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Effect of Hydrostatic Pressure on the Phase Transitions in Ferroelectric $RbHSO_4$ and $RbDSO_4$

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Effect of hydrostatic pressure on the ferroelectric Curie temperatures of $RbHSO_4$ and $RbDSO_4$ was studied by dielectric constant measurements at high pressures. The observed pressure coefficients of the Curie temperature were 12.0 ± 0.1 deg kbar^{-1} for $RbHSO_4$ and 12.7 ± 0.2 deg kbar^{-1} for $RbDSO_4$. A pressure-induced phase was found for $RbHSO_4$ above about 7.5 kbar.

§ 1. Introduction

Rubidium bisulfate $RbHSO_4$ is ferroelectric below a Curie temperature of -9.4°C.[1]* The crystal structures of the paraelectric phase (denoted as Phase I in this paper) and the ferroelectric phase (Phase II) are respectively considered to be isomorphous with the higher temperature paraelectric phase (Phase I) and the ferroelectric phase (Phase II) of NH_4HSO_4.[1,2] Therefore, a common mechanism would be invoked for the I-II transitions in these two bisulfates. A marked difference in the phase transitions of these two bisulfates is that NH_4HSO_4 is ferroelectric between two Curie temperatures while $RbHSO_4$ does not show a lower Curie temperature down to liquid helium temperature.[3] These compounds show a peculiar isotope effect for substituting hydrogens by deuteriums; the deuterization depresses the Curie temperature (the upper Curie temperature for the case of NH_4HSO_4) unlike other hydrogen containing ferroelectrics.[4,5]

Bridgman[6] studied the pressure-temperature phase diagram of NH_4HSO_4 above room temperature and found that the room temperature phase (Phase I) transforms to a high pressure phase (Phase II_B) at about 0.5 kbar at room temperature. The phase boundary between Phases I and II_B extrapolates itself to the lower Curie temperature at 0 kbar. Although it is somewhat questionable that Phase II_B is identical with the low temperature non-ferroelectric phase of Phase III,[7] the ferroelectric phase of NH_4HSO_4 is restricted in a rather narrow region in the p-T plane.[8]

The present work intended to draw the pressure-temperature phase diagram of $RbHSO_4$ in order to decide whether the ferroelectric state of $RbHSO_4$ is also restricted in a limited region in the p-T plane. A part of the present work was published.[9] The presnet paper reports in a wider pressure region up to about 8 kbar. A first order phase transition has been observed above about 7.5 kbar. The pressure dependence of the Curie temperature of $RbDSO_4$ was also determined to compare the results of $RbHSO_4$.

§ 2. Experimental

Single crystals of $RbHSO_4$ were prepared by means of slow evaporation of an aqueous solution at room temperature. A single crystal of $RbDSO_4$ was kindly provided by Dr. I. Tatsuzaki. Several c-plates were cleaved out of a single crystal. After attached silver-paste electrodes, the specimen was set in a high pressure bomb. Two types of pressure bomb were used; one was an internal furnace type for high temperature measurements, and the other was a Cu-Be one for low temperatures. Each bomb has seven electrical terminal plugs. Kerosene was used as the pressure transmitting fluid. The dielectric constant was measured at 100 kHz with an LCR meter and recorded on an x-y recorder. Detailed descriptions of the high pressure system and the procedure of dielectric measurements at high pressures were reported elsewhere.[10,11]

§ 3. Results

Figure 1 shows the temperature dependence

* Pepinsky *et al.*[1] reported the Curie temperature of $RbHSO_4$ to be about -15°C, but more recent studies showed that it is around -10°C. The value -9.4°C was obtained by Chihara[3] from a heat capacity measurement.

of the dielectric constant along the polar direction of the *c*-axis at various hydrostatic pressures. The dielectric constant peak shifts towards high temperatures as pressure increases. At 6.85 kbar, immediately after reaching the

