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**Effect of Hydrostatic Pressure  
on the Ferroelectric Phase Transitions  
in  $\text{CsH}_2\text{PO}_4$  and  $\text{CsD}_2\text{PO}_4$**

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Ferroelectric activity in  $\text{CsH}_2\text{PO}_4$  and  $\text{CsD}_2\text{PO}_4$  was first reported by Levstik *et al.*<sup>1)</sup> They reported a large isotope effect on the ferroelectric Curie point; the Curie point of  $\text{CsH}_2\text{PO}_4$ ,  $T_c^H = -119.5^\circ\text{C}$  is increased to  $T_c^D = -5.55^\circ\text{C}$  by deuteration. Recent X-ray diffraction study by Uesu and Kobayashi<sup>2)</sup> showed that the crystal structure of  $\text{CsH}_2\text{PO}_4$  at room temperature belongs to the monoclinic system (space group:  $P2_1/m$ ) unlike to other  $\text{KH}_2\text{PO}_4$ -type ferroelectrics in which the paraelectric phases belong to the tetragonal system. The lattice parameters at room temperature are  $a = 7.90065 \text{ \AA}$ ,  $b = 6.36890 \text{ \AA}$ ,  $c = 4.87254 \text{ \AA}$  and  $\beta = 107.742^\circ$ .<sup>2)</sup> (The crystal structure can be described as a pseudo-orthorhombic system  $a' = 15.801 \text{ \AA}$ ,  $b' = 6.36890 \text{ \AA}$ ,  $c' = 4.8725 \text{ \AA}$  and  $\beta' = 89.78^\circ$  by taking  $a' = 2a + c$ ,  $b' = b$  and  $c' = c$ .) The spontaneous polarization is parallel to the  $b$ -axis. Slightly different mechanism of the ferroelectric transition has been suggested for  $\text{CsH}_2\text{PO}_4$  from that for  $\text{KH}_2\text{PO}_4$ .<sup>2,3)</sup>

In the present note we report the effect of hydrostatic pressure on the ferroelectric phase transitions in  $\text{CsH}_2\text{PO}_4$  and  $\text{CsD}_2\text{PO}_4$ . This work aimed to see whether  $\text{CsH}_2\text{PO}_4$  shows a different pressure effect from other  $\text{KH}_2\text{PO}_4$ -type ferroelectrics. The compound  $\text{CsH}_2\text{PO}_4$  was synthesized by the reaction,  $\text{Cs}_2\text{CO}_3 + 2\text{H}_3\text{PO}_4 = 2\text{CsH}_2\text{PO}_4 + \text{H}_2\text{O} + \text{CO}_2$ . Single crystals were grown by slow evaporation of an aqueous solution. The deuterated analogue  $\text{CsD}_2\text{PO}_4$  was synthesized by the similar way;  $\text{Cs}_2\text{CO}_3 + 2\text{D}_3\text{PO}_4 = 2\text{CsD}_2\text{PO}_4 + \text{D}_2\text{O} + \text{CO}_2$ . Deuterated phosphoric acid (deuteration rate 99%) was obtained from E. Merk Co. Ltd. The Curie point of thus grown deuterated compound was about  $-11^\circ\text{C}$ . It was slightly raised to  $-8.5^\circ\text{C}$  after two successive recrystallizations from 99.7%  $\text{-D}_2\text{O}$  solution. Further recrystallizations from  $\text{D}_2\text{O}$  solution did not seem to increase the Curie point drastically. The

Curie point of the deuterated specimen used in the present work was slightly lower than that reported by Levstik *et al.*<sup>1)</sup> but almost equal to that reported by Semmingen *et al.*<sup>3)</sup>

Several  $b$ -plate specimens were cut from the single crystals and gold foil was attached on the surfaces as electrodes. A Cu-Be bomb was served for the high pressure measurements. The pressure-transmitting fluid used was 1:1 mixture of  $n$ - and  $iso$ -pentane. The capacitance was measured with an LCR-meter and recorded on an x-y recorder as a function of temperature at various pressures. At the Curie point pronounced peak in the capacitance was observed both for  $\text{CsH}_2\text{PO}_4$  and for  $\text{CsD}_2\text{PO}_4$ .

In Fig. 1 the observed pressure-temperature phase diagrams of  $\text{CsH}_2\text{PO}_4$  and  $\text{CsD}_2\text{PO}_4$  are indicated. In  $\text{CsH}_2\text{PO}_4$ , the Curie point decreases with increasing pressure. The pressure range studied in the present work was limited because of the solidification of the pressure-transmitting fluid used. The pressure dependence of the Curie point  $T_c^H$  can be approximated by a linear relation of  $T_c^H = T_c^H(0) + K^H p$  with the parameters of  $T_c^H(0) = -119.8 \pm 0.3^\circ\text{C}$  and  $K^H = -5.6 \pm 0.3 \text{ deg kbar}^{-1}$ .

