Brief Reports

Coupling of displacive and order-disorder transformations in hydrogen-bonded ferroelectrics

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Bistable hydrogen bonds are shown to induce systematic displacements in arrangement of molecules or ions in the structures of ferroelectric crystals: methods of calculating the magnitudes of the displacements, and characteristic structural transformations on disordering of the H atom above T_c are described. The displacements are correlated with T_c, and their contribution to the isotope effect on T_c, and to the differences in T_c between isostructural ferroelectric crystals are discussed.

The structural origin of ferroelectric properties in hydrogen-bonded crystals, in which the hydrogen atom is bistable and becomes disordered above T_c, was initially explained by the "ice rule" proposed for KH_2PO_4 (KDP) crystals by Slater.[1,2] KDP-type ferroelectrics attracted much attention both as simple model compounds for order-disorder transitions and for their practical applications. They were also considered a valuable source of information about hydrogen bonds. Observation of a strong isotope effect increasing T_c when the H atom is substituted by a deuterium atom led to the pseudospin model proposed by Blinc,[3] assuming that the isotope effect is due to the tunneling of H/D. Ichikawa[4-6] argues that the isotope effect is due to the so-called Ubbelohde effect of increased $O \cdots O$ and $H--O$ distances on deuteration.[7] The pressure dependence of T_c (Refs. 8, 9) confirmed the interdependence between hydrogen-bond dimensions and T_c; however, high-resolution structural studies[10,11] indicated that the isotope effect cannot be accounted for by the Ubbelohde effect alone. Kobayashi introduced a coupled mode theory for KDP, in which the tunneling mode of protons or deuterons is coupled with transverse optic vibrational modes involving ions PO_4 and K.[12] The model implies that the vibrations of heavy atoms "freeze" into displacements below T_c; thus the phase transitions in KDP-type crystals were termed as "mixed," exhibiting both order-disorder and displacive behavior. This classification of the KDP-type ferroelectrics, as lying between order-disorder and displacive extremes, is now commonly accepted.[13,14] However, the nature of the displacements or the structural origin of spontaneous polarization (usually nearly perpendicular to the $O \cdots O$ direction) have not been explained. While most of the studies on the atomic-scale transformations of KDP-type ferroelectrics have been concerned with the geometry of the hydrogen bonds, separation between the

hydrogen-atom sites, and deformations of the hydrogen bonded molecules or ions,[15-17] in this paper a mutual relation between the H-atom position and displacements of the molecules or ions is presented. A set of parameters for measuring the displacements is given, which, like the hydrogen-bond dimensions, can be correlated with T_c changes.

Most recently, we described geometric effects of H-atom disordering in KDP-type ferroelectrics, resulting from the combination of differences between the electronic structure of the oxygen atoms involved in the $-OH--O=$ hydrogen bonds, and the symmetry requirements in paraelectric-phase structures.[18] It can be shown that the differences between the electronic structure of the oxygen atoms involved in the hydrogen bond lead to displacements of the hydrogen-bonded molecules or ions. These displacements together with the ordered hydrogen atom contribute to the distortions of (anti)ferroelectric structures from the higher symmetry of paraelectric structures, or, in the case of ferroelastic crystals, to distortions of orientational states from prototypic structures. The functional interdependence between the H-atom position and displacements of the donor and acceptor groups has the simplest form for the hydrogen bonds in which the donor and acceptor groups become C_{2h}-symmetry related in the paraelectric phase, and for this symmetry the equations for calculating the magnitudes of the displacements will be derived here. A pseudo-C_{2h}-symmetric hydrogen bond shown in Fig. 1 (a) is a fragment of the antiferroelectric phase structure of squaric acid. The different electronic structure of the oxygen atoms can be observed both in molecular dimensions (bond lengths and valency angles), and in the directions of formation of the hydrogen bond, i.e., angles $R-O-H$ (denoted η_d) and $H--O'=R'$ (η_a). The electronic structure of the donor oxygen atom O can be described as
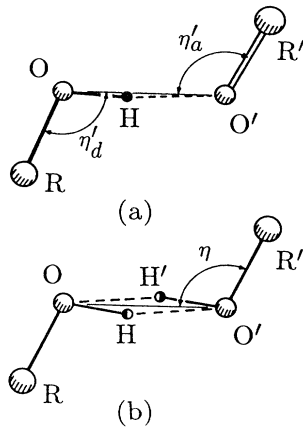
FIG. 1. A pseudo-C_{2h}-symmetric –OH––O= hydrogen bond in ferroelectric phase (a), and a C_{2h}-symmetric hydrogen bond with disordered hydrogen atom in paraelectric phase (b). Angles R–O–H are denoted η_d; H––O$'$–R', η_a; O–H––O$'$, η_H; R–O$\cdots$O$'$, η_d'; O$\cdots$O$'$–R', η_a'; distances O–H, d_d; and H––O$'$, d_a; R stands for the atoms to which the oxygen atoms are chemically bonded.

