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Geometric effects of H-atom disordering in hydrogen-bonded ferroelectrics

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Geometric restraints resulting from differences in the electronic structure of the oxygen atoms involved in the —OH- -O= hydrogen bonds are analyzed in terms of their consistency with the symmetry requirements in ferroelectric crystals. The interdependence between these restraints and the symmetry combines the effect of H-atom disordering with displacements of all the atoms involved in the hydrogen bond, and it allows one to evaluate the changes induced by phase transitions in dimensions of hydrogen bonds, in the arrangement of molecules and ions or even the anomalous changes in the unit-cell dimensions and strain tensor of the crystal. Characteristic structural features observed in the KDP-type (where KDP is KH_2PO_4) ferroelectric crystals above T_c, like shortening of the O···O distance, or the inclination angle between the O···O direction and the H-atom hopping trajectory, are explained. Consistence of the calculated structural parameters with those measured experimentally by neutron diffraction for several classes of prototypical KDP-type ferroelectric crystals (squaric acid, $PbHPO_4$, and KH_2PO_4) is structural evidence of the ferroelectric-phase symmetry of the electronic structure in the KDP-type ferroelectric crystals at their paraelectric phase.

I. INTRODUCTION

Since the discovery of ferroelectric-phase transitions much effort and numerous research investigations have been carried out to describe precisely structural changes of the ferroelectric crystals taking place at T_c.[1–5] Of several types of ferroelectric crystals, the materials in which the phase transitions are connected with the transformation of —OH- -O= hydrogen bonds, have been particularly widely and thoroughly studied. The ferroelectric crystals of this type are often referred to as KDP-type ferroelectrics. A potential energy of such crystals can be described with a double-well function depending on the position of the hydrogen atom in the hydrogen bond.[6] Above T_c, the hydrogen atom is dynamically disordered over the two sites with equal occupancy. When temperature is lowered below T_c the onset of ordering of the hydrogen atom breaks the symmetry element relating the two oxygen atoms involved in the hydrogen bonding. The symmetry of the paraelectric phase is lowered in the ferroelectric domains or ferroelastic orientational states,[7] due to the H-atom ordering and small displacements of the nonhydrogen atoms. With the hydrogen bond playing an essential role in the phase transition, many structural studies were undertaken to describe the structural changes it undergoes during the transformation.[8,9] Structures of several KDP-type crystals, KH_2PO_4 (hereafter KDP), KD_2PO_4, RbH_2PO_4, CsD_2PO_4, $PbHPO_4$, squaric acid ($C_4H_2O_4$), and others, in their ferroelectric and paraelectric phases, were precisely determined. However, interpretation of the results proved more complicated and not as satisfactory as for other types of ferroelectric crystals.[10] One of the results, for example, was that the two sites of the disordered hydrogen atom in the paraelectric phase are not located colinearly with the two oxygen atoms involved in the hydrogen bond.[8] When first noticed, the inclination between these directions (the angle ψ between H···H and O···O lines is about 10°) appeared inconsistent with the seemingly apparent back and forth movement of the H atom along the hydrogen bond.[9] Similar difficulties were encountered in attempts to find systematic changes in the H-bond dimensions, e.g., O···O distance, as a function of temperature. While most works on this problem connected the observed H-bond geometry changes with displacements of the heavy atoms (i.e., the atoms other than H or D), or with the anharmonic vibrations of the oxygen atoms forming the hydrogen bond,[9] the approach presented in this paper considers the differences in electronic structure between the donor and acceptor oxygen atoms. This model is based on the coupling of the dynamical disorder of the electronic structure of the donor and acceptor oxygen atoms with the dynamical disorder of the H atom in the hydrogen bond. It gives a fundamental interpretation of the structural geometrical effects and allows to calculate the dimensions of a disordered H bond in the paraelectric phase from its dimensions below T_c. This model also affords explanation and quantitative calculations of atomic displacements, changes in arrangement of molecules or ions or even an anomalous thermal expansion of the crystal close to T_c. The main advantage of the presented model is its simplicity and that it allows us to connect the atomic-scale transformations with macroscopic properties of ferroelectric crystals.

II. H-BOND STRUCTURE IN KDP-TYPE FERROELECTRICS

The common feature of hydrogen bonds in all the KDP-type ferroelectric crystals is that the hydrogen

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atom is bistable in two off-center sites[6] and the electronic charge-density functions of the donor and acceptor oxygen atoms are different. This difference manifests itself not only in the H-atom position, but also in the structural dimensions of the donor and acceptor groups. For example, the bond length of the oxygen atom in the donor group (e.g., P—O or C—O) is always longer than the corresponding bond length in the acceptor group, as shown in Table I. In the crystal of squaric acid the electronic density of the donor and acceptor oxygen atoms can be described by sp^3 and sp^2 hybridizations, respectively. These hybridizations are disturbed by a strong conjugation of single and double bonds in the squaric acid molecule and by the strong hydrogen bonding between the oxygen atoms,[14] however, the characteristic features of the hybridizations are apparent.[15] Similarly, characteristic features of the O_{sp^3} and O_{sp^2} atoms can be distinguished for the donor and acceptor oxygen atoms in the prototypical ionic ferroelectric crystals of KH_2PO_4 or RbH_2PO_4 (Table I), even though a clear definition of double and single bonds in the $H_2PO_4{}^-$ or $HPO_4{}^{2-}$ anions is not as straightforward as in the molecule of squaric acid, and it combines double, single, and coordination bonds. Because the main point of the further discussion concerns the differences in electronic structure between the donor and acceptor oxygen atoms resulting from the differences of their chemical bonds, for simplification we will refer to these electronic structures as hybridizations sp^3 and sp^2, respectively. Irrespective of the extent of the departures from the ideal hybridizations, the donor oxygen atom is always closer to the sp^3 hybridization than the acceptor oxygen atom, and the acceptor O atom has a stronger sp^2 character than the donor O atom. Figure 1 shows a schematic drawing of a hydrogen bond between oxygen atoms in the ideal sp^3 and sp^2 hybridizations. One of the consequences of these different hybridizations is that the two oxygen atoms have different favorable directions of formation of hydrogen bonds. These directions can be conveniently described with the R—O—H (denoted η_d, R stands for the atom of the ion or molecule to which the O atom is chemically bonded, e.g., C or P) and $R' =$ O′- -H (η_a) angles. Ideally, the η_d angle is about 109° and η_a is about 120°.[15] In the real crystal structures these ideal values of angles η_d and η_a are usually not preserved: they can be changed due to the disturbed electronic structure of the oxygen atoms or due to the intramolecular or intermolecular interactions in the crystal lattices, especially where strong electrostatic forces or other short hydrogen bonds are present. Table II gives the η_d and η_a angles observed in (anti)ferroelectric phases of squaric acid, KH_2PO_4, and RbH_2PO_4. In KH_2PO_4 the difference between the η_d and η_a angles is only of about 1.3°. Even such a small difference between these angles brings about significant structural consequences, when the H atom changes its site or becomes disordered in the hydrogen bond. For an adequate parametrization it is necessary to include in the H-bond description, apart from the usually applied distances O—H (hereinafter denoted d_d), H- -O′ (d_a), O· · ·O′ (r) and angle O—H- -O′ (η_H),[16] also angles η_a and η_d to characterize the positions of the atoms to which the oxygen atoms are chemically bonded and the arrangement of the H-bonded molecules or ions.[15] In certain cases this arrangement should be additionally described by the torsion angle, τ, measured in Newman's projection along O· · ·O′ between the adjacent bonds to the oxygen atoms, as shown in Fig. 1(b). Angle τ is referred to as the conformation of a hydrogen bond.[15] While the potential energy barrier separating two H-atom sites depends on r,[17,18] the difference between the

