PHYSICAL REVIEW B VOLUME 50, NUMBER 22 1 DECEMBER 1994-II

Isotope effects in KH_2PO_4-type crystals

Satoshi Tanaka
Department of Physics, Kinki University, Kowakae 3-4-1, Higashi-Osaka, Osaka, 577, Japan

(Received 22 June 1994)

A number of isotope effects can be seen in some hydrogen-bonded crystals as deuterium atoms are substituted for hydrogen atoms. In KH_2PO_4-type crystals in particular, a rise in the ferroelectric transition temperature, an increase in spontaneous polarization, and an expansion of the hydrogen-bonded distance can be seen. The mechanism behind these isotope effects is explained theoretically by introducing a relation form between the hydrogen-bonded distance and distortions of PO_4 ions without reference to proton tunneling.

I. INTRODUCTION

In some hydrogen-bonded crystals such as tetragonal KH_2PO_4-type crystals (hereafter referred to as KDP-type crystals), remarkable isotope effects are exhibited on the ferroelectric transition temperature T_C, the spontaneous polarization P_S, and the pressure dependence of T_C (dT_C/dP) by substituting hydrogen atoms for deuterium atoms.[1-4]

Recently, Ichikawa and co-workers[5-9] proposed some empirical relations after analyzing some recent data from x-ray and neutron-diffraction experiments of KDP-type crystals. These relations can be outlined as follows:

(i) There exists a correlation, known as the geometric isotope effect, between R_H and $\Delta R(=R_D-R_H)$, where R_H denotes the O-O distance of the hydrogen bond (O-H-O) and R_D that of deuterium bond (O-D-O). The expansion of ΔR upon deuteration is about 2.44–2.64 Å for R_H with a maximum value of 0.027 Å.

(ii) There exists a strong correlation

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

between O-O distance R (in units of Å) and the ferroelectric transition temperature T_C (in units of K). This relationship holds irrespective of whether the crystals are hydrogenated or deuterated. Nelmes[10] has recently improved the relation (1) a little by analyzing the data more accurately.

From a judgment based on these empirical relations, Ichikawa has pointed out that the appearance of the remarkable isotope effects concerning T_C, P_S, and the like originates not in the proton tunneling motion but in the geometric isotope effect.

Recently, Sugimoto and Ikeda[11] have calculated energies and wave functions for a proton in KDP (or a deuteron in DKDP). In this model, as a potential acting on the proton, an asymmetric potential $F_{i,j}d$ induced by distortions of PO_4 ions has been considered in addition to a potential (double-Morse potential) between two oxygens and a proton. It has been shown that the ground-state wave function is localized on one of the two potential minima when $F_{i,j}d=1.5$ eV and a saturated polarization in DKDP crystals, which is calculated by using the observed value of that in KDP crystals, agrees well with the observed value by Samara.[12] Furthermore, Sugimoto *et al.* have estimated the ferroelectric transition temperature T_C for DKDP in order to examine the geometric isotope effect and obtained $T_C=458$ K at the O-O distance $d=2.52$ Å and $T_C=275$ K at $d=2.5$ Å (the observed value for DKDP is $T_C=213$ K). Sugimoto *et al.* have concluded that the geometric isotope effect gives an important contribution to a change in T_C and is caused by a difference in the zero-point energies of proton and deuteron.

In a previous paper,[13] we noticed the geometric isotope effect and explained the mechanism behind it. Anharmonic vibrations of proton [or deuteron, hereafter referred to as the H(D) ion] in a one-dimensional hydrogen-bonded crystal have been studied on the basis of the quantum-mechanical self-consistent Einstein model without reference to the proton tunneling motions. The cause of the geometric isotope effect has been shown to be the difference in anharmonic fluctuations (zero-point vibrations) of proton and deuteron under double-minima potential conditions. This agrees, in principle, with the conclusion of Sugimoto and Ikeda.[11] The mechanism behind this geometric isotope effect is described by the following phenomena:

(i) When the potential acting on a H(D) ion is of the double-minima type, the density of H(D) ion near the center of the hydrogen bond [or deuterium bond, hereafter referred to as the H(D) bond] attracts both oxygen atoms strongly, thus resulting in a shortening of the O-O distance. This shortened O-O distance yields a lower potential barrier and increases the density near the center.