closer to sp^3 hybridization than the electronic structure of the acceptor oxygen atom O$'$; the electronic structure of the O$'$ atom is closer to sp^2 hybridization. Thus, the R–O bond is longer than R'=O$'$, and the angle η_d is smaller than η_a. For example,[18] the η_d and η_a angles in squaric acid are equal to 112.65(7)° and 118.15(5)°, and in KH$_2$PO$_4$ to 112.07(7)° and 113.41(5)°, respectively. It occurs from high-resolution neutron-diffraction measurements that the transformation of a KDP-type ferroelectric to paraelectric phase does not change markedly such hydrogen-bond distances as O–H (denoted d_d), H––O$'$ (d_a), and angles η_d and η_a. This results from the ability of the electronic structure of the oxygen atoms to adjust quickly following the hopping of the hydrogen atom between its two favorable sites, despite the averaging of the molecular dimensions of the donor and acceptor groups, e.g., bond lengths R–O and O$'$–R'. The new symmetry element relating the donor and acceptor groups requires that for both the oxygen atoms the d_d, d_a, η_d, and η_a parameters assume the same values, which leads to characteristic geometric effects in hydrogen bonds with a disordered H atom: sharpening of angle O–H––O$'$ (denoted η_H), shortening of distance O$\cdots$O (r), or an inclination angle of about 10° between directions H$\cdots$H$'$ and O$\cdots$O$'$. The magnitudes of these effects, and the separation between the two H sites, H$\cdots$H$'$ [δ; see Fig. 1(b)], can be calculated and agree with experimental results.[18]

The relative orientation of the donor and acceptor groups in C_{2h}-symmetric hydrogen bonds is determined by the three angles η_d, η_a, and η_H; additional parameters are required for the other possible symmetries C_i or C_2.[18] Only pseudosymmetric bistable hydrogen bonds, in which angle η_H decreases the misalignment of the donor and acceptor groups from the orientation required by the symmetry relating the H-bonded groups in paraelectric phase, are observed in KDP-type ferroelectric

crystals,[18,19] and only this type of hydrogen bond is discussed in this paper. To describe relative positions of the donor and acceptor groups it is convenient to apply angles R–O$\cdots$O$'$, denoted η_d', and O$\cdots$O$'$=R', η_a'. It occurs that despite the compensating role of angle η_H in pseudosymmetric hydrogen bonds of ferroelectric phases, the η_d' angle is always smaller than the η_a' angle. This results from a strong tendency of short hydrogen bonds to be linear (η_H close to 180°).[20] Any symmetry element relating the donor and acceptor groups, and the sites of the disordered hydrogen atom, requires that angles η_d' and η_a' become equal in the paraelectric phase; their common value is denoted η. The differences

$$\Delta\eta_d' = \eta_d' - \eta, \qquad (1)$$

$$\Delta\eta_a' = \eta_a' - \eta \qquad (2)$$

are convenient parameters for measuring the displacements of the donor and acceptor groups in the ferroelectric phase from their position assumed above T_c. The magnitudes of the displacements can be visualized by plotting angles η_a' versus η_d', as shown for prototypical ferroelectric structures of KH$_2$PO$_4$, KD$_2$PO$_4$, squaric acid (C$_4$H$_2$O$_4$ and C$_4$D$_2$O$_4$), RbHSeO$_4$, and RbH$_2$PO$_4$ (Refs. 21–26) in Fig. 2. For C_{2h}-symmetric hydrogen bonds it is possible to calculate equivocally the magnitudes of $\Delta\eta_d'$ and $\Delta\eta_a'$ from parameters d_d, d_a, η_d, and η_a, described above, according to the formulas

$$\Delta\eta_d' = \tan^{-1}\left(\frac{d_a \sin\mu}{d_d + d_a \cos\mu}\right) - \tan^{-1}\left(\frac{d_a \sin\eta_H}{d_d - d_a \cos\eta_H}\right), \qquad (3)$$