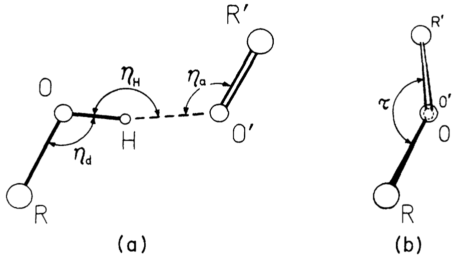

FIG. 1. A schematic drawing of an —OH· · ·O= hydrogen bond. The R—O—H, O—H- -O′ and H- -O′ = R' angles are denoted η_d, η_H, and η_a, respectively. Generally, the R—O and O′ = R' bonds are not coplanar and the conformation of the hydrogen bond can be described with a torsion angle R—O· · ·O′ = R', τ, as shown in Newman's projection in (b).

TABLE I. Selected geometrical dimensions of the donor and acceptor groups and the O· · ·O′ distance in several ferroic crystals in their (anti)ferroelectric phase.

Crystal	Squaric acid[a] at 298 K	KH_2PO_4 at 102 K	RbH_2PO_4 at 77 K
R—OH	1.289(1) Å 1.287(1)	1.5719(6) Å	1.58(1) Å
R=O	1.227(1) 1.230(1)	1.5158(6)	1.51(1)
O—H (d_d)	1.030(1) 1.037(1)	1.0564(12)	1.06(1)
H- -O (d_a)	1.524(1) 1.517(1)	1.4410(11)	1.430(15)
O· · ·O (r)	2.5530(11) 2.5541(11)	2.4974(6)	2.489(11)
Reference	11	12	13

[a] There are two symmetry-independent hydrogen bonds in the antiferroelectric phase of squaric acid.

TABLE II. Angular dimensions of the hydrogen bonds in the (anti)ferroelectric phases of squaric acid, KH_2PO_4, and RbH_2PO_4 calculated from the positional parameters given in Refs. 11, 12, and 13, respectively. Angles η_d, η_a, and η_H are defined in Fig. 1 and in the text.

	η_d (deg)	η_a (deg)	η_H (deg)
Squaric acid[a]	112.65(7)	118.15(5)	177.43(9)
at 298 K	113.6(7)	116.24(5)	177.85(9)
KH_2PO_4	112.07(7)	113.41(5)	179.54(10)
at 102 K			
RbH_2PO_4[b]	114.2(12)	114.8(8)	175.4(18)
at 77 K			

[a] See the footnote in Table I.

[b] Powder neutron-diffraction data.

potential energy of the two minima depends on chemical differences between the two oxygen atoms[19] and on the differences in the arrangement of the donor and acceptor groups.[20,21] It can be derived from angles η_d, η_a, and η_H, whether the donor and acceptor groups are related by a pseudosymmetry element located at the midpoint between the oxygen atoms or not. The pseudosymmetric and asymmetric geometries of hydrogen bonds have been discussed elsewhere.[15] The further discussion will pertain only to the double-well pseudosymmetric or disordered-symmetric hydrogen bonds occurring in the KDP-type ferroelectrics, as distinguished from single-well hydrogen bonds, which often are referred to as centered H bonds.

Several geometrical features are characteristic of the hydrogen bonds in the KDP-type ferroelectrics. These features are directly connected with the ability of the H atom to interchange its donor and acceptor sites in the hydrogen bond. Such hydrogen bonds are usually shorter than 2.55 Å because in short hydrogen bonds the potential-energy barrier is low, and proton transfer can be easily activated. Another feature is that the hydrogen bonds are pseudosymmetric in the ferroelectric phases, i.e., the donor and acceptor sites are related by a pseudosymmetry element: a pseudo-C_i (e.g., $PbHPO_4$), pseudo-C_2 (KH_2PO_4, RbH_2PO_4), pseudo-C_{2h} (squaric acid), or a pseudo-C_s. It is characteristic that the structure of ferroelectric phase approximates a higher symmetry of the paraelectric-phase space group. The same applies to the orientational-state structure approximating the symmetry of the prototype structure for ferroelastic crystals.[7] Thus, the arrangement of the C_4O_4 groups in the antiferroelectric phase of squaric acid, monoclinic space group $P2_1/m$, closly approximates the symmetry of the tetragonal space group $I4/m$; the arrangement of the K^+ cations and PO_4 groups in KDP in the ferroelectric phase, orthorhombic $Fdd2$, approximates tetragonal space group $I\bar{4}2d$. The symmetry distortions between the donor and acceptor groups can be conveniently described and measured by the difference between angles R—O$\cdots$O′ (hereafter η'_d) and O$\cdots$O′—R′ (η'_a). Angle η'_d is usually smaller than η'_a (Table III). For pseudosymmetric H bonds, angles η'_d and η'_a assume values between 109° and 120°: η'_d is somewhat more open than η_d, and η'_a is somewhat sharper than η_a.[15] The difference between η'_d and η'_a measures the displacements of the donor and acceptor groups, which must be eliminated when the phase transition of the ferroelectric structure to the paraelectric phase takes place.

TABLE III. Angles η'_d and η'_a for the hydrogen bonds in squaric acid at (T_c–76) K, KH_2PO_4 at (T_c–20) K and RbH_2PO_4 at (T_c–69) K, calculated from atomic positions determined by neutron diffraction (Refs. 11, 12, and 13).

	η'_d (deg)	η'_a (deg)	τ (deg)
Squaric acid[a]	114.18(5)	117.10(5)	0
at 298 K	114.88(5)	115.37(5)	0
KH_2PO_4 at 102 K	112.17(3)	113.60(2)	76.81(5)
RbH_2PO_4 at 77 K	114.4(6)	116.8(5)	77.9(11)

[a] See the footnote in Table I.

