# High-Pressure Phase Relations of CsD$_2$PO$_4$

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The high-pressure phase diagram of CsD$_2$PO$_4$ to 4.5 GPa and temperatures between 0 and 470°C is reported. Comparisons are made with CsH$_2$PO$_4$ and correlated with the isotope effect on the high-temperature high-pressure phase relations of KH$_2$PO$_4$.

## Introduction

The effect of deuteration on the ferro-electric phase transition in the potassium dihydrogen phosphate (KH$_2$PO$_4$) class of compounds has been extensively studied (*1–5*).

Recently, the effect of deuteration on the high-temperature and high-pressure phase relations of KH$_2$PO$_4$ has been reported (*6*). The present work is a similar study of the high-pressure phase relations of deuterated cesium dihydrogen phosphate (CsD$_2$PO$_4$ or DCDP).

At room temperature CsD$_2$PO$_4$ has a monoclinic (*7*) paraelectric structure with space group $C_{2n}^2 - P_{2_1}/m$. Below the Curie point the ferroelectric phase is monoclinic (*8*) space group $C_2^2 - P_{2_1}$. The Curie point in CsH$_2$PO$_4$ lies at $-119.5$°C (*9*), while in CsD$_2$PO$_4$ it lies at $-5.5$°C (*10*). The large shift in the ferroelectric–paraelectric transition temperature is attributed to the role of the hydrogen bond in the transformation,

and is similar to the shift observed on deuteration of KH$_2$PO$_4$ (*9*). It should be noted, however, that the ferroelectric and paraelectric phases of KH$_2$PO$_4$ and CsH$_2$PO$_4$ are not isomorphous.
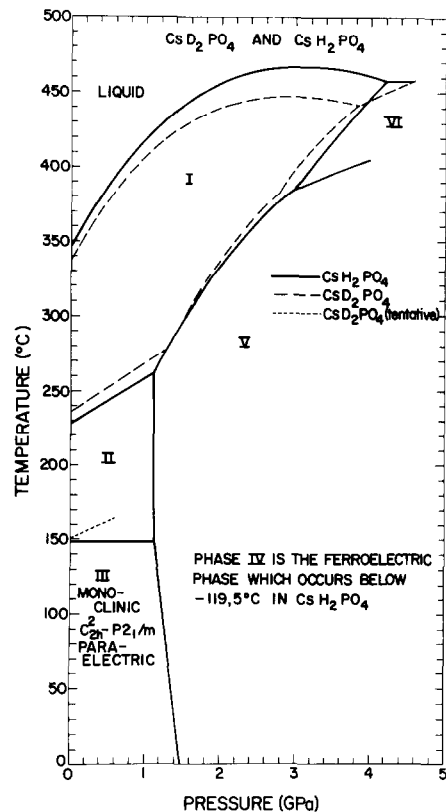
## Experimental

Single-crystal CsD$_2$PO$_4$ was grown by slow evaporation of an aqueous solution of Cs$_2$CO$_3$ and deuterated phosphoric acid. The 99% deuterated D$_3$PO$_4$ was obtained from Merck. The Curie point of the thus-grown deuterated compound was about $-11$°C. It was slightly raised to $-8.5$°C after two successive recrystallizations from D$_2$O solution. The Curie point of the deuterated specimen used in the present work was slightly lower than that reported by Levstik *et al.* (*10*), but almost equal to that reported by Semmingsen *et al.* (*11*). As expected, the CsD$_2$PO$_4$ shows the identical X-ray diffraction pattern as its undeuter-
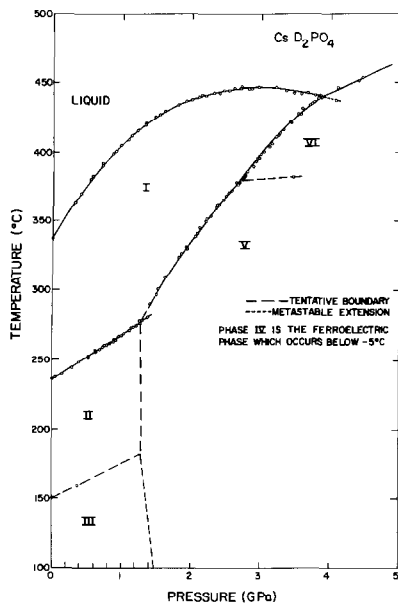
FIG. 1. Phase diagram of $CsD_2PO_4$.



