

Crystal Structure of a New Monoclinic Form of Potassium Dihydrogen Phosphate Containing Orthophosphacidium Ion, $[\text{H}_4\text{PO}_4]^+$

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Received July 23, 1993; in revised form January 14, 1994; accepted March 9, 1994

The crystal structure of a new monoclinic form of potassium dihydrogen phosphate, KH_2PO_4 , has been determined by single crystal X-ray diffraction. Crystals are monoclinic, space group $P2_1/c$ with $a = 7.4399(7)$, $b = 7.2634(9)$, $c = 9.3629(13)$ Å, $\beta = 127.696(8)^\circ$, $V = 400.35(9)$ Å³, $d_m = 2.25$, $d_c = 2.257$ Mg m⁻³ for $Z = 4$, $\mu = 17.9$ cm⁻¹, $F(000) = 272$, $T = 293$ K. The structure was refined to $R = 0.022$ and $R_w = 0.038$ for 740 reflections with $I \geq 3\sigma(I)$. The crystal structure consists of a compact assembly of potassium and phosphate ions, arranged in columns along the b -axis, bound by $\text{K}\cdots\text{O}$ ionic bonds and $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds in a three-dimensional network as in all other forms of KH_2PO_4 and KD_2PO_4 . The two crystallographically nonequivalent phosphate groups appear to exist as an orthophosphacidium ion, $[\text{H}_4\text{PO}_4]^+$ and a PO_4^{3-} ion rather than as the expected H_2PO_4 ions. This study provides the first example of crystal structure determination of the $[\text{P}(\text{OH})_4]^+$ ion. © 1995 Academic Press, Inc.

Potassium dihydrogen phosphate, KH_2PO_4 (KDP), is the prototype for a series of hydrogen-bonded ferroelectrics whose properties have attracted wide and sustained interest (1, 2). In order to gain a better understanding of these transitions, KDP and the deuterated analog, KD_2PO_4 (DKDP), have been the subject of several structural studies, of X-ray and neutron diffraction, and have been studied as a function of temperature and pressure (2–11). At room temperature, both KDP and DKDP are paraelectric and belong to the tetragonal space group $I4_2d$. There are no practical differences between these structures except for slight differences in the lengths of the $\text{O}-\text{H}-\text{O}$ bonds (5). On cooling, both KDP and DKDP

undergo a transition to an orthorhombic ($Fdd2$) ferroelectric phase, and again the structures of KDP and DKDP are nearly identical (6). The transition temperature is profoundly influenced, however, by the degree of substitution of D for H. High-temperature phase transitions from the tetragonal to the monoclinic form (space group $P2_1$ or $P2_1/m$) have also been reported for KDP and DKDP (10–13). DKDP is known to crystallize in the monoclinic form from aqueous solution at room temperature, whereas KDP does not (10). During the course of our investigation of calcium/potassium phosphates, we have isolated single crystals of a new monoclinic form of KDP from solution. The crystals are relatively stable in air for several months, unlike the monoclinic DKDP which reverts to tetragonal form on exposure to the air (9). The crystal structure of this new monoclinic form of KH_2PO_4 is reported here.

EXPERIMENTAL

In order to prepare crystals of calcium potassium phosphates/pyrophosphates, a solution containing a small amount of calcium acetate monohydrate and an excess of 1:1 mixture of KH_2PO_4 and $\text{K}_4\text{P}_2\text{O}_7 \cdot 3\text{H}_2\text{O}$ (initially adjusted to pH 10.0 by adding KOH) was kept at 45°C for about 2 weeks and then left at room temperature in a partially sealed container. After several months, it was noted that the bulk precipitate contained an appreciable amount of clear, rectangular, platy, single crystals. These crystals were handpicked and washed with acetone.

Preliminary precession photographs indicated monoclinic symmetry, space group Pc or $P2_1/c$. A well-formed crystal, with the approximate dimensions $0.20 \times 0.18 \times 0.13$ mm, was mounted along the longest dimension and used for X-ray measurements; Enraf–Nonius CAD4 diffractometer; graphite-monochromatized MoK_α , $\lambda = 0.7107$ Å; cell parameters and crystal orientation from a least-squares refinement of the angular settings of 25 reflections with $18 < 2\theta < 51^\circ$; $a = 7.4399(7)$, $b =$

¹ Certain commercial materials and equipments are identified in this paper to specify the experimental procedure. In no instance does such identification imply recommendation or endorsement by the National Institute of Standards and Technology or the ADA Health Foundation, or that the material or equipment identified is necessarily the best available for the purpose.