$$\Delta\eta_a' = \tan^{-1}\left(\frac{d_d \sin\mu}{d_a + d_d \cos\mu}\right) - \tan^{-1}\left(\frac{d_d \sin\eta_H}{d_a - d_d \cos\eta_H}\right), \qquad (4)$$

where $\mu = \eta_a - \eta_d$ is constant. Angle η_H can vary in the ferroelectric phase, while in the paraelectric phase it must assume a value close to $\eta_H = 180° - \mu$, for which the two $\Delta\eta'$ displacements are equal 0° [Eqs. (3), (4)]. Most importantly, Eqs. (3) and (4) demonstrate that displacements $\Delta\eta_d'$, $\Delta\eta_a'$, and the distance between the sites of a disordered H atom, δ, are interdependent, because the displacements and δ depend on the set of parameters d_d, d_a, η_d, and η_a reflecting the electronic structure of the oxygen atoms [see Eq. (7) of Ref. 18]. Several forms of the dependence of T_c on δ were postulated.[27,11] The above argument shows that T_c can be equally dependent on displacements $\Delta\eta_d'$ and $\Delta\eta_a'$.

To assess the significance of the atomic displacements for ferroelectric transformations a combined displacive parameter $\Delta\eta'$ is defined:

$$\Delta\eta' = \Delta\eta_d' + \Delta\eta_a'. \qquad (5)$$

The interdependence between $\Delta\eta'$, T_c, and δ is presented in Fig. 3, in which temperatures T_c and distances δ are plotted against displacements $\Delta\eta'$ for a series of prototypical (anti)ferroelectric crystals, for which precise structural data are available.[21–25] In the antiferroelectric monoclinic phase of squaric acid there are two symmetry-
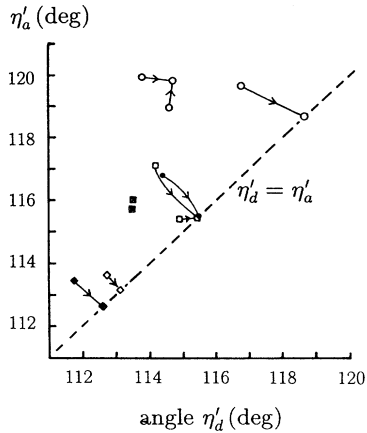
η'_a (deg)

FIG. 2. Angles η'_a plotted versus η'_d, for the crystals of KH$_2$PO$_4$ ($\Diamond$), KD$_2$PO$_4$ ($\blacklozenge$), RbH$_2$PO$_4$ ($\bullet$), squaric acid C$_4$H$_2$O$_4$ ($\Box$, two symmetry-independent hydrogen bonds in the antiferroelectric phase), C$_4$D$_2$O$_4$ ($\blacksquare$), and RbHSeO$_4$ ($\circ$, three symmetry-independent hydrogen bonds in the ferroelectric phase, one of which becomes disordered above T_c and the two other related by a twofold screw axis). The dashed line represent values $\eta'_d = \eta'_a$, arrows and thin lines joining the points indicate changes in (η'_d, η'_a) on transformation from (anti)ferroelectric to paraelectric phases.

independent hydrogen bonds, which on transformation to the paraelectric tetragonal phase become disordered and symmetry related[23] (see Fig. 2); the displacements of the two hydrogen bonds were added to obtain one cumulative $\Delta\eta'$ plotted in Fig. 3. The same procedure of calculating $\Delta\eta'$ was applied for the structure of RbHSeO$_4$, containing three symmetry-independent hydrogen bonds in the ferroelectric phase, one of which becomes disordered in the paraelectric phase above $T_c = 374$ K, and the
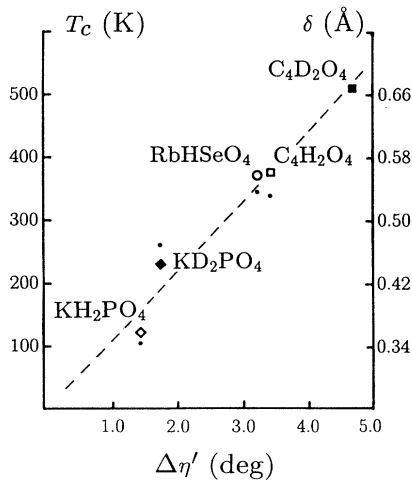
FIG. 3. Temperatures T_c, and distances between the sites of a disordered H atom, δ, plotted against displacement parameters $\Delta\eta'$ for the structures of KH$_2$PO$_4$ ($\Diamond$), KD$_2$PO$_4$($\blacklozenge$), RbHSeO$_4$ ($\circ$), squaric acid C$_4$H$_2$O$_4$ ($\Box$), and C$_4$D$_2$O$_4$ ($\blacksquare$); H$\cdots$H separations δ are represented as dots.

