

$\pm 0.2$  deg kbar<sup>-1</sup> up to about 2.5 kbar. The Curie temperature at 1 atm was  $-(21.9 \pm 0.1)^\circ\text{C}$  for the present specimen, which is in accord with  $-(21.4 \pm 0.5)^\circ\text{C}$  reported by Yamada and Kamiyoshi.<sup>4)</sup>

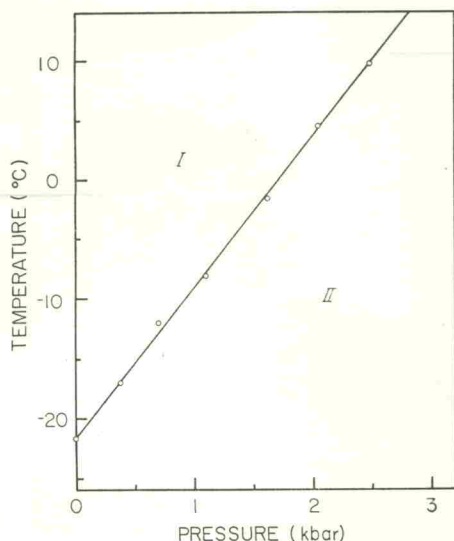


Fig. 4. Temperature dependence of the ferroelectric Curie temperature of RbDSO<sub>4</sub>.

#### § 4. Discussion and Conclusive Remark

The plus sign of the pressure coefficients of the Curie temperatures of RbHSO<sub>4</sub> and RbDSO<sub>4</sub> indicates that an order-disorder process of hydrogens (or deuteriums) in hydrogen bonds is not responsible to the ferroelectric phase transitions in these materials.<sup>12)</sup> The above result is consistent with the peculiar isotope effect of RbHSO<sub>4</sub>, and also with the results of recent deuterium quadrupole resonance study by Kasahara and Tatsuzaki<sup>13)</sup> which showed that the deuteriums are in acentric positions even in the paraelectric state of RbDSO<sub>4</sub>.

According to Chihara<sup>9)</sup> the change in the specific heat at the Curie temperature of RbHSO<sub>4</sub> is  $8.6 \text{ J deg}^{-1} \text{ mol}^{-1}$ , then the Ehrenfest relation together with the present result of  $dT_c/dp = 12.0 \text{ deg kbar}^{-1}$  and density of  $2.89 \text{ g cm}^{-3}$ <sup>2)</sup> yields a change in the cubic thermal expansion coefficient at the Curie temperature as  $\Delta\alpha = -6.2 \times 10^{-5} \text{ deg}^{-1}$ . Yamada and Shimazu<sup>14)</sup> showed that the changes in the linear thermal expansion coefficients along the *b*- and *c*-axis are  $-1.25 \times 10^{-4} \text{ deg}^{-1}$  and  $2.5 \times 10^{-5} \text{ deg}^{-1}$ , respectively. Then, the change in

the temperature coefficient of  $(a \cdot \sin \beta)$  should be  $3.8 \times 10^{-5} \text{ deg}^{-1}$ . The result indicates that the change in the linear thermal expansion of RbHSO<sub>4</sub> at the Curie temperature is rather uniaxial along the monoclinic axis of *b*.

The existence of the pressure induced Phase III of RbHSO<sub>4</sub> showed that the ferroelectric state of RbHSO<sub>4</sub> is restricted in a limited region in the *p*-*T* plane alike to NH<sub>4</sub>HSO<sub>4</sub>. This would provide an important piece of information for those who intend to understand the ferroelectricity in these two isomorphous bisulfates on a common basis. The equilibrium II-III phase boundary was not determined because of very long time constant for the III-II transition especially at low temperatures. Thus, whether RbHSO<sub>4</sub> has a lower Curie temperature at 1 atm in equilibrium seems still to be open to question; even if Phase III is stabilized at low temperatures at 1 atm, it would need very long time to realize the final equilibrium state.

#### Acknowledgement

The authors would thank Professor I. Tatsuzaki of Hokkaido University for providing a single crystal of RbDSO<sub>4</sub>. Thanks are also deboted for Dr. N. Yamada of Tohoku University and for Professor H. Chihara of Osaka University who showed experimental results prior to publication.

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the final equilibrium state. I aim, it would need very long time to realize Phase III is stabilized at low temperatures at Curie temperature at 1 atm in equilibrium. Thus whether RbHSO<sub>4</sub> has a lower for the III-II transition especially at low temperatures determined because of very long time constant equilibrium II-III phase boundary was not phase disulfates on a common basis. The stand the ferroelectricity in these two isomorphous information for those who intend to understand This would provide an important piece of region in the p-T plane alike to NH<sub>4</sub>HSO<sub>4</sub>. state of RbHSO<sub>4</sub> is restricted in a limited III of RbHSO<sub>4</sub> showed that the ferroelectric

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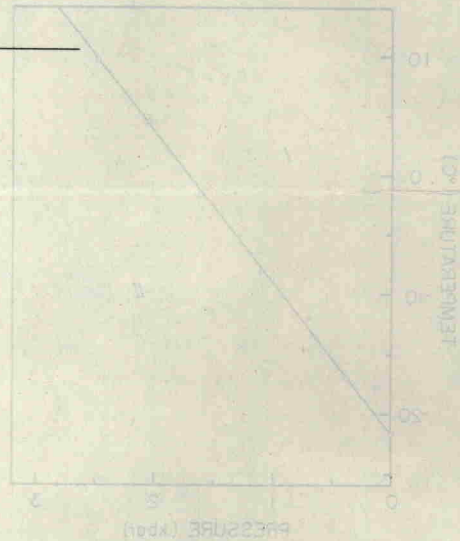


Fig. 4 Temperature dependence of the ferroelectric Curie temperature of RbDSO<sub>4</sub>.

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