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Negative evidence for a proton-tunneling mechanism in the phase transition of KH_2PO_4-type crystals

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We have found a linear relation between the transition temperature T_c (in K) and the hydrogen-bond length R (in Å) for tetragonal KH_2PO_4-type crystals, $T_c = 2290(R - 2.428)$, irrespective of whether the crystals are deuterated or undeuterated; this finding supplies negative evidence for the proton-tunneling mechanism in the phase transition. We deduce from this relation that the isotope effect in the initial pressure derivative of T_c, dT_c/dp, reflects not the isotope effect in dT_c/dR, so far regarded as supporting evidence of proton tunneling, but that in dR/dp. Some R and dR/dp values at T_c are predicted.

During the fifty years since the discovery of ferroelectric KH_2PO_4 (KDP), the problem of its phase transition and the large isotope effect on such physical quantities as the transition temperature T_c has been one of the most interesting topics in this field.[1] Among the various theoretical models that have been proposed, the coupled proton-lattice model with proton tunneling has been most widely accepted,[2] since it is supported by light scattering[3] and high-pressure measurements.[4,5] Recently, however, some serious doubts have been thrown upon the proton-tunneling model. Ichikawa has pointed out the importance of the length and symmetry of the hydrogen bond (H bond) and the H-bond-length isotope effect (geometric isotope effect) in inducing the occurrence of a large isotopic shift of the transition temperature ΔT_c (Ref. 6) and he has proposed an empirical relation that connects ΔT_c and the intersite separation of a proton in the H bond.[7] This indicates that the large ΔT_c might be interpreted without invoking proton tunneling. Recently, too, two groups cooperatively[8] have interpreted the Brillouin and Raman scattering data of KDP in terms of an order-disorder dynamics of the PO_4 dipole without recourse to the proton-tunneling model, on the basis of (1) the existence of a central component (< 20 cm^{-1}) that increases in intensity as the temperature approaches T_c, (2) the assignment of the broad mode ($\lesssim 150$ cm^{-1}) in the $x(yx)y$ Raman spectra to the librational motion of PO_4 tetrahedron, and (3) the C_2 local site symmetry of the PO_4 tetrahedron above T_c. In spite of these doubts, the tunneling model is still thought to be an attractive explanation of the isotope effect on T_c and its pressure derivative dT_c/dp. We report negative evidence for proton tunneling during the phase transition of tetragonal KDP-type crystals on the basis of an empirical relation between T_c and the H-bond length $R(O \cdots O)$.

Figure 1 shows the relation between T_c and $R(O \cdots O)$ (abbreviated as R) in tetragonal KDP-type crystals. A linear regression analysis gives the relation

$$T_c = 2290(R - 2.428) \ , \tag{1}$$

where T_c is expressed in K, R in Å. Here only tetragonal crystals are included among the various KDP-type crystals that share the same environment as the constituent ions and H bond. It is noticeable that T_c correlates very nicely with R, since R in the KDP-type crystals is distributed in a rather narrow range of width 0.04 Å. The data obtained from high-pressure experiments for KDP and KD_2PO_4 (DKDP) by Tibballs, Nelmes, and McIntyre[14] are also plotted in Fig. 1 (triangles). The high-pressure data fit fairly well along the regression line. Furthermore, when they used the P-T dependence of the H-bond length obtained the from high-pressure data, they got an H-bond length of 2.428(7) Å at the critical pressure 17 kbar, where the ferroelectricity of KDP vanishes ($T_c = 0$). This is the same value as the one obtained by extrapolation of the regression line to 0 K [Eq. (1)]. These results are consistent with our own.