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TABLE 1
Final Atomic Parameters in KH_2PO_4

| Atom | x | y | z | $B(\text{eq})^a$ |
|-------|------------|------------|-----------|------------------|
| K(1) | 0.5000 | 0.0544(1) | 0.7500 | 2.36(1) |
| K(2) | 0.0000 | 0.3695(1) | 0.2500 | 1.84(1) |
| P(1) | 0.5000 | 0.5721(1) | 0.7500 | 1.56(1) |
| P(2) | 0.0000 | -0.1127(1) | 0.2500 | 1.19(1) |
| O(11) | 0.2748(2) | 0.4479(2) | 0.6144(2) | 2.19(3) |
| O(12) | 0.5405(2) | 0.6986(2) | 0.6299(2) | 1.88(3) |
| O(21) | 0.0818(2) | 0.0144(2) | 0.4128(2) | 1.78(3) |
| O(22) | -0.1982(2) | 0.7702(2) | 0.2060(2) | 2.08(3) |
| H(11) | 0.309(5) | 0.380(6) | 0.714(4) | 9.6(1.5) |
| H(12) | 0.441(4) | 0.288(4) | 0.023(3) | 4.4(7) |

Note. The hydrogen atoms were refined with isotropic temperature factors.

$$^a B_{\text{eq}} = (4/3) \sum \sum_{ij} \beta_{ij} a_i \cdot a_j.$$

7.2634(9), $c = 9.3629(13)$ Å, $\beta = 127.696(8)^\circ$, $V = 400.35(9)$ Å³, $d_m = 2.25$, $d_c = 2.257$ Mg m⁻³ for $Z = 4$, $\mu = 17.9$ cm⁻¹, $F(000) = 272$, $T = 293$ K. The possible doubling of the b -axis, as reported for monoclinic KDP and DKDP (9–11), was carefully checked with both precession photographs and the diffractometer, but no doubling was observed. Intensities were collected by $\omega/2\theta$ scans, $2\theta < 54^\circ$, in one hemisphere, $h = -9$ to 9, $k = 0$ to 9, $l = -11$ to 11; three check reflections were monitored periodically, maximum variation 2.1%; empirical absorption corrections by phi-scan data from 3 reflections, transmission factors 0.937–0.999; 1741 total data measured, equivalent reflections merged into a set of 874 independent reflections ($R_{\text{int}} = 0.014$), 740 with $I \geq 3\sigma(I)$ used in the structure solution and refinements.

The structure was solved by the heavy atom method with Patterson synthesis and subsequent Fourier analyses; full-matrix least-squares refinements, $\sum w(|F_0| - |F_2|)^2$ minimized, with $w^{-1} = [\sigma^2(F_0) + (0.02 F_0)^2]$; correction for secondary isotropic extinction (14) applied, $g = 0.58(2) \times 10^{-5}$; all nonhydrogen atoms refined with anisotropic thermal parameters, all H atoms from difference Fourier synthesis, refined with individual isotropic temperature factors. The difference Fourier map indicated two reasonable positions for the H atom on O11 (H11 and H11a, with $\text{H11} \cdots \text{H11a} = 0.35$ Å) indicating some disorder. Attempts to refine these H atoms independently (with half occupancies) were not successful. When either of these positions was used as a H atom with full occupancy, it gave a high temperature factor and the maximum residual electron density was at the other possible H position. Atomic scattering factors for neutral atoms were taken from (15); final R and R_w and S were 0.022 and 0.038 and 1.38, respectively; parameter Δ/σ of 0.01 (max) on H11; maximum Δ/ρ of $0.41 \text{ e} \text{ \AA}^{-3}$.

The possible disorder of the H atoms on O11 could

mean a lower crystal symmetry than the $P2/c$ assumed in the refinement. Attempts were made to refine the structure in the noncentric space group Pc . The space group Pc would require no symmetry constraints on the two independent PO_4 groups. Comparisons of refinements under the two possible space groups (with K and P anisotropic and O isotropic) indicated the R -ratio test (16) to be significant at the $p < 0.005$ level, but the P–O bond lengths and angles remained nearly identical to those in the space group $P2/c$. During additional refinements, with anisotropic thermal parameters for the oxygen atoms, one O atom (O21) became nonpositive-definite, and the refined positional parameters were not significantly different from those in $P2/c$. Further discussion of the structure is based on the refinement in the space group $P2/c$.