(ii) When the O-O distance is sufficiently large, the vibration levels of the H(D) ion drop below the potential barrier, and the density becomes low at the center of the H(D) bond. Consequently, the H(D) ion near the center does not attract the oxygens very much. At a suitable O-O distance, the lowest level of proton approaches the top of the potential barrier, but that of deuteron still lies below this barrier. As a result, the proton density near the center becomes remarkably high compared to that of deuteron. Consequently, the O-O distance of the hydrogen bond becomes shorter than that of the deuterium bond, and the geometric isotope effect is exhibited remarkably.

As a second step, it should be possible to reveal a relationship between the geometric isotope effect and the remarkable isotope effects concerning T_C, P_S, and the like. The purpose of this paper is, theoretically, to clarify the mechanism behind the relationship of the base of the idea in the previous paper. In order to reveal this relationship, we introduce a model in Sec. II, where we will propose a relation form between the O-O distance and the distortions of PO_4 ions accompanied with the dipole moments of K-PO_4. In Sec. III, the theoretical results developed in Sec. II are analyzed numerically and graphically.

II. MODEL

In order to reveal the relationship, it is important to consider an interaction form between the O-O distance and dipole of K-PO_4. Sugimoto *et al.*, as mentioned above, have proposed an asymmetric potential $F_{i,j}d$ as this interaction form. To date, however, a mechanism of this interaction has not yet been made clear. Then, we consider the mechanism as follows: (i) At a suitable hydrogen-bonded distance, the deuterium-bonded distance expands by substituting hydrogen atoms for deuterium atoms. This fact has been already shown in the previous paper. (ii) An expansion of the O-O distance causes larger distortions of two tetrahedral PO_4 ions at both ends of H(D) bond. An appearance of dipole moment of K-PO_4 originates in the distortion in the PO_4 ion. (iii) Consequently, by this substitution, the distortions of PO_4 ions (or dipole moments of K-PO_4) in deuterium-bonded crystals becomes larger than that of hydrogen-bonded crystals. As the result, it is expected that the ferroelectric transition temperature T_C and the spontaneous polarization P_S rises on deuteration and remarkable isotope effects appear.

We assume that the distortion of a tetrahedral PO_4 ion takes only two states $\sigma=1$ and -1 and the interaction form between the O-O distance and the distortions of PO_4 ions at both ends is represented as follows:

$$R_{j,j+\rho}=R_0+C\sigma_j\sigma_{j+\rho}\ , \tag{2}$$

where σ_j denotes the state of the distortion of jth PO_4 ion, then it also gives the state of the dipole moment of jth K-PO_4. $R_{j,j+\rho}$ is the O-O distance between neighboring jth and $(j+\rho)$th PO_4 ions ($\rho=1\cdots4$). When a system is in the paraelectric phase (that is, when thermal-averaged value $\langle\sigma\rangle$ is equal to zero), the O-O distance comes to R_0. We assume the parameter C to be positive. This means the O-O distance expands when the system is in the ferroelectric phase ($\langle\sigma\rangle\neq0$).

The O-O distance can also be closely related with the interaction energy between a H(D) ion and two oxygen atoms at both ends on the H(D) bond. In a previous paper,[13] this interaction energy was given by double Morse-type potentials. In this paper, instead of the double Morse-type potentials, we introduce the following simple type potential:

$$V_{j,j+\rho}=-a(R_{j,j+\rho}-R_C)x_{j,j+\rho}^2+bx_{j,j+\rho}^4 \tag{3}$$

as a potential acting on a H(D) ion along the H(D) bond between neighboring jth and $(j+\rho)$th PO_4 ions. The $x_{j,j+\rho}$ denotes the position of the H(D) ion from the center of the H(D) bond between jth and $(j+\rho)$th PO_4 ions. We call it H(D)'s position hereafter. We assume the parameters a and b to be positive. The potential $V_{j,j+\rho}$ is of a double-minima type when $R_{j,j+\rho}$ is larger than a critical length R_C. On the contrary, when $R_{j,j+\rho}<R_C$, the potential is of a single-minimum type.

Additionally, at this point, we introduce a term $J_0\sigma_j\sigma_{j+\rho}$ which represents an ordinary dipole-dipole interaction of the order-disorder type between dipole moments of neighboring jth and $(j+\rho)$th K-PO_4, where J_0 is a magnitude of the dipole-dipole interaction.