The first important point to emerge from our result is that T_c in the KDP-type crystals is regulated only by the H-bond length, irrespective of whether the crystals are deuterated or undeuterated. This indicates that ΔT_c is not due to proton tunneling. For, if the proton-tunneling mechanism were really effective, the tunneling frequency in the D bond, Ω_D, would be lower than that in the H-bond, Ω_H, for the same bond length, and consequently the deuterated crystal would show a higher T_c than the undeuterated crystal: but in fact, however, both of them agree within the scatter of the data, i.e., $\Omega_H = \Omega_D$. Recently, however, Matsushita and Matsubara proposed another interpretation that, under the condition that Ω is much smaller than the interaction term, proton tunneling plays an indirect role in ΔT_c, i.e., that proton tunneling drives the H-bond-length isotope effect and the latter drives ΔT_c.[15] This condition leads to $kT_c \gg \Omega$, resulting

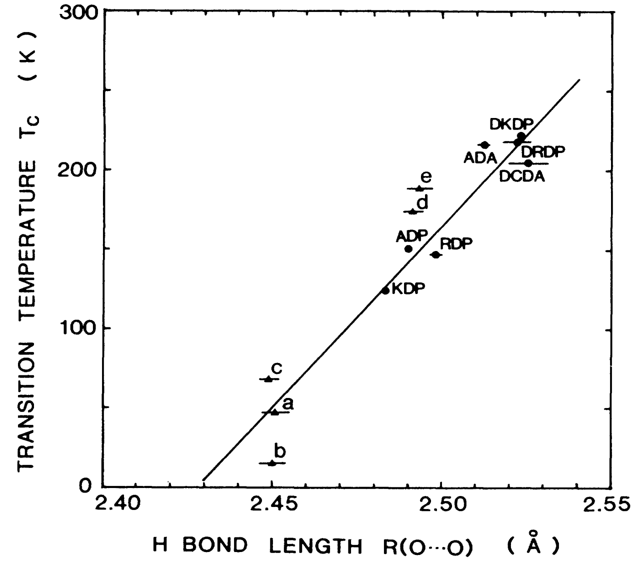

FIG. 1. The transition temperature T_c vs hydrogen-bond length $R(\mathrm{O}\cdots\mathrm{O})$ in tetragonal KH_2PO_4-type crystals. The least-squares line was obtained from seven member compounds denoted by circles. Their chemical formulas are given in Table I. Data on the transition temperature were taken from Ref. 9. H-bond length data are cited from Ref. 10 for KDP and DKDP, Ref. 11 for RDP and DRDP, Ref. 12 for DCDA (58% deuterated), Ref. 13 for ADP and ADA. Where data close to T_c are unavailable, those at room temperature were used. The triangles denote the high-pressure data for KDP (*a*, *b*, and *c*) and for DKDP (*d* and *e*) (Ref. 14), where the H-bond lengths at the transition temperature were derived to T_c by linear extrapolation using temperature derivative at atmospheric pressure when the experiment had been performed at room temperature.

in $\Omega \ll 100\ \mathrm{cm}^{-1}$. The small isotopic difference $\Delta\Omega$ ($\ll 100\ \mathrm{cm}^{-1}$), therefore, must entirely induce the H-bond isotope effect (~ 0.02 Å). Furthermore, the above Ω value ($\ll 100\ \mathrm{cm}^{-1}$) is one order of magnitude smaller than the recently reported value ($320\ \mathrm{cm}^{-1}$) derived under the assumption of tunneling for KDP.[16] Taking these points into consideration, it seems difficult to account for ΔT_c by this other interpretation. Thus we believe that the H-bond-length isotope effect, which is irrelevant to proton tunneling, is responsible for the large ΔT_c. If we take the general theory of the first-order phase transition, which holds for KDP-type crystals, we get

$$\Delta U = T_c \Delta S \ , \tag{2}$$

where ΔU is a change of the internal energy at T_c and ΔS is the transition entropy. It is natural in the first approximation to assume that ΔS is a constant among the KDP-type crystals. T_c is then determined by ΔU alone. Although we cannot go further into the substance of ΔU, we note that ΔU should be interpreted as an interaction energy, which possibly includes the K-PO_4 interaction, PO_4 distortion,[17] the H-bond energy, and other unrevealed interactions as well as Slater-like configuration interactions. However, Eq. (1) requires that ΔU should be related linearly to the H-bond length. This also indicates that ΔU depends linearly on the intersite separation in the symmetric H bond, δ, since δ can be regarded as linearly dependent on R in the narrow range we have been considering.[14,18]