In  $\text{CsD}_2\text{PO}_4$ , the Curie point also decreases with increasing pressure. Up to about 6 kbar, a linear relation  $T_c^D = T_c^D(0) + K^D p$  holds with the

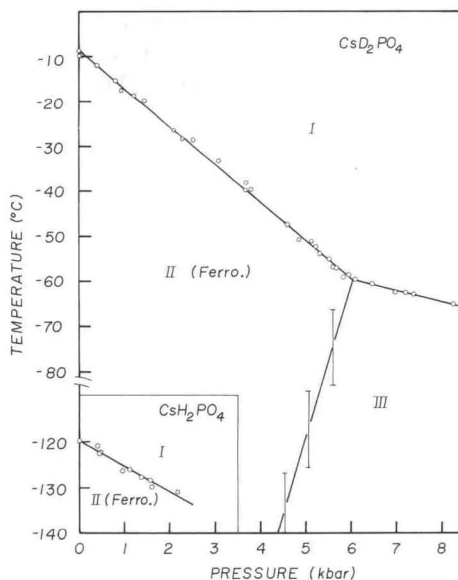


Fig. 1. Pressure-temperature phase diagrams of  $\text{CsH}_2\text{PO}_4$  (insert) and  $\text{CsD}_2\text{PO}_4$ . The vertical bars indicate thermal hysteresis of the II-III transition.

parameters of  $T_c^D(0) = -8.5 \pm 0.2^\circ\text{C}$  and  $K^D = -8.5 \pm 0.1 \text{ deg kbar}^{-1}$ . Above about 6 kbar a  $\lambda$ -type maximum of the dielectric constant of  $\text{CsD}_2\text{PO}_4$  is not observed, instead a step-like discontinuity is seen. The transition point vs. pressure relation lies on another straight line than the  $T_c^D$  vs.  $p$  above 6 kbar. This indicates that there is a pressure-induced phase above 6 kbar, and the phase is called Phase III in this note. The pressure slope of the I-III transition point is  $dT_c^{\text{I-III}}/dp = -2.5 \pm 0.2 \text{ deg kbar}^{-1}$ . The transition from Phase II (the ferroelectric phase) to Phase III is characterized by a discontinuous jump in the dielectric constant and marked thermal hysteresis of  $15\text{--}17^\circ\text{C}$  as shown in Fig. 1. The I-II-III triple point exists at  $p_{\text{tr}} = 6.04 \pm 0.2 \text{ kbar}$  and  $T_{\text{tr}} = -59.8 \pm 0.3^\circ\text{C}$ . The estimation of the pressure coefficient of the II-III transition point in equilibrium is difficult because of the large thermal hysteresis, but very roughly it is  $\sim 33 \text{ deg kbar}^{-1}$ . Ferroelectric activity of  $\text{CsD}_2\text{PO}_4$  in Phase III has not been recognized so far.

The present results show that the effects of deuteration and of hydrostatic pressure on the Curie points of  $\text{CsH}_2\text{PO}_4$  are quite similar to those in  $\text{KH}_2\text{PO}_4$ : That is, the ratio of the Curie point of deuterated compound to that of normal compound  $T_c^D(0)/T_c^H(0)$  is 1.74 for  $\text{CsH}_2\text{PO}_4$  and 1.73 for  $\text{KH}_2\text{PO}_4$ .<sup>4)</sup> The fractional pressure coefficient of the Curie point of the normal compound  $d(\ln T_c^H)/dp$  is  $-0.036 \text{ kbar}^{-1}$  for  $\text{CsH}_2\text{PO}_4$  and  $-0.037 \text{ kbar}^{-1}$  for  $\text{KH}_2\text{PO}_4$ .<sup>4)</sup> The similarity

suggests that the proton tunneling motion plays an important role in the ferroelectric process in  $\text{CsH}_2\text{PO}_4$  as in the case of  $\text{KH}_2\text{PO}_4$ .

The Curie constant  $C$  have been reported to be  $4.3 \times 10^4 \text{ K}$  and  $3.2 \times 10^4 \text{ K}$  for  $\text{CsH}_2\text{PO}_4$  and  $\text{CsD}_2\text{PO}_4$ , respectively.<sup>1)</sup> Then, the volume electrostrictive coefficients  $Q_h$  are estimated to be  $0.82 \times 10^{-12} \text{ cgs esu}$  for  $\text{CsH}_2\text{PO}_4$  and  $1.67 \times 10^{-12} \text{ cgs esu}$  for  $\text{CsD}_2\text{PO}_4$  by using the relation  $Q_h = (-2\pi/C) \cdot (dT_c/dp)_{p=0}$  together with the observed pressure coefficients of the Curie points. The electrostrictive coefficient of  $\text{CsH}_2\text{PO}_4$  is comparable with  $Q_h = Q_{12} + Q_{22} + Q_{32} = 0.6 \times 10^{-12} \text{ cgs esu}$  obtained from thermal expansion measurements by X-ray diffraction.\*

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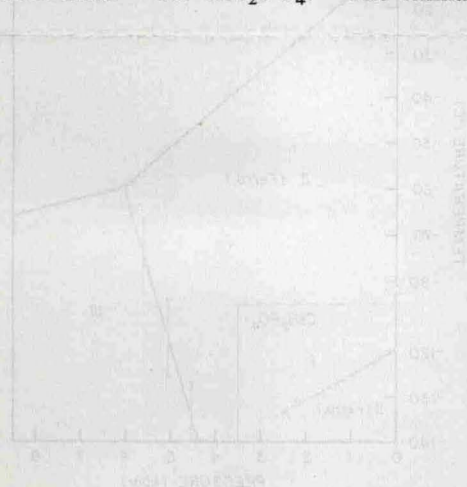


Fig. 1. Pressure-temperature phase diagram of  $\text{CsH}_2\text{PO}_4$  (open) and  $\text{CsD}_2\text{PO}_4$  (filled circles). The vertical bar indicates thermal hysteresis of the II-III transition.