The total Hamiltonian H of the system constituted with N molecules of $KH(D)_2PO_4$ can be expressed as

$$H=H_\sigma+H_{x,\sigma}\ , \tag{4}$$

where

$$H_\sigma=-\frac{1}{2}\sum_{j=1}^{N}\left\{\sum_{\rho=1}^{4}J_0\sigma_j\sigma_{j+\rho}+h_e\sigma_j\right\} \tag{5}$$

and

$$H_{x,\sigma}=\frac{1}{2}\sum_{j=1}^{N}\sum_{\rho=1}^{4}\left\{\frac{p_{j,j+\rho}^2}{2m}+V_{j,j+\rho}\right\} \tag{6}$$

and by placing Eq. (2) into Eq. (3), one obtains

$$V_{j,j+\rho}=-a(R_0+C\sigma_j\sigma_{j+\rho}-R_C)x_{j,j+\rho}^2+bx_{j,j+\rho}^4\ . \tag{7}$$

The parameter h_e represents the external electric field applied to the dipole moment of jth K-PO_4 and p and m are the momentum and mass of the H(D) ion, respectively. Equation (7) includes an interaction between the H(D) ion and the distortions of two neighboring PO_4 ions. This is significant for an appearance of the isotope effects.

Let us analyze the Hamiltonian of Eq. (4) with Eqs. (5), (6), and (7) systematically and approximately by the use of a variational principle method. In order to execute this method, we define a trial Hamiltonian H_0:

$$H_0=-\sum_{j=1}^{N}K\sigma_j+\frac{1}{2}\sum_{j=1}^{N}\sum_{\rho=1}^{4}\left\{\frac{p_{j,j+\rho}^2}{2m}+\frac{m\omega^2}{2}\delta x_{j,j+\rho}^2\right\}\ , \tag{8}$$

where $\delta x_{j,j+\rho}$ is the vibrational displacement, along the H(D) bond between jth and $(j+\rho)$th PO_4 ions, about the equilibrium H(D)'s position $\langle x_{j,j+\rho}\rangle=\langle x\rangle$, namely,

$$\delta x_{j,j+\rho}=x_{j,j+\rho}-\langle x\rangle\ , \tag{9}$$

and the bracket $\langle\cdots\rangle$ represents the thermal average defined by

$$\langle\cdots\rangle=\frac{\mathrm{Tr}\{\cdots\exp(-\beta H_0)\}}{\mathrm{Tr}\{\exp(-\beta H_0)\}}\ . \tag{10}$$

The parameters K and ω in Eq. (8) are the trial mean-field exerted on the PO_4 ion and the trial Einstein frequency of the H(D) ion, respectively. These trial parameters are determined by minimizing the trial free energy:

$$F_t=\langle H\rangle-\langle H_0\rangle-\beta^{-1}\ln[\mathrm{Tr}\{\exp(-\beta H_0)\}] \tag{11}$$

with respect to K and ω. The result yields two following self-consistent equations:

$$K=4\langle\sigma\rangle\{J_0+aC(\langle x\rangle^2+\langle\delta x^2\rangle)\}+h_e \tag{12}$$

and

$$\frac{m\omega^2}{2}=-a(R_0-R_C)+6b(\langle x\rangle^2+\langle\delta x^2\rangle)-aC\langle\sigma\rangle^2\ , \tag{13}$$

where $\langle\sigma\rangle$ is nothing less than an order parameter of the ferroelectric transition and $\langle\delta x^2\rangle$ gives the mean-square vibrational amplitude of the H(D) ion. These are specifically represented in terms of K and ω as follows:

$$\langle\sigma\rangle=\tanh(\beta K) \tag{14}$$

and

$$\langle\delta x^2\rangle=\frac{\hbar}{2m\omega}\coth\left[\frac{\beta\hbar\omega}{2}\right]\ . \tag{15}$$