III. STRUCTURE OF DISORDERED —OH- -O═ BONDS

When the H atom becomes dynamically disordered above T_c, the heavy atoms assume the positions that are average between their sites in possible ferroelectric domains or ferroelastic orientational states. Thus, for example, the double and single bonds in the molecule of squaric acid, clearly identified by their lengths in the antiferroelectric phase, assume an averaged length intermediate between the double and single bonds. This situation arises from the fact that the nonhydrogen atoms are too heavy to adjust their positions in phase with quick changes of the electronic structure of the molecule or ion coupled with the H-atom hopping.[6] The averaged R—O bond lengths are not characteristic of any stable electronic structures of the molecules or ions.[22] At high temperatures or pressures, when the back and forth tunneling and/or thermal vibrations of the H atoms become random with no correlation between neighboring structural units, the H atom still introduces local changes in the electronic structure of the oxygen atoms. The crystallographic symmetry element, relating the positions of the heavy atoms and the averaged over long-measurement-time sites of the disordered H atom, does not apply to the instantaneous H atom positions or to the electronic structures of the donor and acceptor groups. In other words, in a disordered R—OH- -O′$=R'$ hydrogen bond the electronic structure of the O atoms depends on the instantaneous H-atom site. Most recently, this was confirmed by experimental evidence of spectroscopic measurements.[23,24] Also, a survey of the H-bond dimensions in ferroelectric and paraelectric phases shows that the phase transitions do not significantly alter distances d_d and d_a and angles η_d and η_a. This is a natural consequence of the preserved electronic structure of the oxygen atoms. Therefore, it is reasonable to assume that the H-bond dimensions depending mainly on the molecular and electronic structure of molecules or ions, in particular d_d, d_a, η_d, and η_a, are unlikely to be significantly changed during a ferroelectric phase transition.

At the same time, the transformation of the pseudosymmetry element into a new crystallographic symmetry element, relating the two sites of the hydrogen atom and the donor and acceptor groups means that the η'_d and η'_a angles become equal. One of significant consequences of the higher symmetry of the crystal is that the donor and acceptor groups have fewer degrees of freedom to adjust their positions to minimize the strains in the hydrogen bond. Owing to the symmetry element these dimensions involving each site, H and H′, must assume identical values, as shown in Fig. 2. The structural changes taking place at a phase transition, including both the displacements of the H-bonded groups and changes in H-bond dimensions, lead to the arrangement that satisfies both the favored dimensions of the H bond (i.e., conservation of d_d, d_a, η_d, and η_a) and the symmetry

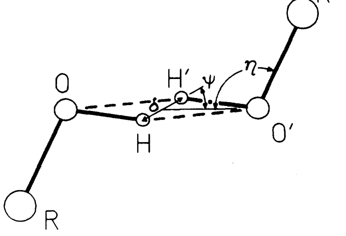

FIG. 2. A C_{2h}-symmetric (τ=180°) hydrogen bond with a disordered H atom in paraelectric phase of squaric acid: the atoms lie in the plane of the drawing and the H-bonded groups are related by a center of symmetry and a two-fold axis at the midpoint of the H bond. Angle ψ has been increased in this drawing for clarity.

requirements. The structural conditions described above for a paraelectric structure above T_c can be expressed by the following system of formulas:

$$\mathbf{d}_{OR} \cdot \mathbf{d}_{OH} = d_{OR} d_d \cos\eta_d, \tag{1}$$

$$\mathbf{d}_{O'R'} \cdot \mathbf{d}_{O'H} = d_{O'R'} d_a \cos\eta_a, \tag{2}$$

$$\mathbf{d}_{OR} \cdot \mathbf{d}_{OH'} = d_{OR} d_a \cos\eta_a, \tag{3}$$

$$\mathbf{d}_{O'R'} \cdot \mathbf{d}_{O'H'} = d_{O'R'} d_d \cos\eta_d, \tag{4}$$

where $\mathbf{d}_{OR}$ is a vector between atoms O and R (see Fig. 2) and d_{OR} is the length of this vector, the primed labels refer to the (pseudo)symmetry-related atoms. Above T_c the atomic coordinates are related by matrix $\underline{S}$ of the symmetry element located in the midpoint between O and O′: $\underline{O'} = \underline{SO}$, $\underline{H'} = \underline{SH}$, and $\underline{R'} = \underline{SR}$. Below T_c only two of equations (1)–(4) remain valid: (1) and (2) when the hydrogen atom is ordered in site H (see Fig. 1), or (3) and (4) when it is ordered into site H′. Bondlengths d_{OR} and $d_{O'R'}$ are temperature dependent and

$$\text{for } T < T_c,\ d_{OR} \neq d_{O'R'}, \tag{5}$$

$$\text{for } T > T_c,\ d_{OR} = d_{O'R'}. \tag{6}$$

Averaging of the molecular or ionic dimensions, such as P—O or C—O bond length, is of secondary importance in this discussion, and thus will be ignored. Below, the structural changes depending on H-bond transformations are analyzed for the possible H-bond symmetries in KDP-type crystals.

A. C_{2h}-symmetric H-bond

A disordered C_{2h}-symmetric hydrogen bond (Fig. 2) is present in the paraelectric phase of squaric acid. Owing to the symmetry requirements all the atoms involved in this hydrogen bond are coplanar and the calculations of the H-bond dimensions, satisfying the condition that parameters η_d, η_a, d_d, and d_a remain unchanged, reduce to simple trigonometric relations. Thus, the distance between two sites H and H′, δ, can be obtained from Carnot's formula:

$$\delta = \sqrt{d_d^2 + d_a^2 - 2 d_d d_a \cos\mu}, \tag{7}$$

where μ is the H—O$\cdots$H′ angle, $\mu = \eta_a - \eta_d$ (see Fig. 2). The OH$\cdots$O′ angle η_H is

$$\eta_H = 180^\circ - \mu. \tag{8}$$

The O$\cdots$O′ distance r is

$$r = \sqrt{d_d^2 + d_a^2 - 2 d_d d_a \cos\eta_H}. \tag{9}$$

The C—O$\cdots$O angle η is

$$\eta = \eta_a - \mu_a = \eta_d + \mu_d, \tag{10}$$

where

$$\mu_a = \tan^{-1}\left(\frac{d_d \sin\mu}{d_d \cos\mu + d_a}\right) \tag{11}$$

and

$$\mu_d = \mu - \mu_a. \tag{12}$$

μ_d and μ_a are the O′$\cdots$O—H and O$\cdots$O′--H angles, respectively. The inclination angle between the lines drawn through H$\cdots$H′ and O$\cdots$O′ ψ is

$$\psi = \sin^{-1}\left(\frac{2 d_d \sin\mu_d}{\delta}\right). \tag{13}$$

Table IV gives the dimensions of the disordered H bond observed in the neutron-diffraction measurement carried out for the paraelectric phase of squaric acid at 394 K,[25] and the dimensions of this disordered H bond calculated with formulas (7)–(13) using the η_d, η_a, d_d, and d_a dimensions of the H bond in the antiferroelectric phase as the starting parameters. The calculated dimensions agree within 3 estimated standard deviations (ESD's) with the experimentally measured data. It must be stressed that the experimental data in Table IV was not corrected for vibrations of the atoms, although at 394 K this effect can lead to significant systematic descrepancies.[26,27] At the same time by applying the d_d and d_a values measured at 394 K,[25] of 1.014 and 1.536 Å, respectively, and the η_d and η_a from the antiferroelectric phase

TABLE IV. Experimental (Ref. 25) and calculated dimensions of the disordered H bond in paraelectric phase of squaric acid.

