Isotope Effects in Hydrogen-Bonded Crystal KH_2PO_4

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The energies and wave functions of both the ground and excited states are calculated for a proton in KDP (KH_2PO_4) and a deuteron in DKDP (KD_2PO_4), respectively. On the basis of these calculations, the isotope effects on the saturated polarization and the transition temperature of the ferroelectric phase are examined. It is shown from these results that remarkable isotope effects are caused by the isotope dependence of changes in the ground-state energy induced by a distortion of PO_4 tetrahedrons.

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One of the striking features of hydrogen-bonded crystals, such as KH_2PO_4 (KDP), is that there is a large isotope effect on the transition temperature T_c from a ferroelectric phase to a paraelectric phase. For example, KDP and its deuterated isomorph DKDP undergo phase transitions at 122 and 213 K, respectively. To account for this remarkable isotope effect, a tunneling motion of protons, in addition to interactions between neighboring protons, has been introduced by Blinc [1] and by Tokunaga and Matsubara [2]. In this model, the change in T_c is qualitatively explained by a large difference of tunneling matrix elements due to the mass difference between a proton and a deuteron. Kobayashi [3] has taken account of an optical phonon mode coupled with the tunneling motion, showing that the transition is of a displacive type and is accompanied by a softening of the optical mode, which is called a "soft mode." Since this conclusion seemed to be supported by many experiments, including observations of the soft mode, his model has been accepted as the mechanism of the phase transition of KDP-type crystals.

Recent experiments concerning KDP and DKDP, however, indicate that there are some doubts regarding the validity of this model [4]. In particular, Tominaga and co-workers [5,6] concluded from Raman-scattering experiments for KDP and DKDP the following: The mechanism of the phase transition is of an order-disorder type; the mode which has usually been assigned to the soft mode comprises two components of a polarization-fluctuation mode and a libration mode of PO_4 tetrahedrons. Futhermore, Ichikawa [7] found that the increase in T_c upon deuteration can be attributed to an accompanying increase in the oxygen-oxygen distance between two PO_4 tetrahedrons (d) and in the displacement of a proton (or a deuteron) from the center of the oxygen-oxygen distance. He called this the "geometric isotope effect." Later, Nelmes [8] reexamined the high-resolution neutron-diffraction results for KDP and DKDP, and insisted that a part of the increase (about 40 K) is caused by a direct tunneling effect, although there is also the geometric isotope effect.

We propose a new model in which a strong coupling between the protons and distortions of PO_4 tetrahedrons is assumed, and the interaction between protons is disregarded. Based on this model, we performed numerical calculations on KDP and DKDP, including the energies and the wave functions of the proton and deuteron, and some of the properties of the ferroelectric phase. The purpose of this Letter is to show that a consistent account of the isotope effects can be obtained from the knowledge of the energies and wave functions of the proton and deuteron.

Let us consider a system which comprises N distorted PO_4 tetrahedrons and $2N$ protons connecting two neighboring tetrahedrons. We can write the total energy of this system as

$$E_{\rm tot}=\frac{A}{2}\sum_{i=1}^{N}\mu_i^2+\frac{1}{2}\sum_{i,j}^{N}D_{ij}\mu_i\mu_j-\sum_{\langle ij\rangle}^{2N}E_{ij}^0 . \tag{1}$$

It is assumed here that all distortions of PO_4 lie along the c axis in a KDP crystal and that the distortion of tetrahedron i is proportional to its electric dipole moment μ_i. The first term in this expression represents the elastic energy associated with the mechanical deformation of the tetrahedrons. Accordingly, the parameter A must be positive. The second term expresses the interaction energy between dipoles. The last term is the energy of $2N$ protons, where E_{ij}^0 is the ground-state energy of a proton connecting two neighboring tetrahedrons i and j. E_{ij}^0 and its excitation energies can be obtained by solving the Schrödinger equation for the proton, i.e.,

$$[(-\hbar^2/2m)\nabla^2+U]\Psi_n=E_{ij}^n\Psi_n . \tag{2}$$

The potential acting on the proton, $U(r)$, is described by involving an asymmetric potential $F_{ij}x$ induced by μ_i and μ_j as follows:

$$\begin{aligned}U(r)=&\frac{f}{2}(\alpha_i^2+\alpha_j^2)+\frac{g}{2}(\beta_i^2+\beta_j^2)\\&+V([(x-x_i)^2+y^2+z^2]^{1/2})\\&+V([(x-x_j)^2+y^2+z^2]^{1/2})+F_{ij}x ,\end{aligned} \tag{3}$$

where α_i and β_i are bending angles defined by

$$\alpha_i = \sin^{-1}\{y/[(x-x_i)^2+y^2]^{1/2}\}$$

and

$$\beta_i = \sin^{-1}\{z/[(x-x_i)^2+z^2]^{1/2}\}.$$

x_i and x_j are $-d/2$ and $+d/2$, respectively. $V(r)$ is the Morse potential,

$$V(r) = \varepsilon\{\exp[-2a(r-r_0)] - 2\exp[-a(r-r_0)]\}.$$

The coordinate axes used here are shown in Fig. 1.

In order to solve the Schrödinger equation, we adopt a numerical method which was derived, for the first time, by Kimball and Shortely [9] and applied to hydrogen in metals by Sugimoto and Fukai [10]. Regarding parameters f and g in Eq. (3), $f=0.2$ eV and $g=1.2$ eV are used. Matsushita and Matsubara [11] determined the values of ε, a, and r_0 in order to reproduce the empirical relation between d and the oxygen-hydrogen distance found widely in various hydrogen-bonded crystals. We slightly adjusted their values and used $\varepsilon=2.0$ eV, $a=3.0$ Å^{-1}, and $r_0=0.98$ Å.

Using the above values and $d=2.50$ Å, we calculated both the energies and wave functions of the ground state and the excited states of a proton in KDP, with various values of F_{ij}. Calculations on DKDP were also performed using the same formula by substituting the deuteron mass in Eq. (2) and by adopting $d=2.52$ Å, which is the observed value of d in DKDP.

The F_{ij} dependences of the excitation energies of a proton (ΔE_x, ΔE_y, and ΔE_z) obtained from these calculations are shown in Fig. 2. Here, ΔE_x is the energy difference between the ground state and the first excited state of motion in the x direction. Similarly, the differences for the y and z directions are denoted by ΔE_y and ΔE_z, respectively. The results show that ΔE_x increases with increasing F_{ij}, whereas both ΔE_y and ΔE_z decrease. Shibata and Ikeda [12] performed inelastic neutron-scattering measurements on KDP, observing vibration modes in the x direction at 28 and 160 meV as well as on the plane perpendicular to the x direction at 125 and 160 meV. At $F_{ij}d=1.5$ eV, we can show that $\Delta E_x=0.16$, $\Delta E_y=0.12$, and $\Delta E_z=0.16$ eV. These results agree well with their experimental results if the mode observed at 28 meV is one coupled with PO_4 tetrahedrons. Accordingly, we shall use below the following potential parameters: $f=0.2$ eV, $g=1.2$ eV, $\varepsilon=2.0$ eV, $a=3.0$ Å^{-1}, and $r_0=0.98$ Å.

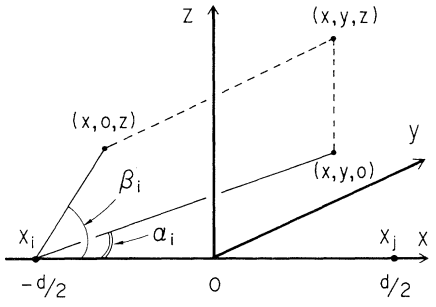

FIG. 1. The coordination axes used here.

In Figs. 3(a) and 3(b) are shown profiles of the potential wave functions for a proton along the x direction at $F_{ij}d=0$ and $F_{ij}d=1.5$ eV, respectively. At $F_{ij}d=0$, the potential has a hump at the bottom of the broad potential well. However, the wave function for the ground state extends over the broad potential well and the maximum of its amplitude is located at the center of the oxygen-oxygen distance. At $F_{ij}d=1.5$ eV, the ground-state wave function is strongly localized on one of the two potential minima, which is deepened by the asymmetric term F_{ij}. The maximum of its amplitude is at about 0.18 Å from the center, which is in good agreement with the experimental result obtained from a neutron-diffraction measurement [13]. We emphasize here that there is no tunneling motion in our potential model.