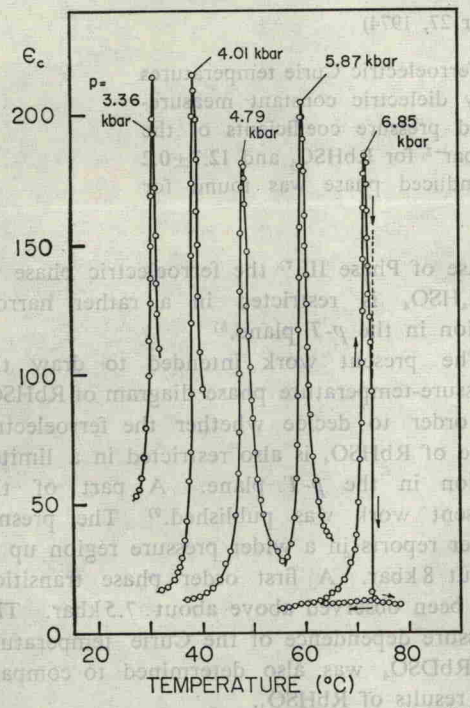

Fig. 1. Temperature dependence of the dielectric constant ε_c along the *c*-axis of $RbHSO_4$ at various hydrostatic pressures. For the curve at $p=6.85$ kbar, the transition from Phase II to Phase III is indicated by the vertical slashed line and arrow. Frequency: 100 kHz.

maximum at the Curie temperature, the dielectric constant discontinuously decreases and it is not recovered even if temperature was lowered far below the corresponding Curie temperature. The discontinuous change in dielectric constant evidently corresponds to a first order phase transition to a pressure-induced phase which is denoted as Phase III in this paper. Figure 2 indicates a isothermal variation of the dielectric constant with pressure at 36°C. At about 7.5 kbar, a discontinuous change accompanying the II-III transition is seen. The decrease in dielectric constant at the II-III transition was not recovered by lowering pressure to 1 atm. The fact indicates that the high pressure III Phase can be brought to atmospheric pressure as a metastable structure.

The resultant pressure-temperature phase diagram of $RbHSO_4$ is illustrated in Fig. 3. The ferroelectric Curie temperature linearly increases with increasing pressure with a slope of $dT_c/dp=12.0\pm0.1$ deg kbar^{-1}. The Curie temperature at 1 atm was $-(9.5\pm0.1)$°C which is in good agreement with $-(9.4\pm0.1)$°C obtained by a recent heat capacity measure-

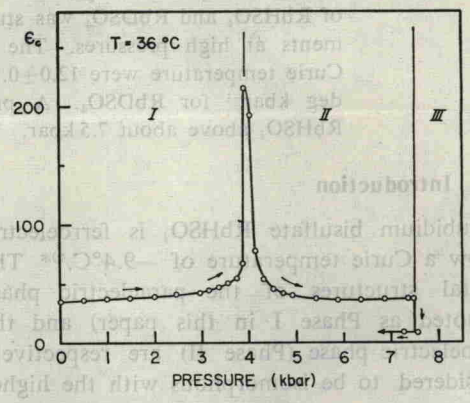

Fig. 2. Pressure dependence of the dielectric constant ε_c along the *c*-axis of $RbHSO_4$ at $T=36$°C. Frequency: 100 kHz.

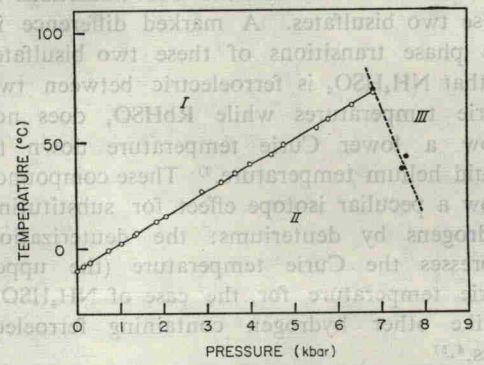

Fig. 3. Pressure-temperature phase diagram of $RbHSO_4$.

ment by Chihara.[8] Since the specimen was cracked when it was once brought into Phase III, the equilibrium II-III (or I-III) phase boundary was not determined. In Fig 3, an estimated II-III phase boundary is represented only for increasing pressure run (or increasing temperature run) by a slashed line. The I-II-III triple point is roughly estimated to be at $T=73$°C, $p=6.9$ kbar.

The pressure dependence of the Curie temperature of $RbDSO_4$ is shown in Fig. 4. The pressure coefficient of the Curie temperature of $RbDSO_4$ was determined as $dT_c/dp=12.7$