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Comment on "Does the structural superionic phase transition at 231 °C in CsH₂PO₄ really not exist?" [J. Chem. Phys. 110, 4847 (1999)]

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Superionic materials have intrigued researchers because they exhibit structural transitions from the paraelectric to the superionic phase which are accompanied by an increase of the electrical conductivity as much as five orders of magnitude. Notwithstanding the number of studies and variety of experiments that have been carried out on superprotonic crystals of the KH₂PO₄ type, no generally agreed-upon model describing the structural and chemical features that induce superionic transitions exists. Discrepancies between the high-temperature results reported by different groups of scientists have been well summarized in recent papers.^{1,2}

Lee¹ has discussed the similarities of the phase transitions in the KH₂PO₄-type compounds and concluded that the high-temperature phenomena of these compounds are not related to physical changes like structural phase transitions, but related to chemical ones and has suggested that the term "high-temperature phase transition" should be replaced by "onset of partial polymerization at reaction sites distributed on the surface of solids."

In order to check if the reported high-temperature phase transitions of CsH₂PO₄ (CDP) are *only* related to thermal dehydration, power x-ray measurements were performed by Ortiz *et al.*² A fresh powder sample was subsequently heat treated 1 min at 130, 165, 200, 238, and 250 °C, and their respective x-ray diffraction patterns taken under dry conditions after cooling at room temperature (25 °C) were plotted (see Fig. 3 of Ref. 2). That strategy of the experiment is very good for presenting the thermal decomposition process of CDP as a function of annealing temperature; however, it is insufficient to conclude that the reported transition³⁻¹² associated with endothermic anomaly at ca. 231 °C does not take place and, moreover, that the high conductivity above 231 °C is *only* a consequence of the dehydration of the crystal surface.

Under normal air conditions the high-temperature transition occurs very close to the region where CDP decomposes by dehydration and these two simultaneous effects considerably complicate the interpretation of the phase relation.

Ten years ago the Bond method of precise lattice parameter determination was applied as a sensitive monitor of the structural changes occurring in the CDP crystal.⁹ Lattice parameters of CDP were calculated on the basis of the measurements of the Bragg angles of the reflections with high θ angles using the least-square method. The accuracy of the measurements of 2θ , which was better than 10" of arc, al-

lowed the determination of the lattice parameters to an accuracy better than 3×10^{-5} . Investigations of the lattice parameters of CDP above room temperature have revealed that up to ca. 137 °C all parameters are almost linear. In the vicinity of 149 °C a discrepancy of the linearity of the lattice parameters has been noticed, but the space group ($P2_1/m$) of the crystal above room temperature up to ca. 231 °C does not change. The investigation of the single-crystal samples of CDP with the Bond diffractometer above 207 °C appeared to be difficult because of the decreasing intensity and considerable broadening of the profiles of some Bragg reflections. It was only possible to find the temperature dependence of the lattice parameter b on the basis of the very strong (080) reflection in the temperature range from room temperature to ca. 231 °C. The polycrystallization of the sample due to a phase transition and/or a decomposition process of the sample above 231 °C caused a drastic decrease of the intensity of the (080) reflection and the Bond method of investigation above this temperature appeared to be impossible.

The powder x-ray study performed in a normal air atmosphere (from 127 °C to 327 °C on heating with a rate 0.1 °C per minute) using the high-temperature Guinier-camera⁹ allowed study of structural changes and thermal decomposition of CDP. Slightly above 227 °C the powder diffraction pattern shows the transformation of the monoclinic cesium dihydrogen phosphate CsH₂PO₄ to the orthorhombic cesium hydrogen pyrophosphate Cs₂H₂P₂O₇ with the lattice parameters $a = 4.571(7)$ Å, $b = 8.150(9)$ Å, and $c = 11.405(6)$ Å (at 247 °C, $\lambda = 1.54179$ Å). Further heating of the sample causes the conversion of the compound at ca. 267 °C to the monoclinic cesium metaphosphate CsPO₃ with the lattice parameters $a = 12.744(9)$ Å, $b = 4.344(5)$ Å, $c = 6.829(6)$ Å and $\beta = 84.60(7)^\circ$ (at 297 °C, $\lambda = 1.54179$ Å). The powder data of Cs₂H₂P₂O₇ and CsPO₃ have been submitted to the International Centre for Diffraction Data (file nos. 45-619 and 45-617, respectively).