The F_{ij} dependences of the ground-state energy E_{ij}^0 for KDP and DKDP are shown in Fig. 4. E_{ij}^0 can be reproduced by the function

$$E_{ij}^0 = (h^2+I^2F_{ij}^2)^{1/2} - h, \tag{4}$$

with $h=0.110$ eV and $I=0.222$ Å for KDP, and with $h=0.058$ eV and $I=0.225$ Å for DKDP, respectively.

In order to proceed, we assume the following relation:

$$F_{ij} = K(\mu_i+\mu_j). \tag{5}$$

Furthermore, we adopt a mean-field approximation for the dipole-dipole interaction. This approximation is expected to be valid for an interaction with a long-range character. By introducing the averaged interaction constant (D) and the order parameter of the system ($\bar{\mu}$) we can replace Eq. (1) with

$$E_{\text{tot}} = \frac{A}{2}\sum_{i=1}^{N}\mu_i^2 + \frac{D}{2}\bar{\mu}\sum_{i}^{N}\mu_i - \sum_{\langle ij\rangle}^{2N}\{[h^2+I^2K^2(\mu_i+\mu_j)^2]^{1/2}-h\}. \tag{6}$$

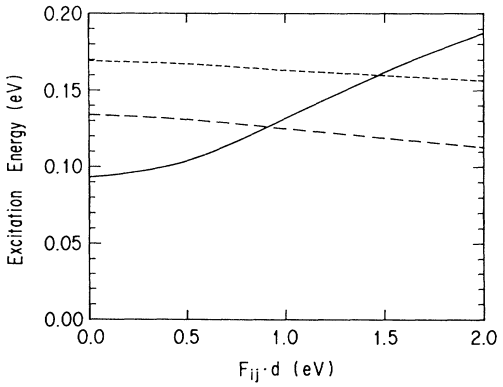

FIG. 2. Variation of the excitation energies of a proton with the asymmetric parameter F_{ij}. ΔE_x, ΔE_y, and ΔE_z are denoted by solid, long-dashed, and dashed lines, respectively.

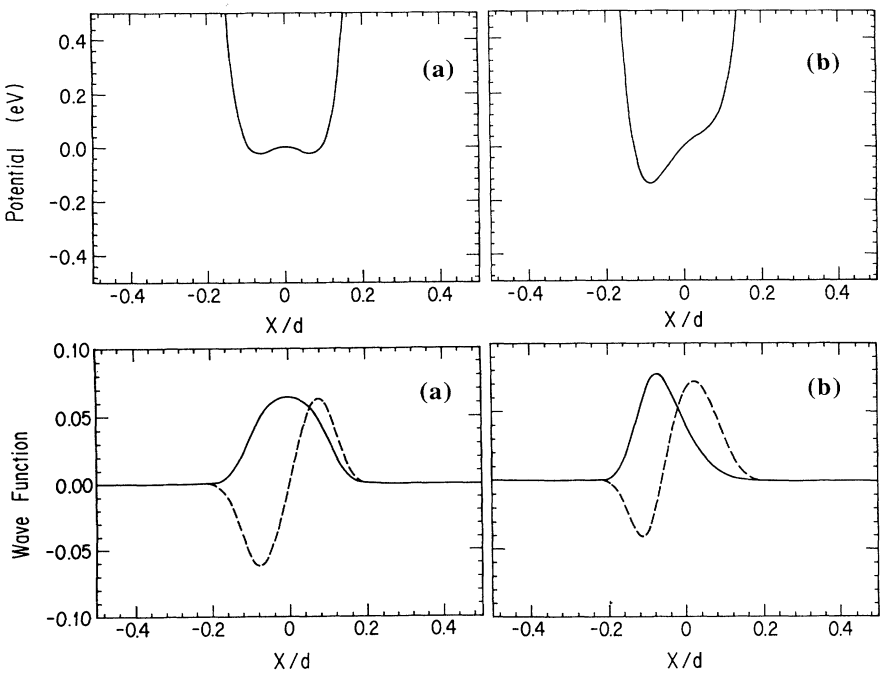

FIG. 3. Profiles of the potential and wave functions of a proton along the x direction (a) at $F_{ij}d=0$ and (b) at $F_{ij}d=1.5$ eV. The wave functions of the ground and first excited states are shown by solid and dashed lines, respectively.