H-bond dimensions		Experimental data, 394 K	Calculated values	
d_d	(Å)	1.014(4)	1.033[a]	1.014[b]
d_a	(Å)	1.536(5)	1.521[a]	1.536[b]
η_d	(deg)	113.1(3)	113.13[a]	113.13[a]
η_a	(deg)	117.0(2)	117.19[a]	117.19[a]
η_H	(deg)	176.2(4)	175.94	175.94
η	(deg)	115.43(5)	115.55	115.58
r	(Å)	2.5491(10)	2.5525	2.5485
δ	(Å)	0.529(8)	0.4960	0.5294
ψ	(deg)	8.9(10)	10.12	9.41

[a] Averaged dimensions of two symmetry-independent hydrogen bonds in squaric acid at 298 K (Ref. 11), used for the calculations.

[b] Experimental lengths of d_d and d_a measured at 394 K.

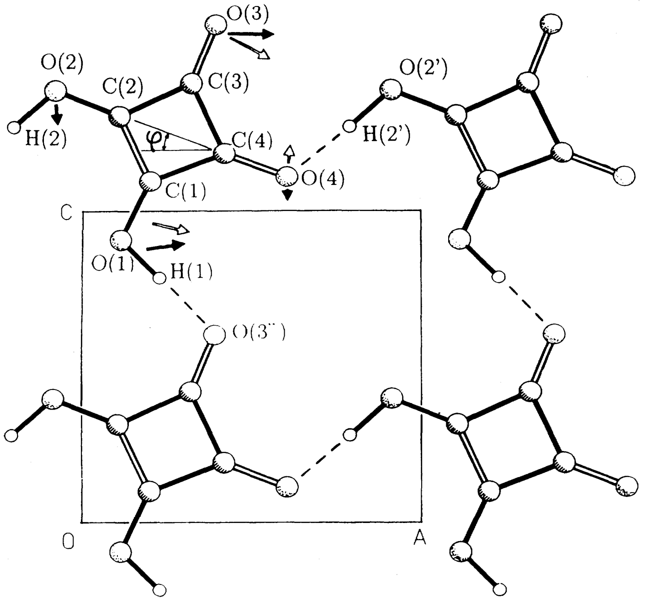

FIG. 3. One layer of the H-bonded molecules in the antiferroelectric phase of squaric acid. H bonds are represented as the dashed lines. Arrows with full arrowheads show the displacements of the oxygen atoms calculated as described in the text, the open arrowheads show the displacements measured experimentally (Ref. 25). Angle φ defines the orientation of the molecule (see the text).

the calculations give all the H-bond dimensions identical with those measured experimentally (Table IV). The consistency between the observed and calculated dimensions of the disordered H-bond in squaric acid confirms the origin of the structural effects accompanying this antiferroelectric–paraelectric phase transition, also common for other disordered C_{2h}-symmetric H bonds.

1. Direction of H-atom motion

A straightforward consequence of the angular requirement concerning η_d and η_a is that in the C_{2h}-symmetric H bond the direction of H-atom motion between its sites $H\cdots H'$ must be inclined to the $O\cdots O'$ direction, i.e., the H-atom vibrations cannot proceed along the hydrogen bond. The calculated inclination angle ψ (Table IV) well agrees with the experimental results.

2. Molecular reorientations and displacements

As already described, the H-bond disordering requires that the η'_d and η'_a angles (Table III) become equal η at T_c (Table IV). This, in turn, must be accommodated by reorientations of the H-bonded molecules or ions and by changes in molecular dimensions. Figure 3 shows one layer of the H-bonded molecules of squaric acid in the antiferroelectric phase. Angle φ describes the orientation of the planar C_4O_4 group and is defined as the angle between the axis x and the line drawn through atoms O(2) and O(4) of one molecule. The arrows in Figure 3 indicate the directions of displacements of the oxygen atoms required for the η'_d or η'_a angles to become equal η, the lengths of the arrows corresponding to the $(\eta'_d - \eta)$ or $(\eta'_a - \eta)$ differences: 1.25, 0.55, 1.67, and 0.06° for O(1), O(2), O(3), and O(4), respectively. The lengths of these arrows are consistent with the experimentally observed magnitudes of displacements of the oxygen atoms between the antiferroelectric and paraelectric phases of squaric acid, which are indicated by the arrows with the open arrowheads in Fig. 3; compare also Fig. 4 of (Ref. 25). Angle φ observed in the antiferroelectric phase at 298 K (Ref. 11) is 21.96(1)° and above T_c angle φ only slightly decreases to 21.90(1)° (Ref. 28). This very small change in φ results from the compensating directions of changes in the O-atom positions.

3. Sharpening of O—H- -O′ angle η_H

Statistical analyses of O—H- -O′ hydrogen bonds show a pronounced tendency of these bonds to be linear; this tendency is much stronger for short hydrogen bonds, like those in ferroelectric crystals, than for long hydrogen bonds.[16,29] For a hydrogen bond in an (anti)ferroelectric phase there are no symmetry restrictions limiting this tendency [Eqs. (1) and (2)]. In the paraelectric phase, however, owing to the disorder of the H atom and symmetry of the H bond [Eqs. (1)–(4)], the η_H angle becomes dependent on angles η_d and η_a [Eq. (8)]. This dependence leads to the sharpening of angle η_H in the paraelectric phase of squaric acid: compare Tables II and IV. A similar sharpening of the η_H angle is common for all the structures discussed in this paper.

4. Shortening of $O\cdots O'$ distance r

Sharpening of angle η_H, with the d_d and d_a distances constant, automatically causes a shortening of the r length (Tables I and IV). This shortening can directly affect the unit-cell dimensions and is responsible for the anomalous changes in the strain tensors of the KDP-type crystals near T_c. In squaric acid the shortening of r causes a contraction of the crystal along the directions within

TABLE V. Unit-cell dimensions for squaric acid measured at 292 K (Ref. 28), 298 K (Ref. 11), and 394 K (Ref. 25).

Temperature	a (Å)	b (Å)	c (Å)	β (deg)
292 K	6.1256(5)	5.2681(7)	6.1368(5)	90.027(7)
298 K	6.143(2)	5.286(2)	6.148(2)	90.04(1)[a]
394 K	6.137(2)	5.337(2)	$=a$	90

[a] ESD estimated from the ESD's of a, b, and c (Ref. 11).

the layers (see Fig. 3) with increasing temperature (i.e., negative $\partial a/\partial T$ and $\partial c/\partial T$ close to T_c). The unit-cell dimensions given in Table V show that despite the thermal expansion of a and c between 294 and 298 K, a contraction of a and c is observed at 394 K compared with these dimensions at 298 K. This anomalous contraction can be attributed to the shortening of the O···O′ distances.