Final atomic parameters are listed in Tables 1 and 2; bond lengths and angles are given in Table 3.³

DISCUSSION

The crystal structure of this monoclinic form of KDP (Fig. 1) consists of a compact assembly of K^+ and phosphate ions bound by $\text{K} \cdots \text{O}$ ionic bonds and $\text{O}-\text{H} \cdots \text{O}$ hydrogen bonds in a three-dimensional network and is similar to other forms of KDP and DKDP. The close similarity in the structures of tetragonal and monoclinic KDP is illustrated in Fig. 2.

Potassium and phosphate ions are arranged in columns (along the b -axis) and within each column, K and P are separated by about $b/2$, as in tetragonal KDP (t-KDP). The relative positions of K and P in adjacent columns are quite different from those of t-KDP. Columns of K and phosphate ions at the corners of a square in t-KDP are shifted to the corners of a rhombus in the monoclinic form (Fig. 2). However, the environments of both K and phosphate ions are quite similar to those in t-KDP; each K is coordinated to eight O atoms, and each O of the phosphate groups is coordinated to two K ions.

The most significant feature of this structure is that the two crystallographically nonequivalent phosphate groups appear to exist as a $(\text{H}_4\text{PO}_4)^+$ and a PO_4^{3-} rather than as the expected H_2PO_4 groups. The P–O bond lengths in $\text{P}(2)\text{O}_4$ [$\text{P}(2)-\text{O}(21) = 1.553(2)$ and $\text{P}(2)-\text{O}(22) = 1.525(2)$ Å] are in good agreement with the mean value of 1.536 Å calculated for a large number of orthophosphate groups (17). The longer $\text{P}(2)-\text{O}(21)$ may be the result of two

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TABLE 2
Anisotropic Thermal Parameters in KH_2PO_4

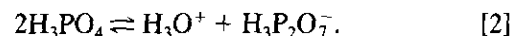
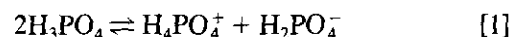
| Atom | U_{11} | U_{22} | U_{33} | U_{12} | U_{13} | U_{23} |
|------|-----------|-----------|-----------|------------|-----------|------------|
| K1 | 0.0217(2) | 0.0235(3) | 0.0209(2) | 0 | 0.0111(1) | 0 |
| K2 | 0.0229(2) | 0.0225(3) | 0.0389(2) | 0 | 0.0162(1) | 0 |
| P2 | 0.0163(2) | 0.0160(3) | 0.0150(2) | 0 | 0.0105(1) | 0 |
| P1 | 0.0194(2) | 0.0210(3) | 0.0178(2) | 0 | 0.0107(1) | 0 |
| O11 | 0.0284(5) | 0.0309(8) | 0.0198(4) | -0.0130(5) | 0.0126(3) | -0.0057(5) |
| O12 | 0.0211(4) | 0.0285(8) | 0.0196(4) | -0.0037(5) | 0.0114(3) | 0.0027(4) |
| O22 | 0.0280(4) | 0.0318(7) | 0.0208(4) | -0.0137(5) | 0.0157(3) | -0.0054(5) |
| O21 | 0.0273(4) | 0.0242(7) | 0.0198(4) | -0.0071(5) | 0.0163(3) | -0.0074(4) |

Note. The thermal parameters are of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + U_{12}hka^*b^* + U_{13}hla^*c^* + U_{23}klb^*c^*)]$.