FIG. 2. Comparison of the phase diagrams of $CsH_2PO_4$ and $CsD_2PO_4$.

ated analog. No other impurities could be discerned by this technique.

Chips of single-crystal $CsD_2PO_4$ were finely ground and loaded into niobium capsules which had been redesigned to minimize leakage (12). All handling was done in a glovebox under a dry nitrogen atmosphere to minimize hydrogen isotope exchange. Pressures of up to 4.8 GPa were generated in a piston–cylinder device (13) using supported pistons. Phase transformations were studied by means of differential

thermal analysis (DTA) with chromel-alumel thermocouples. Heating/cooling rates varied between 0.5 and 0.8°C/sec. Signals were taken from two runs on each boundary. The phase boundaries are believed to

TABLE I

PHASE RELATIONS OF $CsD_2PO_4$

| Transition | Fit ($P$ in GPa) | Standard deviation (°C) |
|---|---|---|
| II/I | $t(°C) = 236 + 323\,P$ | 0.5 |
| V/I | $t(°C) = 277 + 89.8\,(P - 1.27)$ $- 12.5\,(P - 1.27)^2$ | 0.9 |
| VI/I | $t(°C) = 382 + 68.9\,(P - 2.74)$ $- 13.5\,(P - 2.74)^2$ | 0.7 |
| VI/Liquid | $t(°C) = 441 + 2.21\,(P - 3.87)$ | 0.9 |
| I/Liquid | $t(°C) = 338 + 87.5\,P - 22.2\,P^2$ $+ 1.6\,P^3$ | 0.9 |

be accurate to ±0.05 GPa and ±2°C unless otherwise stated.

Further details of experimental techniques have been reported elsewhere (*14, 15*).

## Results

The phase diagram of $CsD_2PO_4$, based on heating signals only, is shown in Fig. 1. The shape of the boundaries and nature of the transitions are similar to those of $CsH_2PO_4$ determined by Rapoport *et al.* (*6*), and it is concluded that all phases are isostructural. The phase diagrams are compared in Fig. 2. Phase relations are summarized in Table I, and coordinates of triple points collated in Table II.

The quasi-irreversible character of the III/II transition, identical to that of $CsH_2PO_4$, contributed to the difficulty in determining the position of the III/II boundary. A tentative boundary is shown in Fig. 1. Insufficient sample precluded the determination of the III/V and II/V boundaries of $CsD_2PO_4$ by volumetric techniques.

The II/I boundary was followed to the I/II/V triple point at 1.27 GPa, 277°C. The upward shift of the boundary relative to the undeuterated analog is significant, being 6°C at atmospheric pressure, with the triple point being 15°C and 0.17 GPa higher. This results in a significant increase in the temperature and pressure stability field of

phase II. The cooling signals were found 10–12°C below the heating signals. In comparison, the cooling signals of the II/I boundary of $CsH_2PO_4$ were 25–30°C below the heating signals. Typical DTA signals for the II/I transition of $CsD_2PO_4$ are shown in Fig. 3(i).