B. H-bond symmetries C_{2v} and C_s

Although not encountered in ferroelectric crystals, a disordered C_{2v}-symmetric H bond, shown in Fig. 4, is worth considering. The formulas describing the geometry of the C_{2v}-symmetric H bond are similar to those for C_{2h} symmetry, but angle O—H- -O, η_H, is

$$\eta_H = 180° - \nu_H - \nu'_H, \tag{14}$$

where $\nu_H = \sin^{-1}\left(\frac{d_a \sin\mu}{\delta}\right)$, and $\nu'_H = \sin^{-1}\left(\frac{d_d \sin\mu}{\delta}\right)$. Angle η is

$$\eta = \eta_a + \mu_a \tag{15}$$

$$= \eta_d + \mu_d, \tag{16}$$

where $\mu_d = \sin^{-1}\left(\frac{d_a \sin\eta_H}{r}\right)$, and $\mu_a = \sin^{-1}\left(\frac{d_d \sin\eta_H}{r}\right)$.

The dimensions of a hypothetical disordered C_{2v}-symmetric H bond calculated using Eqs. (7), (9), and (13)–(15) and initial parameters d_d, d_a, η_d, and η_a of squaric acid (see Table IV) are unrealistic: angle η_H of 158.98° is sharper, the distance r of 2.5127 Å is shorter, and angle η of 125.67° is more open than these dimensions observed experimentally in the H bonds with similar d_a distance (compare, e.g., Table IV). The contraction of r is nearly ten times stronger than that observed on disordering of the hydrogen bond in squaric acid. It appears that because of the strong changes in the H-bond dimensions required by the conservation of d_d, d_a, η_d, and η_a for two sites H and H′, the ferroelectric crystals with C_{2v}-symmetric H bonds are not encountered. A similarly unfavorable geometry for disordering the H atom is in C_s-symmetric hydrogen bonds (the mirror plane relating the donor and acceptor groups), and this case will not be separately discussed here. It can be also mentioned that even in the aggregates of carboxylic acids with disordered H atoms, where angle τ is restricted to the values close to 0°, a C_s or C_{2v} symmetry of the synperiplanar hydrogen bonds is not observed.[30,31]

C. C_i-symmetric H bond

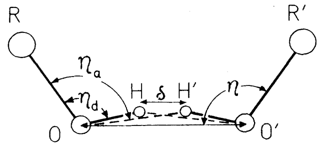

FIG. 4. A C_{2v}-symmetric hydrogen bond (τ=0°) with disordered H atom.

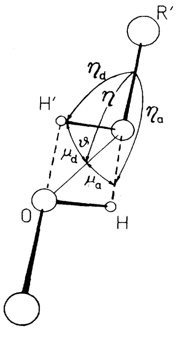

FIG. 5. A disordered C_i-symmetric hydrogen bond. The dimensions in this drawing have been adjusted with priority to a clear definition of angles η_d, η, η_a, μ_d, μ_a, and dihedral angle ϑ.

The geometry of the disordered H bond in C_i symmetry is similar to that in C_{2h} symmetry, with this exception that the H-atom sites, H and H′, are not constrained to lie in the plane of the R, O, O′ and R' atoms, as shown in Fig. 5. Consequently, the dimensions of the disordered C_i-symmetric H bond depend, apart from d_d, d_a, η_d, and η_a, also on the angle between the planes through R, O, O′, R' and O, H, H′, O′; this dihedral angle will be denoted ϑ; see Fig. 5. The angular dimensions of the disordered C_i-symmetric H bond are interconnected by the following set of equations:

$$\begin{aligned} \cos\eta_d &= \cos\mu_d \cos\eta + \sin\mu_d \sin\eta \cos\vartheta, \\ \cos\eta_a &= \cos\mu_a \cos\eta - \sin\mu_a \sin\eta \cos\vartheta, \\ d_d \sin\mu_d &= d_a \sin\mu_a, \end{aligned} \tag{17}$$

where μ_d and μ_a are the O′···O—H and O···O′- -H angles, respectively. The other dimensions of the H bond, δ, η_H, r, and ψ, can be calculated from Eqs. (7), (8), (9), and (13), given for the C_{2h}-symmetric H bond. Owing to angle ϑ, which is not constrained by the symmetry, the other dimensions of the H bond are not univocally determined.

A disordered C_i-symmetric hydrogen bond is present in the paraelectric phase of the crystals isostructural

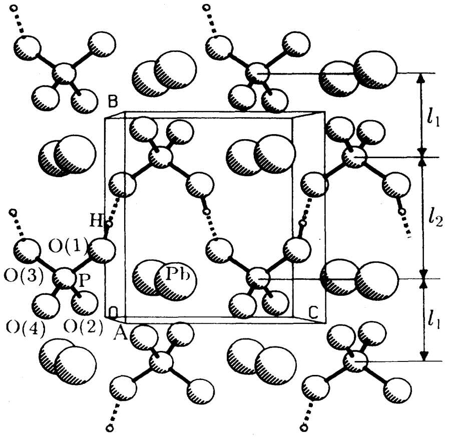

FIG. 6. A perspective diagram of the lead monohydrate phosphate structure in the ferroelectric phase viewed down x axis. The hydrogen bonds are represented as the dashed lines.

TABLE VI. Dimensions of the C_i-symmetric H bond in the paraelectric phase of lead monohydrogen phosphate at 316 K calculated from experimentally determined atomic positions (Ref. 32), and calculated from Eqs. (17), (7)–(9), and (13) for the d_d, d_a, η_d, and η_a dimensions experimentally determined and two ϑ values of 0° and 38.5°.

H-bond dimensions		Experiment 316 K	Calculated values	
ϑ	(deg)	38.5(27)	0[a]	38.5[a]
d_d	(Å)	1.049(2)	1.049[a]	1.049[a]
d_a	(Å)	1.424(2)	1.424[a]	1.424[a]
η_d	(deg)	118.50(17)	118.50[a]	118.50[a]
η_a	(deg)	122.56(13)	122.56[a]	122.56[a]
η	(deg)	120.85(2)	111.54	120.85
η_H	(deg)	174.82(27)	175.94	174.78
δ	(Å)	0.392(3)	0.3849	0.3912
r	(Å)	2.4702(5)	2.4715	2.4705
ψ	(deg)	16.2(8)	12.85	16.35

[a] Initial dimensions used for the calculations.

with lead monohydrogen phosphate, $PbHPO_4$ (hereafter LHP),[33,34] the crystals are monoclinic, space group $P2/c$. Below $T_c = 310$ K an onset of ordering of the H atom induces a ferroelectric phase transition in LHP and lowers the crystal symmetry to space group Pc.[33] The LHP structure is shown in Fig. 6. The H-bond dimensions of the paraelectric phase are given in Table VI. The dihedral angle ϑ is 38.5(27)° in this structure. It is difficult to specify exactly the physical factors that influence the ϑ angle. Equations (17) define the interdependence of angles ϑ and η, the letter describing the arrangement of the H-bonded anions. It appears that in the particular crystal structures changes of η can minimize intermolecular or ionic forces or accommodate local strains, while the ϑ angle can partly depend on the H bond surrounding and on the intermolecular or interionic forces. Figure 7 shows the dependence of selected H-bond dimensions on angle ϑ. A characteristic feature of all H-bond dimensions, not only of those plotted in Fig. 7, is that between $\vartheta = 0°$ and 40° they are weakly dependent on changes in ϑ. Above $\vartheta \cong 40°$ the dependence becomes strong and a significant increase of ϑ above 40° changes the H-bond dimensions so markedly that they assume unrealistic values. Due to such a dependence of the H-bond dimensions versus ϑ, angle ϑ, and others connected with it H-bond dimensions, can adjust without a significant increase in the potential energy of the system within the ϑ range of about 40°. It can be noted that within the range of ϑ to 40°, the dependence on ϑ of parameters η_H and r is much weaker than the dependence of δ and ψ; however these dimensions are interdependent and they derive from the H-bond symmetry and from its parameters d_d, d_a, η_d, η_a, and η or ϑ.

