Negative evidence for a proton-tunneling mechanism in the phase transition
of KH$_2$PO$_4$-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$_2$PO$_4$-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$_2$PO$_4$ (KDP), the problem of its phase transition and the large isotope effect on such physical quantities as tric KH$_2$PO$_4$ (KDP), the problem of its phase transition cooperatively have interpreted the Brillouin and Raman models that have been proposed, the coupled proton-lattice model with proton tunneling has been most widely accepted, since it is supported by light scattering and high-pressure measurements. Recently, however, some serious doubts have been thrown upon the proton-tunneling model, on the basis of (1) the existence of a central component $\nu$ (x-y) in the Raman spectra to the librational motion of PO$_4$ tetrahedron, and (2) the assignment of the broad mode $\nu$ (x-y) in the KDP-type crystals is restricted only by the H-bond length, irrespective of whether the crystals are deuterated or undeuterated. This indicates that the large $\Delta T_c$ might be interpreted without invoking proton tunneling. Recently, too, two groups cooperatively 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-y-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

$$T_c = 2290(R - 2.428),$$

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$_2$PO$_4$ (DKDP) by Tibbals, Nelmes, and McIntyre 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 from the 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 $\Delta T_c$ is not due to proton tunneling. For, if the proton-tunneling mechanism were really effective, the tunneling frequency in the D bond, $\Omega_D$, would be lower than that in the H-bond, $\Omega_H$, 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, Matsushita and Matsubara proposed another interpretation that, under the condition that $\Omega$ is much smaller than the interaction term, proton tunneling plays an indirect role in $\Delta T_c$, i.e., that proton tunneling drives the H-bond-length isotope effect and the latter drives $\Delta T_c$. This condition leads to $kT_\beta \gg \Omega$, resulting...
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FIG. 1. The transition temperature \(T_c\) vs hydrogen-bond length \(R(O\cdots O)\) 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 \(\Omega \approx 100 \text{ cm}^{-1}\). The small isotopic difference \(\Delta \Omega\) (\(\ll 100 \text{ cm}^{-1}\)), therefore, must entirely induce the H-bond isotope effect (\(-0.02 \text{ Å}\)). Furthermore, the above \(\Omega\) value (\(\ll 100 \text{ cm}^{-1}\)) is one order of magnitude smaller than the recently reported value (320 cm\(^{-1}\)) derived under the assumption of tunneling for KDP.\(^{16}\) Taking these points into consideration, it seems difficult to account for \(\Delta T_c\) 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 \(\Delta T_c\). If we take the general theory of the first-order phase transition, which holds for KDP-type crystals, we get

\[
\Delta U = T_c \Delta S ,
\]

where \(\Delta U\) is a change of the internal energy at \(T_c\) and \(\Delta S\) is the transition entropy. It is natural in the first approximation to assume that \(\Delta S\) is a constant among the KDP-type crystals. \(T_c\) is then determined by \(\Delta U\) alone. Although we cannot go further into the substance of \(\Delta U\), we note that \(\Delta U\) should be interpreted as an interaction energy, which possibly includes the K-PO\(_4\) interaction, PO\(_4\) distortion,\(^{13}\) the H-bond energy, and other unrevealed interactions as well as Slater-like configuration interactions. However, Eq. (1) requires that \(\Delta U\) should be related linearly to the H-bond length. This also indicates that \(\Delta U\) depends linearly on the intersite separation in the symmetric H bond, \(\delta\), since \(\delta\) 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

\[
\frac{dT_c}{dp} = \frac{dT_c}{dR} \cdot \left(\frac{dR}{dp}\right).
\]

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 Zekš\(^{19}\) the isotope effect is entirely attributed to the \(d^2T_c/dR^2\) 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 \(X-O\) onto the \(x-y\) plane 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>
<thead>
<tr>
<th>Compound</th>
<th>(R(O\cdots O)) (Å)</th>
<th>(-dR/dp) (10(^{-2}) GPa(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>RbH(_2)PO(_4) (RDP)</td>
<td>(\ldots)</td>
<td>2.71</td>
</tr>
<tr>
<td>RbD(_2)PO(_4) (DRDP)</td>
<td>(\ldots)</td>
<td>2.1</td>
</tr>
<tr>
<td>KH(_2)AsO(_4) (KDA)</td>
<td>2.470</td>
<td>1.15</td>
</tr>
<tr>
<td>KD(_2)AsO(_4) (DKDA)</td>
<td>2.498</td>
<td>0.699</td>
</tr>
<tr>
<td>RbH(_2)AsO(_4) (RDA)</td>
<td>2.476</td>
<td>2.00</td>
</tr>
<tr>
<td>RbD(_2)AsO(_4) (DRDA)</td>
<td>2.502</td>
<td>1.18</td>
</tr>
<tr>
<td>CsH(_2)AsO(_4) (CDA)</td>
<td>2.493</td>
<td>2.46</td>
</tr>
<tr>
<td>CsD(_2)AsO(_4) (DCDA)</td>
<td>(\ldots)</td>
<td>1.76</td>
</tr>
<tr>
<td>NH(_4)H(_3)PO(_4) (ADP)</td>
<td>(\ldots)</td>
<td>1.48</td>
</tr>
<tr>
<td>ND(_4)D(_2)PO(_4) (DADP)</td>
<td>2.531</td>
<td>0.624</td>
</tr>
<tr>
<td>NH(_4)H(_3)AsO(_4) (ADA)</td>
<td>(\ldots)</td>
<td>0.860</td>
</tr>
<tr>
<td>ND(_4)D(_2)AsO(_4) (DADA)</td>
<td>2.561</td>
<td>0.576</td>
</tr>
</tbody>
</table>
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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2See, for example, T. Matsubara, in Proceedings of the Sixth International Meeting on Ferroelectricity, Kobe, August, 1985 [Jpn. J. Appl. Phys. 24, Suppl. 24-2, 1 (1985)].
4See, for example, G. A. Samara, in Advances in High Pressure Research, edited by R. S. Bradley (Academic, New York, 1969), Vol. 3.