We have already stated that the pressure-derivative data for the transition temperature dT_c/dp also favor the proton-tunneling model. Since three pieces of pioneering work were published in 1967,[4] the dT_c/dp data have revealed a striking isotope effect in KDP-type crystals. We should like to discuss this problem using the present result. dT_c/dp is written as

$$\frac{dT_c}{dp} = \frac{dT_c}{dR}\left[\frac{dR}{dp}\right] . \tag{3}$$

Equation (3) establishes the second important point: The isotope effect of dT_c/dp does not represent the isotope effect of dT_c/dR considered so far, but that of dR/dp, since dT_c/dR is constant from Eq. (1). On the other hand, in the theoretical analysis of dT_c/dp data by Blinc and Žekš[19] the isotope effect is entirely attributed to the dT_c/dR term. The isotope effect of dT_c/dp does not therefore support the notion of proton tunneling.

Combining Eq. (1) and Eq. (3) makes it possible to predict dR/dp values for KDP-type crystals, other than KDP and DKDP, not measured so far. The dR/dp of tetragonal KDP crystals is expressed by several factors including the temperature effect as

$$\frac{dR}{dp} = \frac{1}{2}\frac{da}{dp} + 2d_{xy}\sin\theta\frac{d\theta}{dp} \ ,$$

where a is the lattice constant, and d_{xy} the projection of the X–O length onto the x-y plane while θ is the rotation angle of the XO_4 ion from the x axis around the c axis in the chemical formula MH_2XO_4 or MD_2XO_4.[14] The predicted dR/dp values are given in Table I together with the predicted values of the hydrogen-bond length at T_c from

TABLE I. The predicted H-bond length and its initial pressure derivative at the transition temperature for tetragonal KH_2PO_4-type crystals. The two predicted values were obtained from Eqs. (1) and (3) using the data of the transition temperature and its initial pressure-derivative taken from Ref. 9.

Compound	$R(\mathrm{O}\cdots\mathrm{O})$ (Å)	$-dR/dp$ (10^{-2} Å GPa^{-1})
RbH_2PO_4 (RDP)	· · ·	2.71
RbD_2PO_4 (DRDP)	· · ·	2.1
KH_2AsO_4 (KDA)	2.470	1.15
KD_2AsO_4 (DKDA)	2.498	0.699
RbH_2AsO_4 (RDA)	2.476	2.00
RbD_2AsO_4 (DRDA)	2.502	1.18
CsH_2AsO_4 (CDA)	2.493	2.46
CsD_2AsO_4 (DCDA)	· · ·	1.76
$NH_4H_2PO_4$ (ADP)	· · ·	1.48
$ND_4D_2PO_4$ (DADP)	2.531	0.624
$NH_4H_2AsO_4$ (ADA)	· · ·	0.860
$ND_4D_2AsO_4$ (DADA)	2.561	0.576

Eq. (1). If we compare the calculated values of the dT_c/dp data with the directly measured value of the high-pressure data, we obtain 0.020 Å GPa^{-1} for KDP and 0.010 Å GPa^{-1} for DKDP. On the other hand, the values 0.023(7) (Å GPa^{-1}) for KDP and 0.024(4) (Å GPa^{-1}) for DKDP were obtained from the high-pressure data, where the R value at 295 K was taken from the three-dimensional data and the values at T_c were obtained by interpolation. If we take into consideration that in experiments under high pressure it is extremely difficult to attain sufficient accuracy to compare the results, especially for DKDP with a slight change in R, the agreement might be said to be fairly good. Finally, we must note that the conclusion drawn from this study totally depends on the validity of Eq. (1) and that the H-bond-length data for crystals not yet measured are therefore needed for further verification of Eq. (1).

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[1] See, for example, R. Blinc and B. Žekš, in *Soft Modes in Ferroelectrics and Antiferroelectrics,* edited by E. P. Wohlfarth (North-Holland, Amsterdam, 1974); M. E. Lines and A. M. Glass, *Principles and Applications of Ferroelectrics and Related Materials* (Clarendon, Oxford, 1977).

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