Figure 7 also illustrates a shortening of r in disordered H bonds, already discussed for C_{2h} symmetry (Sec. III A 4). In a linear H bond the values of d_d (1.05 Å) and d_a (1.45 Å) applied for the calculations shown in Fig. 7 would give the r distance of 2.500 Å. The symmetry effect shortens the r distance to 2.4985 Å for $\vartheta = 0°$, and to 2.4975 Å for $\vartheta = 38°$. In the crystal lattice of LHP the hydrogen bonds lying approximately along the [y] link the perpendicular to [y] layers of electrostatically interacting ions (see Fig. 6). Precise unit-cell measurements showed an anomalous contraction of the unit-cell dimension **b** when the LHP crystal is heated up to the temperatures approaching T_c; no similar anomalous changes were observed in the thermal expansion of other unit-cell parameters. The same results were obtained for the deuterated LHP samples.[35,36] Structural studies of LHP crystal in

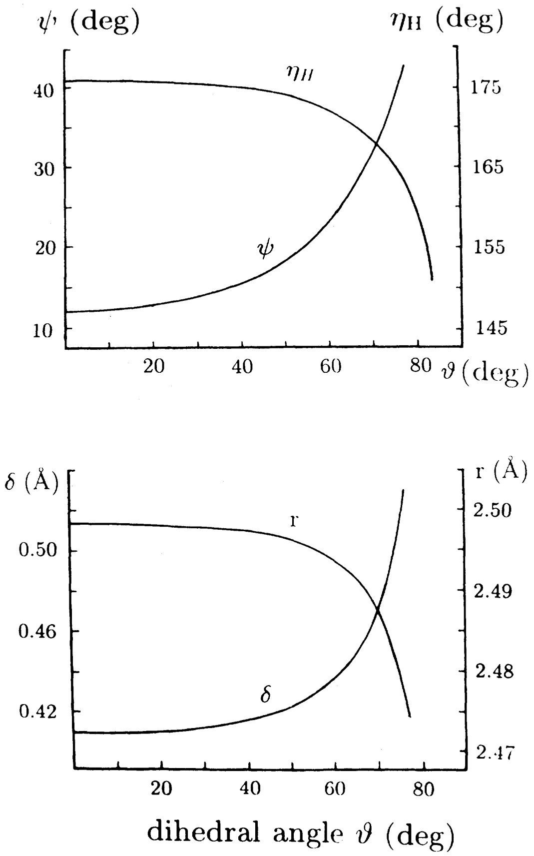

FIG. 7. Changes of η_H, η, δ, and r plotted vs dihedral angle ϑ calculated according to Eqs. (17), (7), (8), (9), and (13); the initial parameters d_d=1.050, d_a=1.450 Å, η_d=118.0°, and η_a=122.0° have been applied for the calculations (see Table VI).

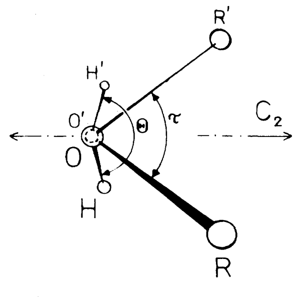

FIG. 8. Newman's projection of a disordered C_2-symmetric hydrogen bond. The dihedral angle between O—H- -O′ and O- -H′—O′ is denoted θ. The distortions of the O—H- -O′ bonds from linearity have been enhanced for clarity.

the function of temperature reveiled that on disordering of the H atom the l_2 interlayer distance becomes shorter, while distance l_1 is constant;[37] see Fig. 6.

D. C_2-symmetric H bond

A disordered H bond in symmetry C_2 is schematically shown in Fig. 8. The H bond of this symmetry is present in the paraelectric phase of the crystals isostructural with KDP (e.g., RbH_2PO_4, CsH_2PO_4, and NH_4AsO_4). The C_2-symmetric H bonds can be antiperiplanar ($\tau \cong 180°$; see Fig. 2), synperiplanar ($\tau \cong 0°$; see Fig. 4) or of intermediate conformations (Fig. 8). The orientation of the O—H- -O′ plane is not constrained by the C_2 symmetry. Thus, in theory, angle θ (see Fig. 8) can assume any value between 0° and 360°. However, in practice, as it has been shown for the C_i-symmetric H bonds, symmetry C_2 favors certain ranges of θ, which additionally depend on the conformation angle τ. The interdependence of the angles describing the geometry of a disordered C_2-symmetric H bond is given by the following set of equations:

$$\cos\eta_d = \cos\mu_d \cos\eta + \sin\mu_d \sin\eta \cos\left(\frac{\theta-\tau}{2}\right),$$

$$\cos\eta_a = \cos\mu_a \cos\eta + \sin\mu_a \sin\eta \cos\left(\frac{\theta+\tau}{2}\right), \quad (18)$$

$$d_d \sin\mu_d = d_a \sin\mu_a .$$

Angle μ depends on μ_d, μ_a, and θ:

$$\cos\mu = \cos\mu_d \cos\mu_a + \sin\mu_d \sin\mu_a \cos\theta. \quad (19)$$

The separation of H-atom sites can be calculated from Eqs. (7) and (19), and angle η_H is

$$\eta_H = 180° - \mu_d - \mu_a . \quad (20)$$

Distance r can be calculated from Eq. (9).

