Pressure-Temperature Phase Diagram of Ferroelectric Ammonium Bisulfate \(NH_4HSO_4\)

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The pressure-temperature phase diagram of ferroelectric \(NH_4HSO_4\) was studied by means of dielectric and differential thermal analysis (DTA) measurements in a pressure and temperature region of \(p \leq 8 \times 10^3\) kg cm\(^{-2}\), \(-120^\circ C \leq T \leq 200^\circ C\). The high pressure phase found by Bridgman above about \(1 \times 10^3\) 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 \(4 \times 10^3\) 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 \(0.6 \times 10^3\) kg cm\(^{-2}\).

§1. Introduction

Ammonium bisulfate \(NH_4HSO_4\) shows two phase transitions at 1 atm: Phase I\(-\)\(\bar{3}\)\(c\), Phase II\(-119^\circ C\) Phase III. Ferroelectric activity of Phase II was first reported by Pepinsky et al.\(^1\). Although Pepinsky et al.\(^1\) showed a polar symmetry \(P1\), ferroelectric activity of Phase III has not been observed so far. Before the discovery of the ferroelectricity Bridgman\(^2\) studied the pressure-temperature phase diagram of \(NH_4HSO_4\) above room temperature up to about \(10^4\) kg cm\(^{-2}\). Bridgman found that three phases are stabilized at high pressures, and denoted them as Phases III, II, 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 \(10^3\) kg cm\(^{-2}\) \(^2\) and the transition pressure increases with increasing temperature. An interesting point is that the I-IV phase boundary given by Bridgman extrapolates itself to \(-119^\circ C\) 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 \(NH_4HSO_4\) was measured by Polandov et al.\(^3\) in a limited pressure range of \(p \leq 1.2 \times 10^3\) 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.\(^4\) 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.\(^1\).

Recently Aizu\(^5\) developed a group theoretical interpretation of the successive phase transitions in \(NH_4HSO_4\). He concluded that the paraelectric room temperature structure of \(B2_1/a\) is ferroelastic and can be deduced from a prototype structure of \(Pmnm\). 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 \(LiH_2(SeO_3)_2\).\(^6\) Since Bridgman\(^2\) 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.\(^3\) 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).\(^7\) 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 NH₄HSO₄.

In the present work, we intended to complete the phase diagram of NH₄HSO₄ in an extended pressure-temperature range of \( p \leq 8 \times 10^3 \, \text{kg cm}^{-2}, -120^\circ \text{C} \leq T \leq 200^\circ \text{C} \). 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 NH₄HSO₄ were grown from an aqueous solution of (NH₄)₂SO₄ and H₂SO₄. 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°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°C), kerosene (between room temperature and 70°C), and 1:1 mixture of iso- and n-pentane (below room temperature). The details of the high pressure arrangements used were published elsewhere.¹⁰,¹¹

Below about 70°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 A-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°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±0.3°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 \( \times 10^3 \, \text{kg cm}^{-2} \).

![Fig. 1. Temperature dependence of the dielectric constant of the (001)-plate of NH₄HSO₄ at \( p = 0.96 \times 10^3 \, \text{kg cm}^{-2} \). The vertical arrows indicate the dielectric anomaly at the II-III transition point.](image)
cm$^{-2}$ corresponding to the II-III transition. On the pressure decreasing process, anomalies corresponding to the II-III and the I-II transitions do not appear down to 1 atm. This indicates that the high pressure phase of III is maintained as a metastable phase at 1 atm as a result of large pressure hysteresis of the transition. The large thermal and pressure hysteresis of the II-III transition makes the determination of the equilibrium phase boundary difficult.

3.2 Dielectric anomaly at the upper Curie point

Figure 4 shows the temperature dependence of the dielectric constant at pressures of $0.93 \times 10^3$ kg cm$^{-2}$ and $1.35 \times 10^3$ kg cm$^{-2}$. The measurements were carried out by keeping pressure within $\pm 2\%$ with a hand pump.
After the measurement of the dielectric constant around the upper Curie point, the specimen was heated up to about 50°C and the pressure was lowered to 1 atm. Pressure variation of the dielectric constant was measured on the pressure decreasing process at 50°C. Detection of the dielectric anomaly of the IV-I transition showed that the dielectric anomalies at $0.93 \times 10^3 \text{ kg cm}^{-2}$ and $1.35 \times 10^3 \text{ kg cm}^{-2}$ shown in Fig. 4 correspond to the I-II and II-IV transitions, respectively. The thermal hysteresis during the heating and cooling processes shows the transitions are of the first order at the cited pressures.

### 3.3 I-IV phase boundary

Figure 5 shows the pressure dependence of the dielectric constant at 44.3±0.5°C and 62.5±0.5°C. The d.c. conductance of the specimen is considerably large above room temperature and surface layer or compatibility of the electrode to the specimen surface severely affects the apparent capacitance of the sample condenser. Then, the dielectric constant shown in Fig. 5 should be considered to be an apparent one. However in spite of the lack of reproducibility in the absolute value of the apparent dielectric constant one may observe a discontinuous jump on the curves as shown by the vertical arrows for the I-IV transition. The pressure hysteresis of the I-IV transition is large and becomes remarkable as temperature approaches to the upper Curie point.

### 3.4 III-IV phase boundary

Above about $1.6 \times 10^3 \text{ kg cm}^{-2}$ peaks of dielectric constant were not found at the extension line of the upper Curie temperature. Instead we found a slight change in the temperature coefficient of the dielectric constant as shown in Fig. 6. We tentatively assigned the dielectric anomaly to the III-IV transition. The results indicate that the high pressure phase found by Bridgman (Phase IV) is not identical with the low temperature non-ferroelectric phase of III.