By the use of self-consistent Eqs. (12) and (13) with Eqs. (14) and (15), the parameters K, ω, $\langle\delta x^2\rangle$, and $\langle\sigma\rangle$ can be expressed as functions of $\langle x\rangle$ and temperature T. Next, by placing the parameters K, ω, $\langle\delta x^2\rangle$, and $\langle\sigma\rangle$, represented in terms of variables $\langle x\rangle$ and T, into F_t [Eq. (11)], one can obtain a free energy $F=F(\langle x\rangle,T)$. We consider a case of zero-pressure hereafter. The thermal-averaged H(D)'s position $\langle x\rangle$ at zero-pressure can be determined to make the free energy $F(\langle x\rangle,T)$ minimum with respect to $\langle x\rangle$. The minimization

$$\left.\frac{\partial F}{\partial\langle x\rangle}\right]_T=0\Longrightarrow$$

yields

$$\langle x\rangle^2=0 \text{ or } \{a(R_0-R_C)+aC\langle\sigma\rangle^2-6b\langle\delta x^2\rangle\}/2b\ . \tag{16}$$

From Eqs. (12)–(16), finally, the mean field K, the frequency ω, the mean-square amplitude $\langle\delta x^2\rangle$, the order parameter $\langle\sigma\rangle$, and the equilibrium H(D)'s position $\langle x\rangle$ are determined as a function of temperature T. The equilibrium O-O distance $\langle R\rangle$ is also determined by

$$\langle R\rangle=R_0+C\langle\sigma\rangle^2\ . \tag{17}$$

Additionally, a Gibbs free energy $G(T)$, which is equivalent to $F(\langle x\rangle,T)$ at zero pressure, is also written as

$$\begin{aligned}G(T)/N=&2\{J_0+aC(\langle x\rangle^2+2\langle\delta x^2\rangle)\}\langle\sigma\rangle^2\\&+2b\langle x\rangle^4-2a(R_0-R_C)\langle x\rangle^2-6b\langle\delta x^2\rangle^2\\&-\beta^{-1}\ln\{2\cosh(\beta K)\}\\&+2\beta^{-1}\ln\{2\sinh(\beta\hbar\omega/2)\}\ .\end{aligned} \tag{18}$$

Now, we assume the potential acting on the H(D) ion [H(D)'s potential] to be the double-minima type even if the system is in a paraelectric phase ($\langle\sigma\rangle=0$), namely, considering the case of $R_0>R_C$ [see Eq. (7)]. Hereafter, in addition, we discuss the case of the zero external field $h_e=0$.

In order to perform numerical analyses in the next section, we introduce the following parameters:

$$x_0^2=\frac{aR_C}{2b}\ ,\quad \varepsilon_0=\frac{a^2R_C^2}{4b}\ ,\quad \text{and } \omega_0^2=\frac{4aR_C}{m} \tag{19}$$

and furthermore, reduced parameters:

$$t=\frac{1}{\beta\varepsilon_0}\ ,\quad Q=\frac{\hbar\omega_0}{2\varepsilon_0}\ ,\quad \xi_0=\frac{R_0-R_C}{R_C}\ ,\quad S=\langle\sigma\rangle\ ,\quad \alpha=\frac{C}{R_C}$$

and

$$\gamma=\frac{J_0}{\varepsilon_0}\ . \tag{20}$$

The H(D)'s potential of the double-minima type in a paraelectric phase, expressed by replacing $R_{j,j+\rho}$ with R_0 in Eq. (3), has a minimum value $-\varepsilon_1=-\varepsilon_0\xi_0^2$ at positions $x_1=\pm s_0\sqrt{\xi_0}$ as is clear from the relation:

$$-a(R_0-R_C)x^2+bx^4=\varepsilon_1\{-2(x/x_1)^2+(x/x_1)^4\}$$

when $R_0>R_C$. Then, the relation $m\omega_0^2x_0^2=8\varepsilon_0$ holds among x_0, ε_0, and ω_0, where ω_0 gives harmonic vibrational frequency about the position x_1.

It should be noted that a parameter Q, which represents quantum-effect magnitude of the H(D) ion, originates not in the tunneling motion of the H(D) ion but in the quantum vibration (such as zero-point energy $\hbar\omega_0/2$) of the H(D) ion. The formulas above [Eqs. (12)–(18)] are finally summarized as follows:

(i) O-O distance:

$$\frac{\langle R\rangle-R_C}{R_C}\equiv\xi=\xi_0+\alpha S^2\ . \tag{21}$$

(ii) H(D)'s position:

$$\frac{\langle x\rangle^2}{x_0^2}\equiv\left[\frac{\delta}{2}\right]^2=0 \text{ or } \xi_0-3\lambda+\alpha S^2\ , \tag{22}$$

where δ is defined as the distance between the two equilibrium sites of a H(D) ion on the H(D) bond.