As can be seen in Fig. 8, the midpoint between O and O′ does not lie on the line drawn through the H and H′ sites, except when $\theta = 180°$ (or in the unrealistic case when the H and H′ sites lie on the O· · ·O′ line). Thus, the ψ angle, which was previously said to describe the inclination between the O· · ·O′ and H· · ·H′ lines, requires a redefinition. The inclination angle between line O· · ·O′ and the line drawn through H and through the midpoint between the O· · ·O′ atoms will be denoted ψ_0 and can be calculated from Eq. (13). However, more relevant for the description of the trajectory of the H atom is the inclination angle between the H· · ·H′ line, and the plane containing both the O· · ·O′ line and the twofold axis. This angle, denoted ψ_2, is given by the formula

$$\psi_2 = \sin^{-1}\left\{\frac{2d_d \sin\mu_d \sin(\theta/2)}{\delta}\right\}. \quad (21)$$

Table VII gives the experimentally measured dimensions of the disordered C_2-symmetric H bond in the paraelectric phase of KDP (Ref. 12) and the same dimensions calculated for τ, d_d, d_a, η_d, η_a, and various θ angles using the above equations. It can be seen that by applying the τ, d_d, d_a, η_d, and η_a dimensions observed in the ordered H bond the equations give values similar to those above T_c, the application of the d_d, d_a, η_d, and η_a dimensions of the disordered H bond leads to identical values as those obtained in the paraelectric phase. Table VII also shows the H-bond dimensions calculated for various θ angles. The $\theta = 0°$ causes strong changes in all calculated dimensions, similar to those calculated for C_{2v}-symmetric H bond (see Sec. III B). The H-bond dimensions calculated for $\theta = 257.15°$ (i.e., the observed $\tau + 180°$) are similar to those in paraelectric phase, except for angle η (O′· · ·O—P) which is significantly smaller. It can be shown that small θ angle requires more open angles η, and when θ increases angle η becomes sharper. This dependence is much stronger for small θ angles. The interdependence between θ, η, and other H-bond dimensions suggests that angle θ may adjust to the molecular

TABLE VII. Dimensions of the C_2-symmetric disordered H bond in the paraelectric phase of KH_2PO_4 at (T_c+5) K (Ref. 12), and the dimensions calculated for various θ angles (see the text).

H-bond dimensions		Experimental data 127 K	293 K	Calculated values			
τ	(deg)	77.15(2)	77.07(2)	76.81[a]	77.15[b]	77.15[b]	77.15[b]
θ	(deg)	145.7(20)	157.6(27)	145.7[b]	257.15[c]	145.7[b]	0[c]
d_d	(Å)	1.0712(6)	1.0676(15)	1.056[a]	1.0712[b]	1.0712[b]	1.0712[b]
d_a	(Å)	1.4119(6)	1.4276(15)	1.441[a]	1.4119[b]	1.4119[b]	1.4119[b]
η_d	(deg)	112.31(4)	112.18(8)	112.07[a]	112.31[b]	112.31[b]	112.31[b]
η_a	(deg)	113.43(3)	113.93(6)	113.41[a]	113.43[b]	113.43[b]	113.43[b]
η	(deg)	113.15(1)	113.39(2)	113.06	112.30	113.130	116.91
η_H	(deg)	178.22(12)	177.2(3)	177.92	177.36	178.224	169.80
r	(Å)	2.4828(4)	2.4946(6)	2.4970	2.4825	2.4828	2.4735
δ	(Å)	0.3430(12)	0.365(2)	0.3869	0.3436	0.3427	0.3420
ψ_o	(deg)	6.3(5)	9.3(8)	6.62	9.39	6.33	39.27
ψ_2	(deg)	6.0(5)	9.1(8)	6.31	7.33	6.03	0

[a] Dimensions of the ferroelectric phase at 102 K used for the calculations.
[b] Dimensions of the paraelectric phase at 127 K used as the initial parameters.
[c] Hypothetical value of θ used in the set of initial parameters.

TABLE VIII. Dimensions of the disordered C_2-symmetric H bond in the paraelectric phase of RbH_2PO_4 at (T_c+5) K (Ref. 13), and the dimensions calculated with various values of the initial parameters τ, θ, d_d, d_a, η_d, and η_a.

H-bond dimensions		Experimental data, 127 K	Calculated values				
τ	(deg)	76.39(10)	77.90[a]	76.39[b]	76.39[b]	76.39[b]	76.39[b]
θ	(deg)	169(22)	169.0[b]	200.0[c]	169.0[b]	100.0[c]	50.0[c]
d_d	(Å)	1.051(5)	1.060[a]	1.051[b]	1.051[b]	1.051[b]	1.051[b]
d_a	(Å)	1.436(5)	1.430[a]	1.436[b]	1.436[b]	1.436[b]	1.436[b]
η_d	(deg)	114.6(4)	114.20[a]	114.6[b]	114.6[b]	114.6[b]	114.6[b]
η_a	(deg)	116.0(3)	114.80[a]	116.0[b]	116.0[b]	116.0[b]	116.0[b]
η	(deg)	115.5(3)	114.57	115.22	115.47	116.10	116.66
η_H	(deg)	177.6(11)	179.06	177.64	177.78	177.54	176.40
r	(Å)	2.486(2)	2.4899	2.4865	2.4865	2.4864	2.4858
δ	(Å)	0.387(7)	0.3705	0.3882	0.3879	0.3871	0.3865
ψ_o	(deg)	6.3(37)	3.09	7.38	6.95	7.73	11.38
ψ_2	(deg)	6.3(40)	3.08	7.27	6.92	5.92	4.78

[a] Dimensions of the ferroelectric phase at 77 K used for calculations.

[b] Dimensions of the paraelectric phase applied as the initial parameters.

[c] Hypothetical values of θ used in the set of initial parameters.

arrangement and molecular or ionic dimensions. A correlation between r and distortions of the tetrahedra in acid phosphate groups was already observed in experimental data.[38] A detailed description of the interdependence between the C_2-symmetric H-bond dimensions goes beyond the scope of this paper. Table VIII compares the experimentally measured[13] and calculated H-bond dimensions in the crystal of RbH_2PO_4, isostructural with KDP. The η_a and η_d angles in RbH_2PO_4 are markedly more open than in KDP. The θ angle in RbH_2PO_4 was determined with a relatively low precision (Table VIII); however, the direction of the change in θ between RbH_2PO_4 and KDP confirms the dependence between η and θ described above and resulting from Eqs. (18): angle θ is more open in RbH_2PO_4 than in KDP. The interdependence between θ and η is also illustrated by the H-bond dimensions calculated for several θ angles given in Table VIII.

As it was observed in other ferroelectric crystals, the direction of anomalous changes in the strain tensor of KDP can be correlated with the directions of hydrogen bonds in the KDP structure. In the paraelectric phase, the KDP crystals are tetragonal, space group $I\bar{4}2d$. In this structure the hydrogen bonds are nearly parallel to the [100] and [010] directions (see Fig. 9): the inclination angle between these directions and O···O lines is only 0.560(4)° at 127 K. At $T_c = 122$ K, the crystal symmetry lowers to orthorhombic space group $Fdd2$. It is convenient to compare the orthorhombic unit-cell dimensions in terms of the pseudomonoclinic subcell corresponding to the choice of axes in the tetragonal unit cell, so the directions of [100], [010], and the H bonds remain nearly parallel, and a direct analysis of the correlation between the changes of the unit-cell dimensions and the O···O distance is possible. The measurements of thermal expansion of KDP crystals were performed in several studies.[39–44] Figure 10 shows the relative changes in the unit-cell dimensions measured by Kobayashi *et al.*;[44] the dimensions of the orthorhombic unit cell have been transformed to the pseudomonoclinic subcell corresponding to the tetragonal body-centered cell (see Table IX). As it was observed for squaric acid and LHP, also in KDP an anomalous contraction of the unit-cell dimensions a and b, which are parallel to the H bonds, is observed when temperature increases through $T_c = 122$ K. The anomalous contraction of a and b can be attributed to shortening of the hydrogen bonds when the H atoms become disordered. Anomalous contraction of parameter c presumably results from small reorientations of PO_4 groups, their deformations, and small displacements of ions in this three-dimensional H-bonded lattice (Fig. 9), as described by the formulas linking the molecular dimensions in the KDP structure with the crystal-lattice dimensions.[45]