strong $\text{K}\cdots\text{O}$ bonds. In the case of the $\text{P}(1)\text{O}_4$ group, however, all four $\text{P}-\text{O}$ bond lengths [$\text{P}(1)-\text{O}(11) = 1.622(2)$ and $\text{P}(1)-\text{O}(12) = 1.617(2)$ Å] are significantly longer than those in $\text{P}-\text{OH}$ groups. The observed $\text{P}-\text{O}$ bond lengths involving $\text{P}-\text{OH}$ systems range from 1.55 to 1.59 Å (17). Those $\text{P}-\text{O}$ bond lengths longer than 1.54 Å have been used as a criterion to indicate the presence of $\text{P}-\text{OH}$ groups. The general lengthening of the $\text{P}-\text{OH}$ bond is compensated for by a decrease in the remaining $\text{P}-\text{O}$ distances so as to preserve the mean $\text{P}-\text{O}$ distance. The increase in the $\text{P}-\text{OH}$ bond is also dependent on the number of $\text{P}-\text{OH}$ groups. The mean $\text{P}-\text{O}$ bond lengths observed in the $\text{P}-\text{O}$ and $\text{P}-\text{OH}$ groups are 1.522 and 1.590 Å in HPO_4 , 1.503 and 1.569 Å in H_2PO_4 , and 1.491 and 1.547 Å in H_3PO_4 , respectively (17). It is clear that the $\text{P}-\text{O}$ bond lengths in $\text{P}(1)\text{O}_4$ do not follow this trend. All four $\text{P}(1)-\text{O}$ bond lengths are identical within experimental error, indicating chemical equivalence. The difference-Fourier maps clearly indicated the positions of H atoms bonded to each oxygen atom of this $\text{P}(1)\text{O}_4$ group. Although the shortest intermolecular $\text{O}\cdots\text{O}$ contact is between a pair of atoms of the $\text{P}(2)\text{O}_4$ group related by a center of inversion [$\text{O}(21)\cdots\text{O}(21') = 2.573(3)$ Å], no possible H position could be located along this direction in difference maps. These results indicate that the $\text{P}(2)\text{O}_4$

exists as a normal PO_4^{-3} ion, while $\text{P}(1)\text{O}_4$ represents a $[\text{P}(\text{OH})_4]^+$ ion.

The present study appears to be the first example of a structure containing $[\text{P}(\text{OH})_4]^+$ ion, although its existence, referred to as orthophosphacidium ion, in the crystalline state was reported nearly a half-century ago (18). Both crystalline and fused anhydrous phosphoric acid exhibit an appreciable ionic conductivity attributed to extensive autoprotolysis according to (19).



In the presence of sulfuric acid, a number of phosphates (ortho, pyro, and poly) are quantitatively converted to $[\text{P}(\text{OH})_4]^+$ ion, which may be represented by (20).

TABLE 3
Bond Lengths (Å) and Angles (°) in KH_2PO_4

| K ions | |
|---|--|
| $\text{K}(1)-\text{O}(21^{i,iii}) = 2.779(2)$ | $\text{K}(2)-\text{O}(11^{i,ii}) = 2.760(2)$ |
| $\text{K}(1)-\text{O}(22^{iv,v}) = 2.822(2)$ | $\text{K}(2)-\text{O}(21^{ii,iii}) = 2.866(2)$ |
| $\text{K}(1)-\text{O}(12^{vi,vii}) = 2.907(2)$ | $\text{K}(2)-\text{O}(12^{x,xi}) = 2.915(2)$ |
| $\text{K}(1)-\text{O}(11^{i,iii}) = 3.160(2)$ | $\text{K}(2)-\text{O}(22^{viii,ix}) = 3.174(2)$ |
| Phosphate ions | |
| $\text{P}(1)-\text{O}(11) = 1.622(2)$ | $\text{P}(2)-\text{O}(21) = 1.553(2)$ |
| $\text{P}(1)-\text{O}(12) = 1.617(2)$ | $\text{P}(2)-\text{O}(22) = 1.525(2)$ |
| $\text{O}(11)-\text{P}(1)-\text{O}(11^{iii}) = 122.44(9)$ | $\text{O}(21)-\text{P}(2)-\text{O}(21^{ii}) = 107.04(9)$ |
| $\text{O}(11)-\text{O}(1)-\text{O}(12) = 108.31(9)$ | $\text{O}(21)-\text{P}(2)-\text{O}(22) = 109.31(9)$ |
| $\text{O}(11)-\text{P}(1)-\text{O}(12^{iii}) = 108.54(9)$ | $\text{O}(21)-\text{P}(2)-\text{O}(22^{ii}) = 109.42(9)$ |
| $\text{O}(12)-\text{P}(1)-\text{O}(12^{iii}) = 110.72(9)$ | $\text{O}(22)-\text{P}(2)-\text{O}(22^{ii}) = 112.19(9)$ |
| Hydrogen bonds | |
| $\text{O}(11)-\text{H}(11) = 0.94(3)$ | $\text{O}(12)-\text{H}(12) = 0.81(2)$ |
| $\text{H}(11)\cdots\text{O}(22) = 1.79(4)$ | $\text{H}(12)\cdots\text{O}(22) = 1.82(2)$ |
| $\text{O}(11)\cdots\text{O}(22) = 2.614(2)$ | $\text{O}(12)\cdots\text{O}(22) = 2.618(2)$ |
| $\text{O}(11)-\text{H}(11)\cdots\text{O}(22) = 145(3)$ | $\text{O}(12)-\text{H}(12)\cdots\text{O}(22) = 170(3)$ |