The application of the Guinier camera was insufficient to accurately study the structural changes related to the reported superionic phase transition. A Philips PW1050 powder diffractometer and a Paar TTK chamber with a heating stage were used to clarify this transition.¹² The measurements were performed in air and in a H₂O-saturated atmosphere. Under normal atmosphere the superionic phase transition is obscured by the simultaneous chemical transformation of CsH₂PO₄ to C₂H₂P₂O₇. Under H₂O-saturated atmosphere the

TABLE I. Powder diffraction data for superionic phase of CDP at 237 °C. CsH_2PO_4 cubic, space group $Pm-3m$, $a=4.961(3)$ Å, $Z=1$. Cu K_α radiation, graphite monochromator.

hkl	2θ (°)	I_{obs}	$I_{\text{cal-1}}^a$	$I_{\text{cal-2}}^b$
100	17.86	28.1	45.5	12.8
110	25.37	100.0	100.0	100.0
111	31.20	7.0	12.4	10.3
200	36.18	11.5	14.7	11.9
210	40.63	15.0	14.0	14.4
211	44.71	16.9	24.3	17.2
220	52.10	3.9	5.9	3.9
300	55.52	3.4	0.8	0.7
221	55.52	3.4	3.3	3.3
310	58.81	4.9	6.3	5.1
311	61.99	0.1	1.8	1.5
222	65.08	0.2	1.2	1.1
320	68.09	1.8	1.1	1.0
321	71.04	5.7	4.2	3.6
400	76.79	1.4	0.3	0.3
410	79.61	0.3	0.4	0.3
322	79.61	0.3	0.4	0.3

^a $I_{\text{cal-1}}$ —calculated for Cs at $x,y,z=0,0,0$ ($U_{\text{iso}}=0.085$ Å²) and P at $x,y,z=0.5,0.5,0.5$ ($U_{\text{iso}}=0.085$ Å²) disregarding oxygen and hydrogen atoms.

^b $I_{\text{cal-2}}$ —calculated like $I_{\text{cal-1}}$ for Cs and P but with four O per unit cell in $x,y,z=0.5,0.25,0.366$ ($U_{\text{iso}}=0.1$ Å²) (Ref. 12).

superionic phase transition takes place at ca. 231 °C without decomposition and is reversible with hysteresis on cooling. Powder diagrams of the superionic phase of CDP exhibit for $2\theta < 80^\circ$ 15 separate and well-resolved reflections which can be indexed as a cubic P -type lattice with $a=4.961$ Å at 237 °C. As a consequence of the lack of systematic absences, the lines correspond to space group symmetry $Pm-3m$ with a unit cell content of one formula unit (Table I). Rietveld refinements lead to a CsCl-type structure with Cs at $x,y,z=0,0,0$ and P at $x,y,z=0.5,0.5,0.5$ and high thermal motion parameters for both. Oxygen and hydrogen atoms of the phosphate group are dynamically disordered.¹² The powder data of the superionic phase of CDP have been submitted to the ICDD (file no 45-618). On transition from the paraelectric phase to the superionic one, the volume per formula unit shows a sudden increase by $\Delta V=3.6$ Å³ and the crystal of CDP is subjected to serious strain. This feature is accompanied by an increase of the electrical conductivity by three orders of magnitude.⁸ Raman spectra of the superionic phase of CDP are characteristic of a plastic phase, implying rapid reorientation of the H_2PO_4^- anions on given sites.¹⁰ Reorientation of the O–H groups leads to the breaking up of the old hydrogen bonds and creating of new ones. This dynamically disordered hydrogen bond network is responsible for the high proton conductivity.

In order to get more information about an irreversible transition at 107 °C¹³ and a quasi-irreversible transition at

149 °C,^{4,5} the crystal structure of CDP was studied at 20 °C and 220 °C using a Philips PW1100 four-circle diffractometer.¹² The crystal structure of CDP at both temperatures turned out to be the same. No evidence was found for a structural phase transition between two monoclinic forms at 107 °C as was earlier suggested.¹³

On the basis of the above results, one can conclude that the CDP crystals undergo a structural and reversible superionic phase transition at ca. 231 °C. The superionic phase of CDP is unstable under normal air condition due to dehydration which leads to the formation of $\text{Cs}_2\text{H}_2\text{P}_2\text{O}_7$. Under H_2O -saturated atmosphere the superionic phase transition of CDP takes place without decomposition. The superionic phase of CDP has cubic symmetry $Pm-3m$. Structural disorder of the superionic phase of CDP has been confirmed. The paraelectric monoclinic phase of CDP does not change its $P2_1/m$ space symmetry group and from the crystallographic point of view is stable over the temperature range from the temperature of the ferroelectric phase transition ($T_c=-120$ °C) to the temperature of the superionic phase transition ($T_s=231$ °C). The model for the superionic phase transition where the increase of symmetry from monoclinic to cubic is used to explain the transition from a low to a high conductivity phase¹⁴ seems to be valid for CDP.

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