### 3.5 Determination of the liquidus line

Figure 7 shows the DTA signal which corresponds to the melting of NH₄HSO₄ at $1.97 \times 10^3 \text{ kg cm}^{-2}$. An anomaly at the III-IV transition is shown by the vertical arrow.
responds to the melting. Since a fairly high rate of temperature change was used for the measurement (\( \sim 20^\circ C \text{ min}^{-1} \)), a thermal hysteresis of about 15°C is apparently seen for the melting point. We determined the equilibrium melting point as the average of the two signals in cooling and heating processes. The melting point monotonically increases with increasing pressure as shown in Figs. 8 and 9. The DTA signal splits into two peaks above about 4.0 \times 10^3 \text{ kg cm}^{-2}. This suggests that there is a new high pressure phase between the two DTA signal peaks. The phase is denoted as Phase VI in the present paper.

§4. Discussion and Conclusion

The resultant pressure-temperature phase diagram of \( \text{NH}_4\text{HSO}_4 \) is shown in Fig. 8. Data obtained in the present work are indicated by open circles and short bars. The short bars indicate the pressure or thermal hysteresis observed for first order transitions. In the figure the transition points reported by Bridgman\(^2\) and Polandov \textit{et al.}\(^3\) are indicated by the closed figures. The present results are fully consistent with those of Bridgman and Polandov \textit{et al.} It should be noted that the points given by Bridgman are representing the equilibrium ones. On the other hand, the experimental points of the II-III transition by Polandov \textit{et al.} are not the equilibrium ones but data for only cooling process. Bridgman already reported a marked volume change accompanying the I-IV transition and stated that the pressure hysteresis of the transition becomes very large as temperature decreases. Polandov \textit{et al.}\(^3\) also pointed out that the thermal hysteresis of the II-III transition gets progressively large as pressure increases. In general, a thermal hysteresis of a first order transition increases as the transition temperature decreases with varying pressure. The thermal hysteresis of the II-III transition in \( \text{NH}_4\text{HSO}_4 \), however, decreases as the transi-

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Fig. 8. Pressure-temperature phase diagram of \( \text{NH}_4\text{HSO}_4 \). Open circles and short bars indicate the present results. Points given by Bridgman\(^2\) and by Polandov \textit{et al.}\(^3\) are indicated by solid circles and triangles, respectively.
tion temperature decreases with lowering pressure as seen in Fig. 8.

The present work reveals that there is a series of phase transitions in NH₄HSO₄ at high pressures; Phase III → Phase IV other than the atmospheric-pressure series of Phase II → Phase I = (The prototype structure; \textit{Pmmn}).

The insignificant dielectric anomaly at the III-IV transition suggests that the structure of Phase IV is a slight modification of Phase III. In fact, Bridgman did not observe a volume change corresponding to the III-IV transition. This would be the reason why the extrapolation of the I-IV boundary tends to the lower Curie point of the II-III transition point at 1 atm. As to the crystal structure of Phase IV, only a powder X-ray study have been available.\(^4\) The reported unit cell dimension of Phase IV is just one third of that of Phase III given by Pepinsky \textit{et al}. at 1 atm.\(^1\) However the space group determination for Phase IV should be postponed until a single crystal structure analysis is done.

The existence of Aizu's prototype phase at high pressures was not directly detected in the present work. However, a change in the curvature of the melting curve at around \(1 \times 10^3\) kg cm\(^{-2}\) seems to suggest that there is a phase in the hatched area in the pressure-temperature plane shown in Fig. 9. Even if there is a high pressure phase in this area the phase boundary between Phase I is so close to the melting that we can not separate the possible DTA signal from the latent heat of melting. At present, we would like to point out only the possibility of the existence of Aizu's prototype phase in a limited region in the cited area.

Recently tricritical points in ferroelectrics have attracted investigators' interest.\(^8,12\) A tricritical point in ferroelectric transition is described in the macroscopic electric field-temperature space, and then, a classical treatment is fully applicable. The order change of the transition at the upper Curie point in NH₄HSO₄ provides a new example of tricritical point in ferroelectric crystal. The critical pressure of the tricritical point of the upper Curie point of NH₄HSO₄ is not determined precisely, but the onset of the thermal hysteresis of the upper Curie point was seen at around \(0.6 \times 10^3\) kg cm\(^{-2}\). Then, the tricritical point exists at this pressure, and above the pressure the transition becomes to be of the first order. The depression of the maximum dielectric constant at the upper Curie point reported by Polandov \textit{et al}.\(^3\) (and also found in the present work) can be explained as a result of the change in the order of the transition similar to the case of TGSe.\(^8\)

From the present results we may conclude the followings:

1. The high pressure phase IV which was first reported by Bridgman should be distinguished from the low temperature non-ferroelectric phase III.
2. The first order nature in the I-IV and II-III transitions becomes more conspicuous as the transitions approach to the upper Curie point with varying pressure.
3. The tricritical point for the upper Curie point exists at around \(0.6 \times 10^3\) kg cm\(^{-2}\). Above the pressure the transition becomes to be of the first order.
4. The III-IV transition is of the second order accompanied with a slight anomaly in dielectric constant. A high pressure series of successive transitions of III→IV is suggested.
5. The liquidus line was newly determined.
6. Above about \(4 \times 10^3\) kg cm\(^{-2}\) a new pressure induced phase of Phase VI is found.
References