Note. Symmetry operations: (i) x, y, z ; (ii) $-x, y, 1/2 - z$; (iii) $1 - x, y, 1/2 - z + 1$; (iv) $-x, -y, 1 - z$; (v) $1 + x, -y, 1/2 + z, -1$; (vi) $x, y - 1, z$; (vii) $1 - x, y - 1, 1/2 - z + 1$; (viii) $x, 1 + y, z$; (ix) $-x, 1 + y, 1/2 - z$; (x) $1 - x, 1 - y, 1 - z$; (xi) $x - 1, 1 - y, 1/2 + z - 1$.

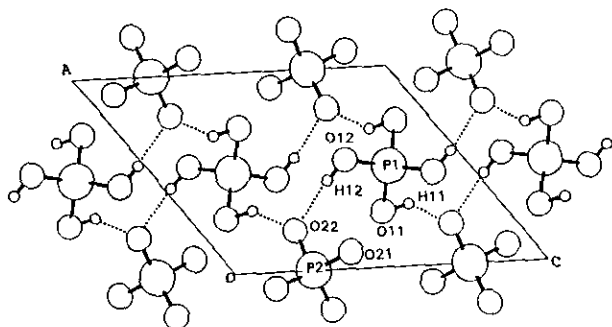


FIG. 1. The structure of KH_2PO_4 projected on the (010) plane. K^+ ions are omitted. $\text{K}(1)$ and $\text{K}(2)$ are in the columns containing $\text{P}(1)$ and $\text{P}(2)$, respectively. The broken lines represent hydrogen bonds.



Similarly, triphenylphosphine oxide, (Ph_3PO), is converted to $[\text{Ph}_3\text{P}(\text{OH})]^+$ ion (20). The formation of $[\text{Ph}_3\text{P}(\text{OH})]^+$ in the crystalline state has also been reported in a nonsulfuric acid medium by the reaction of benzotrifuroxan with triphenylphosphine oxide (21). In subsequent structure analysis, the P–O bond length of 1.639(6) Å in $\text{Ph}_3\text{P}(\text{O}/\text{OH})$ ion has been used (because no hydrogen atom was located) to justify the assignment of a $\text{P}^+ - \text{OH}$ bond and the formula of $[\text{Ph}_3\text{P}(\text{OH})]^+$ (triphenylphosphine oxonium ion) (21). The P–O bond lengths observed in the present study are thus consistent with the formulation of $[\text{P}(\text{OH})_4]^+$.

The dimensions of the probable hydrogen bonds are given in Table 3. All hydrogen atoms are attached to $\text{P}(1)\text{O}_4$ and each P–OH is hydrogen bonded to the O atom of $\text{P}(2)\text{O}_4$. The $\text{O} \cdots \text{O}$ distances (2.614 and 2.618 Å) in these $\text{O} - (\text{H}) \cdots \text{O}$ bonds are longer than those in tetragonal forms of KDP (2.496 Å) and DKDP (2.519 Å). One possible cause may be the "looser" structure associated with the present monoclinic form of KDP, the volume per formula weight being 100.1 Å³ in this monoclinic form compared to 96.8 Å³ for the tetragonal form.

Crystal data for the tetragonal and monoclinic forms of KDP and DKDP are summarized in Table 4. In both KDP and DKDP, there is a slight increase in volume per formula weight (i.e., a decrease in density) associated with the tetragonal-to-monoclinic transition. The difference in the volume of DKDP (97.2/99.1) between the tetragonal and monoclinic phases is much smaller than that of KDP (96.8–100.1), and this smaller difference may explain why DKDP easily crystallizes in the monoclinic form compared to KDP (10). However, this does not account for the stability of the monoclinic form of KDP observed in the present study. The striking similarity in the structure of the tetragonal and monoclinic forms of KDP (Fig. 2)