The order parameter ($\bar{\mu}$) can be obtained from the self-consistent condition $\bar{\mu}=\langle\mu_i\rangle$, where the thermal average $\langle\cdots\rangle$ is defined by

$$\langle X\rangle=\frac{\int d\mu_1\cdots\int d\mu_N[X\exp(-E_{\rm tot}/kT)]}{\int d\mu_1\cdots\int d\mu_N[\exp(-E_{\rm tot}/kT)]}. \quad (7)$$

Note that Eq. (6) is equivalent to that derived by Kojyo and Onodera [14] for CsH_2PO_4 and CsD_2PO_4, except for its dimensionality.

First, let us examine the isotope effects of the saturated polarization (P_s) by using Eq. (6). Since $\mu_i=\mu_s$ holds for all tetrahedrons at $T=0$ K, $E_{\rm tot}$ can be written as

$$E_{\rm tot}=N\{\tfrac{1}{2}(A+D)\mu_s^2-2([h^2+(2IK\mu_s)^2]^{1/2}-h)\}. \quad (8)$$

Considering that μ_s is determined by the condition $\partial E_{\rm tot}/\partial\mu_s=0$, the saturated polarization, $P_s=N\mu_s$, is given by

$$P_s=(N/2IK)\{[2(2IK)^2/(A+D)]^2-h^2\}^{1/2}. \quad (9)$$

By using $P_s=5.0$ μC/cm^2 (the observed value of P_s in KDP), $h=0.110$ eV, $I=0.222$ Å, and $F_{ij}d=1.5$ eV, one can easily estimate $K=6.2\times10^{28}$ eV/μCcm^2 and $A+D=8.7\times10^{41}$ eV/(μCcm)^2. Since K, A, and D are expected to be identical in both KDP and DKDP, the saturated polarization in DKDP can be calculated from Eq. (9), with $h=0.058$ eV and $I=0.225$ Å. The calculated value for DKDP is 6.3 μC/cm^2. This agrees well with the value of 6.2 μC/cm^2 observed by Samara [15].

Next, let us estimate the isotope effect on T_c. We must note here that the lowest excitation energies at $F_{ij}=K(\mu_i+\mu_j)=0$ are 0.08 eV in KDP and 0.05 eV in DKDP, respectively. This means that there is no increase in the entropy of the system when $\mu_i(i=1,\ldots,N)=0$, because the excitation energies are sufficiently larger than the thermal energy at $T\sim T_c$. Accordingly, a transition of the displacive type is impossible in our model.

In order to calculate T_c, we must determine $\bar{\mu}$ self-consistently using Eqs. (6) and (7); this is difficult to do exactly. We therefore assume here that $\mu_i=\mu_s S_i$ ($S_i=1$ or -1 for all i). Under this assumption, $E_{\rm tot}$ can be rewritten as an Ising-type expression,

$$E_{\rm tot}=\frac{D}{2}\mu_s^2\bar{S}\sum_{i=1}^{N}S_i-J\sum_{\langle ij\rangle}^{2N}S_iS_j+E_0', \quad (10)$$

where $\bar{S}=\langle S_i\rangle$ and $J=\frac{1}{2}\{[h^2+(2IK\mu_s)^2]^{1/2}-h\}$. The values of J can be calculated with the estimated values of h, I, K, and μ_s, which were obtained in the above discussion. The calculated values on KDP and DKDP are $J=0.031$ and 0.060 eV, respectively. For simplicity, we again adopt a mean-field approximation for the nearest-neighbor interaction term (the second term). In this approximation, the transition temperature (T_c) is given by

$$T_c=(2J-\tfrac{1}{2}D\mu_s^2)/k_B. \quad (11)$$

By using J, μ_s, and the observed transition temperature in KDP ($T_c=122$ K), the value of D can be determined from Eq. (11): $D=4.42\times10^{41}$ eV/(μCcm)^2. Using this value of D, T_c in DKDP can be calculated. The result is $T_c=458$ K. This value is higher than the observed one of $T_c=213$ K. The origin of this disagreement seems to be