Beyond the I/II/V triple point, the V/I transition had characteristically broader signals than the II/I transition, which is attributed to the steepness of the boundary. Cooling signals were 12–18°C below the heating signals (Fig. 3(ii)), in comparison with ~20°C for $CsH_2PO_4$. The I/V/VI triple point is found at a lower pressure (0.25 GPa) than the corresponding triple point of $CsH_2PO_4$. The V/VI boundary of $CsD_2PO_4$ could not be followed. However, the VI/I transition, with a large associated enthalpy change indicated by large signals (Fig. 3(iii)), could be followed to the I/VI/Liquid triple point at 3.87 GPa, 441°C. This triple point is lower in temperature (16°C) and pressure (0.33 GPa) than the corresponding triple point of $CsH_2PO_4$.

KDP-type materials are known to decompose at atmospheric pressure and elevated temperatures (*16*). At elevated pressures, however, this decomposition is

TABLE II

COORDINATES OF TRIPLE POINTS

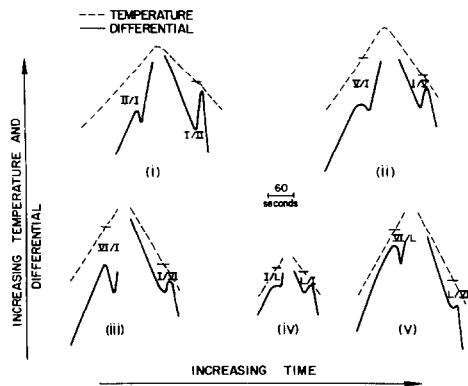| | Compound | |
| | CsH₂PO₄ | CsD₂PO₄ |
| Triple Point | (°C, GPa) | (°C, GPa) |
| --- | --- | --- |
| I/II/V | 262, 1.10 | 277, 1.27 |
| II/III/V | 148, 1.12 | ~180, 1.29 |
| I/V/VI | 385, 2.99 | 382, 2.74 |
| I/VI/Liquid | 457, 4.20 | 441, 3.87 |



FIG. 3. Typical DTA signals for phase transitions of $CsD_2PO_4$. (i) II/I at 1.00 GPa, 267.5°C; (ii) V/I at 2.21 GPa, 349.9°C; (iii) VI/I at 3.12 GPa, 404.6°C; (iv) I/L at 0.56 GPa, 382.5°C; (v) VI/L at 41.0 GPa, 447.0°C.

prevented and melting is observed. This has been confirmed in a number of studies (6, 17, 18). In the case of $CsD_2PO_4$, pressure also suppresses decomposition. The melting point of $CsD_2PO_4$ at atmospheric pressure is depressed by 8°C to 338°C relative to $CsH_2PO_4$. This trend of depressed melting is continued along the entire I/Liquid melting curve to the I/VI/Liquid triple point. Deuteration therefore reduces significantly the range of stability of phase I with both temperature and pressure.

The same broad maximum shown by $CsH_2PO_4$ is apparent in the melting curve of $CsD_2PO_4$. The maximum is estimated to be at 2.86 GPa, 446°C. Typical melting signals are shown in Fig. 3(iv). Beyond the I/VI/Liquid triple point, the VI/Liquid boundary was determined to 4.5 GPa. Freezing signals were about 10°C below the melting signals, as in the case of $CsH_2PO_4$. Typical signals are shown in Fig. 3(v).

## Discussion

The effect of deuteration on the high-temperature and high-pressure phases of $CsH_2PO_4$ may be compared with the deuteration effect of $KH_2PO_4$. Deuteration dramatically extends the region of stability of the monoclinic $KH_2PO_4$ II' phase (19–21). No effect of such magnitude was observed for CDP. However, it should be noted that the decrease in the region of stability of $CsH_2PO_4$ I on deuteration is remarkably similar to the decrease in the stability of $KH_2PO_4$ I (6).

Rapoport et al. (6) have proposed that $CsH_2PO_4$ I and $KH_2PO_4$ I are isostructural on the basis of thermodynamic considerations. As the deuterated phases I of $CsD_2PO_4$ and $KD_2PO_4$ are assumed to be isostructural with their undeuterated analogs, $CsD_2PO_4$ I and $KD_2PO_4$ I are, for the same considerations, likely to be isostructural.

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