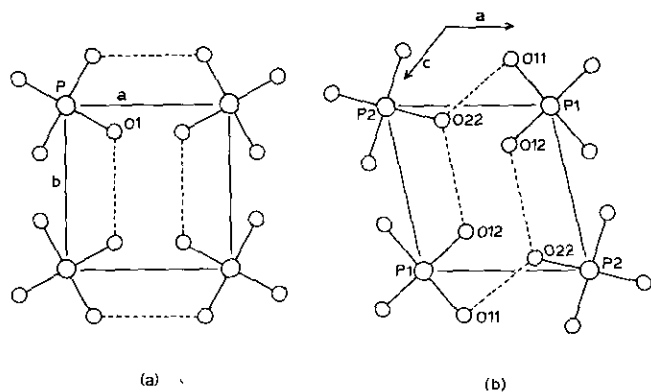


FIG. 2. (a) The structure of tetragonal KDP, projected on (001). All PO_4 groups are equivalent. (b) The structure of monoclinic KDP, projected on (010). K ions are omitted.

TABLE 4
Crystal Data for Tetragonal and Monoclinic Forms of KDP and DKDP

| | Tetragonal | | Monoclinic | | |
|----------------------------|--------------|--------------|------------|--------|-----------|
| | KDP | DKDP | KDP | DKDP | KDP |
| Temperature (K) | 293 | 293 | 468 | 293 | 293 |
| Space group | $I\bar{4}2d$ | $I\bar{4}2d$ | $P2_1$ | $P2_1$ | $P2/c$ |
| <i>a</i> (Å) | 7.451 | 7.467 | 7.471 | 7.47 | 7.440 |
| <i>b</i> (Å) | | | 14.711 | 14.49 | 7.263 |
| <i>c</i> (Å) | 6.973 | 6.975 | 7.167 | 7.33 | 9.363 |
| β (°) | | | 92.34 | 92.2 | 127.70 |
| <i>V</i> (Å ³) | 387.12 | 388.9 | 787.04 | 792.82 | 400.35 |
| <i>Z</i> | 4 | 4 | 8 | 8 | 4 |
| <i>V/Z</i> | 96.8 | 97.2 | 98.4 | 99.1 | 100.1 |
| Reference | 5 | 5 | 11 | 10 | This work |

attests to the stability of this monoclinic form. The columnar arrangement of K and phosphate observed in the *t*-KDP is retained in the monoclinic KDP but not in monoclinic DKDP. The square array of K and phosphate columns in *t*-KDP is shifted to the corners of a rhombus in monoclinic KDP. In spite of the rearrangement of phosphate ions, even the hydrogen bonds appear to be quite similar.

Both KDP and DKDP show two distinct phase transitions, T_p and T_1 , in the temperature range 300 to 500K (10, 12). In DKDP, at least one of these transitions, (T_p), at the lower temperature (383–403K) is also associated with a change from a tetragonal to a monoclinic system, and the crystal remains in the new structure even after cooling back to room temperature. The transition temperature for T_p is also affected by the degree of deuteration, as in the case of ferroelectric transitions, and therefore has been attributed to a change in the hydrogen bond (12). The crystal structure of the monoclinic form of DKDP obtained from solution (9) has been shown to be identical to the monoclinic form (at 386K), corresponding to the transition T_p (11). However, the data and the refinements in both of these studies (9, 11) were inadequate to locate D atoms to establish or rule out the existence of $[\text{P}(\text{OD})_4]^+$ ion. Crystal data for the high temperature monoclinic form of KDP (Table 4) are almost identical to those of the monoclinic form of DKDP and are quite similar to the monoclinic form of KDP used in this study. Thus, it is possible that at least one of the high temperature forms of KDP and DKDP may be similar to the present monoclinic form of KDP.

The paraelectric to ferroelectric phase transitions observed in KDP-type compounds have been explained on the basis of a proton-lattice coupling model, which depends on the dimensions and the configuration of the hydrogen bond. The high-temperature transition to the monoclinic phase is also associated with changes in hydro-

gen bonds (12) that, in turn, may be attributed to the $[P(OH)_4]^+$ ion. Anomalies of thermal expansion coefficients, dielectric constants, and electrical conductivity observed near 180°C (10) may be related to the formation of $[P(OH)_4]^+$ ion. Investigation of the possible role of this ion in the KDP-type transitions is needed.

ACKNOWLEDGMENTS

This investigation was supported, in part, by USPHS Research Grant DE05030 to the American Dental Association Health Foundation by the National Institutes of Health and is part of the dental research program conducted by the National Institute of Standards and Technology in cooperation with the American Dental Association Health Foundation.

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