TABLE I. Values of h (eV), I (Å), K (10^{28} eV/μCcm^2), A [10^{41} eV/(μCcm)^2], D [10^{41} eV/(μCcm)^2], P_s (μC/cm^2), J (eV), and T_c (K) determined from the F_{ij} dependence of E_{ij}^0 obtained using the potential parameters $f=0.2$ eV, $g=1.2$ eV, $\varepsilon=2.0$ eV, $a=3.0$ Å^{-1}, and $r_0=0.98$ Å. Asterisks indicate the experimental values for KDP, which were used to fix the values of K, A, and D. The entries in parentheses indicate the experimental values for DKDP. The unit of d is Å.

	d	h	I	K	A	D	P_s	J	T_c
KDP	2.50*	0.110	0.22	6.2	4.28	4.42	5.0*	0.031	122*
DKDP	2.52	0.058	0.225	6.2	4.28	4.42	6.3	0.060	458
	2.50	0.073	0.215	6.2	4.28	4.42	5.7	0.045	275
	(2.52)						(6.2)		(213)

due to the mean-field approximation and/or the assumption $\mu_i=\mu_s S_i$. More rigorous treatments of Eqs. (6) and (7) are required to confirm the reliability of the present model. However, we emphasize here that the large isotope effect on T_c can be directly derived from our model.

In order to examine the geometrical isotope effect, we again performed similar calculations on DKDP assuming $d=2.50$ Å (which is equal to the value of d in KDP) and obtained $P_s=5.7$ μC/cm^2 and $T_c=275$ K. This result indicates that a change in d gives an important contribution to a change in T_c, and, accordingly, that the geometrical isotope effect is exactly realized in our model. We note here that this enormous change in T_c mainly comes from the change of h: The value of h at $d=2.50$ Å is larger than that at $d=2.52$ Å by about 20%. From the property of the potential function $V(r)$ adopted here, the depth and the form of the potential $U(r)$ produced by $V(r)$ strongly depend on d. At $d\sim2.5$ Å, particularly, $U(r)$ at $F_{ij}=0$ has a hump at the center of the oxygen-oxygen distance [see Fig. 3(a)], and its height ΔU varies from ~0.04 to ~0.02 eV by the decrease of d from 2.52 to 2.50 Å. The decrease in ΔU gives rise to a decrease in the zero-point energy at $F_{ij}\sim0$. The increase of h for a deuteron denoted above is mainly induced by this effect. The enormous increase in T_c by the modest change of d reflects the property of $U(r)$ at $d\sim2.5$ Å. The parameters used in the above discussion and the results obtained are summarized in Table I.

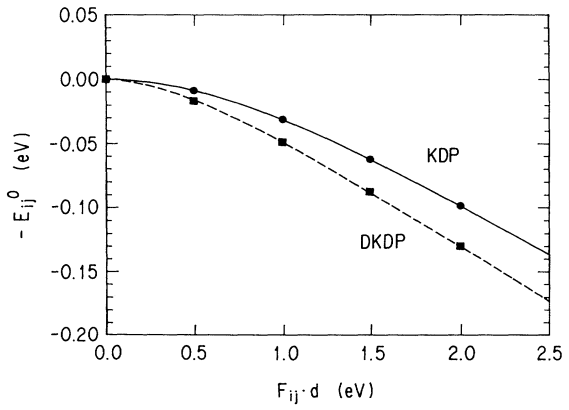

FIG. 4. Variation of the ground-state energy (E_{ij}^0) with F_{ij}. The calculated values for KDP and DKDP are shown by ● and ■, respectively. The curves are the best fits by Eq. (4).

Finally, we emphasize that the isotope dependence of E_{ij}^0 (as shown in Fig. 4) gives rise to isotope effects for P_s and T_c. The isotope dependence of E_{ij}^0 is caused by the dependence of h on d and the mass (see Table I). This indicates that the physical origin of the isotope dependence of E_{ij}^0 obtained here is mainly ascribable to the isotope dependence of a change in the zero-point energy due to the interaction between a proton (deuteron) and dipole moments of PO_4 tetrahedrons.

In our model, no tunneling motion is assumed. Accordingly, our results strongly suggest that the properties of hydrogen-bonded crystals, which have been believed to be due to tunneling motion, should be reexamined on the basis of the present treatment.

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