IV. CONCLUSIONS

Geometric effects resulting from differences in the electronic structure of the oxygen atoms involved in the hydrogen bond and the crystallographic symmetry elements relating the donor and acceptor groups in the paraelectric phase, have been analyzed and the formulas describing quantitatively the magnitudes of these effects have been given. The transformations of the dynamically dis-

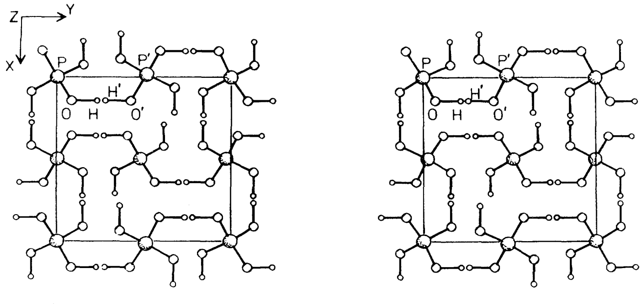

FIG. 9. A stereo-projection of the KH_2PO_4 structure in paraelectric phase. It shows a three-dimensional network of hydrogen bonds, but the H bonds lie along x or y only. The K^{2+} cations have been omitted in this drawing for clarity, they are located 0.5c below and above the P atoms.

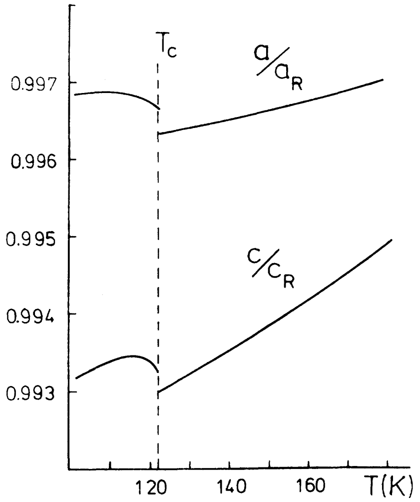

FIG. 10. Relative changes in the unit-cell dimensions of KH_2PO_4 close to T_c, as measured by Kobayashi *et al.* (Ref. 44). The unit-cell dimensions of the orthorhombic phase below T_c have been transformed to the pseudomonoclinic cell corresponding to the tetragonal paraelectric symmetry (see the text).

TABLE IX. Unit-cell dimensions in ferroelectric and paraelectric phases of KDP crystal measured at various temperatures (Ref. 44). Owing to hysteresis, two measurements, one for ferroelectric and one for paraelectric phase, could be performed at the same temperature. The unit-cell dimensions of the orthorhombic phase are transformed to pseudomonoclinic subcell (see the text). The tetragonal, orthorhombic, and pseudomonoclinic cell dimensions are denoted with subscripts t, o, and m, respectively.

	Tetragonal phase		
T (K)	a_t (Å)		c_t (Å)
296.56	7.4524(7)		6.9730(7)
249.86	7.4425(7)		6.9541(8)
173.16	7.4303(7)		6.936
133.36	7.4260(7)		6.9268(7)
122.76	7.4253(7)		6.924
	Orthorhombic phase		
T (K)	$a_m = b_m$ (Å)	c_o (Å)	γ_m (deg)
122.76	7.4275(7)	6.926	90.262
113.56	7.4290(7)	6.9272(7)	90.414
103.86	7.4290(7)	6.9264(7)	90.433

ordered —OH- -O= hydrogen-bond geometry have been illustrated by the calculations performed for model ferroelectric or ferroelastic crystals. Agreement between the results of the calculations and the experimental neutron-diffraction structural data confirms that the electronic structures of the H-bonded oxygen atoms are dynamically disordered in the paraelectric phase. The coupling of the electronic structure of the oxygen atoms with the H-atom positions leads to the characteristic changes in the H-bond geometry, like shortening of O· · ·O′ distance or sharpening of the O—H- -O angle; it also affords a straightforward explanation and exact calculation of the inclination angle between directions H· · ·H′ and O· · ·O′. The interdependence between the process of H-atom disordering and the changes of the hydrogen-bond dimensions combines the order-disorder and displacive structural transformations in the course of the phase transitions in the KDP-type ferroelectrics, which is of crucial importance for understanding the microscopic mechanisms and macroscopic properties of KDP-type ferroelectrics.[46–49] It has been shown for the crystals of squaric acid that the analysis of geometric effects in the disordered H bond also allows us to assess the directions and magnitudes of atomic displacements at T_c. The angular criterion for H-atom position, depending on η_d and η_a, indicates a possibility of coupling of the H-atom hopping in hydrogen bond with rota vibrations of molecules or thermal vibrations of the oxygen atoms in the directions perpendicular to the O· · · O line. Such a coupling between rotations of the hydrogen-bonded molecules with the H-atom site in the hydrogen bond was clearly observed in the phase transition in 1,3-cyclohexanedione crystal.[50,51,15]

The geometry of —OH- -O= hydrogen bonds has been described by the parameters depending on the electronic structure of the H-bonded oxygen atoms. The geometry of the disordered H bonds in ferroelectric crystals can be unequivocally described by a set of parameters, the number of which depends on the H-bond symmetry. In the case of a C_{2h}-symmetric H bond, an independent set of its dimensions can consist of d_d, d_a, η_d, and η_a. For a C_i-symmetric H bond, this set should also include angle ϑ, while for a C_2-symmetric H bond, angles τ and θ should be included. The other dimensions discussed in this paper and commonly applied for H-bond geometry description, like r, η_H, η, δ, or ψ, derive from these basic parameters. The parametrization and understanding of the interdependence between H-bond dimensions is particularly important in the studies connecting the microscopic structure of ferroelectric crystals with their macroscopic properties. For example, several forms of isotope effect in ferroelectric crystals were suggested: $T_c \propto r$,[18,52] $T_c \propto \delta^2$,[53] and $T_c \propto \delta$.[54]

The geometrical effects described for the disordered H bonds in KDP-type ferroelectrics are present in all disordered —OH- -O= hydrogen bonds in any materials. Although the symmetric double-well hydrogen bonds have been analyzed in this paper, the same principles also hold for the disordered H bonds in which the donor and acceptor groups are not symmetry related. They were already successfully applied to explain the proton transfer in the phase transition in 1,3-cyclohexanedione crystals[15,50,51] and to analyze polymorphism or formation of inclusion compounds by hydrogen-bonded molecules.[15] H bonds with donor and acceptor groups not symmetry related are very common, just to mention the double H bridges between the molecules of carboxylic acids, biological macromolecules or liquids. Due to the systematic changes, the disordered and ordered H bonds cannot be statistically compared.[21]

ACKNOWLEDGMENT

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