point at high pressures, and (3) whether a tricritical point is found for the upper Curie point.

## §2. Experimental

Single crystals of  $\text{NH}_4\text{HSO}_4$  were grown from an aqueous solution of  $(\text{NH}_4)_2\text{SO}_4$  and  $\text{H}_2\text{SO}_4$ .<sup>9)</sup> The crystals are transparent, and show a perfect cleavage along the (001) plane. A number of (001) plates were cleaved out from single crystals. After polished with #1,200 mesh emery paper, gold foil was attached on each surface as electrode. The manipulation of specimens was carried out in a dry box filled with dry nitrogen gas.

Two types of pressure bombs were used for the high pressure measurements; one was a Cu-Be bomb used for the measurements below about  $70^\circ\text{C}$ , and the other was an internal furnace type one used for the measurements of melting point and high temperature phase transitions. The pressure-transmitting fluids used were silicone oil (for temperature range above  $70^\circ\text{C}$ ), kerosene (between room temperature and  $70^\circ\text{C}$ ), and 1:1 mixture of *iso*- and *n*-pentane (below room temperature). The details of the high pressure arrangements used were published elsewhere.<sup>10,11)</sup>

Below about  $70^\circ\text{C}$  phase transitions at high pressures were detected by anomalies in the dielectric constant of the (001) plate specimens, but at higher temperatures they were detected by differential thermal analysis (DTA) signals since the measurements of the dielectric constant were difficult because of an increase in the d.c. conductance. The dielectric constant of the specimen was measured by means of a three terminal capacitance bridge at 100 kHz. The DTA signals were amplified and were recorded on an x-y recorder. Since the specimens cracked after passing several times through first

order transitions (such as the I-IV or II-III transition) a number of specimens were used for the determination of the first order phase boundaries.

## §3. Results

### 3.1 Pressure effect on the I-II (the upper Curie point) and the II-III (the lower Curie point) transitions

Figure 1 shows the temperature dependence of the dielectric constant of the (001) plate at a pressure of  $0.96 \times 10^3 \text{ kg cm}^{-2}$ . A sharp  $\lambda$ -type peak is seen at the I-II transition (the upper Curie point), whereas there is a slight step at the II-III transition (the lower Curie point). The dielectric anomaly at the II-III transition is demonstrated in Fig. 2 in some detail. In the figure the transition point is shown by the vertical arrows for the cooling and heating processes. The thermal hysteresis of the II-III transition which is estimated to be about  $10^\circ\text{C}$  at 1 atm becomes more and more conspicuous as pressure increases. Figure 3 indicates the pressure dependence of the dielectric constant at a constant temperature of  $1.5 \pm 0.3^\circ\text{C}$ . On the pressure increasing process a marked peak of dielectric constant is found at about  $0.4 \times 10^3 \text{ kg cm}^{-2}$  corresponding to the I-II transition, and then, there is a slight step at about  $2.05 \times 10^3 \text{ kg}$

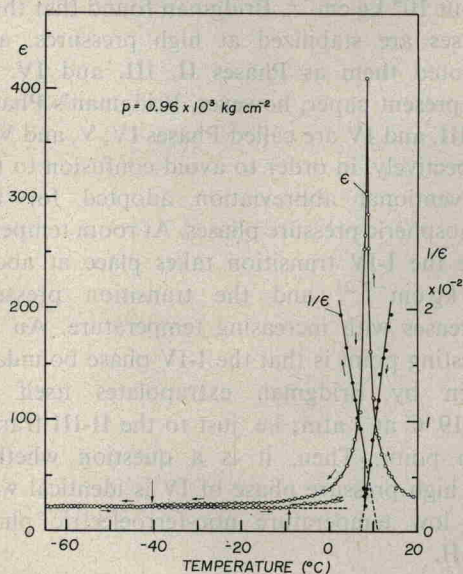


Fig. 1. Temperature dependence of the dielectric constant of the (001)-plate of  $\text{NH}_4\text{HSO}_4$  at  $p = 0.96 \times 10^3 \text{ kg cm}^{-2}$ . The vertical arrows indicate the dielectric anomaly at the II-III transition point.