two other become symmetry related by a twofold screw axis.[25] The results for KH$_2$PO$_4$ and its deuterated analog KD$_2$PO$_4$ show that the deuteration increases both the separation δ between the H-atom sites, and the combined displacement $\Delta\eta'$, and that the ratio of the increase in these two values is similar. An apparent effect of deuteration, increasing $\Delta\eta'$ and δ, is also observed for the crystals of squaric acid. Despite significant structural differences in the lattice interactions and space group symmetries between organic molecular crystals of squaric acid and inorganic ionic crystals of RbHSeO$_4$, the interdependence between $\Delta\eta'$, δ, and T_c is remarkably similar for these two substances. The plot shows an approximately linear correlation between T_c and $\Delta\eta'$, resulting from the same origin of the displacements. The plot also illustrates the interdependence between δ and $\Delta\eta'$, which can be expressed as a function by substituting Eq. (7) of Ref. 18 to Eqs. (3), (4), and (5).

The described interdependence between atomic displacements, H-atom disordering, and T_c temperature offers a means of assessing the transformation temperature, when only ferroelectric structural data are available. For the pseudo-C_{2h}-symmetric H bonds the value of $\Delta\eta'$ can be calculated from Eqs. (3) and (4); values of $\Delta\eta'$ for C_i- or C_2-symmetric hydrogen bonds can be estimated with the difference

$$\Delta\eta' \cong \eta'_a - \eta'_d. \tag{6}$$

The value of $\Delta\eta'$, in turn, can be used for assessing T_c. Moreover, the application of Eq. (6) does not require any knowledge about the H-atom position, which is often not precisely determined in x-ray-diffraction measurements. If so assessed T_c exceeds the melting point of the studied crystal, by applying information about dT_c/dp one can estimate the pressure required to reduce T_c below the melting point.[28,29] This information is often required before planning experiments aimed at the observation of transitions to paraelectric phases when only (anti)ferroelectric data are available; for example, see Refs. 28–31.

The phase transitions in KDP-type ferroelectrics involve several systematic and interdependent structural transformations: (a) disordering of the hydrogen atom; (b) averaging of molecular (ionic) dimensions of the donor and acceptor groups, e.g., lengths of the R–O bonds; (c) displacements of the hydrogen-bonded molecules or ions, consisting of reorientations of the donor and acceptor groups, $\Delta\eta'_d$ and $\Delta\eta'_a$, and systematic changes in hydrogen-bond dimensions, e.g., shortening of r; and (d) in ionic crystals or inclusion compounds, adjustments of the molecules or cations, which are not hydrogen bonded, to the transformed network of hydrogen-bonded molecules or anions. While the averaging of molecular dimensions (b) causes only small and approximately similar changes in various KDP-type structures, the $\Delta\eta'_d$ and $\Delta\eta'_a$ displacements (c) may have larger and very structure-dependent magnitudes. The $\Delta\eta'_d$ and $\Delta\eta'_a$ displacements measure deviations of ferroelectric structures from their paraelectric phases, and therefore are directly connected to the properties of these crystals.

The displacements of the heavy-atom structure and the correlation of their magnitudes with T_c invoke questions concerning the nature of the phase transitions in the KDP-type ferroelectrics. In the light of these results the H bonds induce atomic displacements breaking the symmetry of paraelectric phases. It appears that at temperatures approaching T_c the vibrations of the molecules or ions upset the $\eta'_d < \eta'_a$ relation, and thus destabilize the H-atom position in the hydrogen bonds. In this case the displacements would play a key role in the ferroelectric transformations of the crystals, while the H-atom site would depend on the instantaneous positions of the thermally vibrating heavy atoms, and instantaneous relations between the η'_d and η'_a angles. The R–O bond lengths, in turn, depend on the H-atom posi-

tion in the hydrogen bond; the dimensions of the hydrogen bond are also somewhat changed on disordering of the H atom. This confirms the classification of the phase transitions in KDP-type ferroelectrics as intermediate between displacive and order-disorder structural transformations.[12-15] It also means that although considerably more complicated than initially assumed, the atomic-scale mechanism of the phase transitions in KDP-type ferroelectrics can be described, and magnitudes of the structural transformations can be precisely calculated and applied for evaluating thermodynamic or macroscopic properties of these crystals.

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