(iii) Fluctuation of H(D) ion:

$$\frac{\langle\delta x^2\rangle}{x_0^2}\equiv\lambda=\frac{Q\coth(QW/t)}{8W}\ . \tag{23}$$

(iv) Frequency of H(D) ion:

$$\frac{\omega^2}{\omega_0^2}\equiv W^2=\frac{3(\delta^2+4\lambda)}{8}-\frac{\xi_0}{2}-\frac{\alpha S^2}{2}\ . \tag{24}$$

(v) Order parameter:

$$\langle\sigma\rangle\equiv S=\tanh(4\eta^2S/t)\ , \tag{25}$$

where

$$\eta^2=\gamma+\frac{\alpha(\delta^2+4\lambda)}{2}\ . \tag{26}$$

The second term of right-hand side in Eq. (26) represents an indirect dipole-dipole interaction added to the direct one γ and is due to an effect of the vibrational motion of the H(D) ion upon the distortions of two neighboring PO_4 ions. Then, the value of $\eta S(\equiv\mu)$ means an averaged magnitude of the dipole moment of K-PO_4 at zero external field.

(vi) Gibbs free energy:

$$\begin{aligned}\frac{G(T)}{N\varepsilon_0}&\equiv g(t)\\&=2\{\gamma+\alpha(\delta^2+4\lambda)/2\}S^2+\delta^4/8-\xi_0\delta^2-6\lambda^2\\&\quad-t\ln\{2\cosh(4\eta S/t)\}+2t\ln\{2\sinh(QW/t)\}\ .\end{aligned}\tag{27}$$

Equation (22) shows that there are two types of H(D) positions. One is $\delta=0$, which means a peak of H(D) ion distribution to be on the center of H(D) bond, hereafter, called a symmetric phase. Another is $\delta>0$, which means the peak to be displaced from the center of H(D) bond, hereafter, called an asymmetric phase. Additionally, as is clear in Eq. (25), there exist two types of solutions: paraelectric phase $S=0$ and ferroelectric phase $S>0$. Therefore, the system is divided into four phases:

(a) $\delta=0;S=0$, (b) $\delta=0;S>0$, (c) $\delta>0;S=0$,

(d) $\delta>0;S>0$.

From Eq. (27), then, we can get four "Gibbs energies:"

(a) $g(\delta=0;S=0)$, (b) $g(\delta=0;S>0)$,

(c) $g(\delta>0;S=0)$, (d) $g(\delta>0;S>0)$

corresponding to the four phases above, respectively. Consequently, the phase which has the most minimal "Gibbs energy" among the four gives the final state of the system. In the next section, the theoretical results developed in this section are analyzed numerically and graphically.

III. NUMERICAL ANALYSES

A. Phase diagrams of t vs Q and t vs ξ_0

In order to study upon what conditions each phase mentioned above appears, at first, it is convenient to consider phase diagrams of t vs Q and t vs ξ_0; these are shown in Figs. 1 and 2, respectively. The solid line represents the first-order transition curve (the transition temperature is defined by $T_{C\delta}$), which produces two regions corresponding to the symmetric phase ($\delta=0$) and the asymmetric phase ($\delta>0$). Hereafter this transition is referred to as a symmetric transition. Furthermore, each phase is divided into the ferroelectric phase ($S>0$) and the paraelectric phase ($S=0$) by the broken line, representing the second-order transition curve (the transition temperature is defined by T_{CS}). Hereafter this transition is referred to as a ferroelectric transition.

B. Symmetric transition

The symmetric transition temperature $T_{C\delta}$ (solid lines) goes down according as the quantum-effect magnitude Q increases as shown in Fig. 1 (or the O-O distance R_0 for the paraelectric phase shortens as shown in Fig. 2) and finally comes up to zero at a certain value $Q=Q_C$ (or a certain length $R_0=R_{0C}$, corresponding to $\xi_0=\xi_{0C}$). Especially, as is seen in Fig. 2, a linear relation holds between $T_{C\delta}$ and R_0 except for neighborhood of R_{0C}. This fact, by the extrapolation from the previous paper[13] (in which the geometric isotope effect has been discussed for double-Morse potential at absolute zero temperature), may be explained as follows.

If Q is small enough (or R_0 is sufficiently large) and the temperature is sufficiently low compared with $T_{C\delta}$, namely, the system is in the asymmetric phase ($\delta>0$), then the

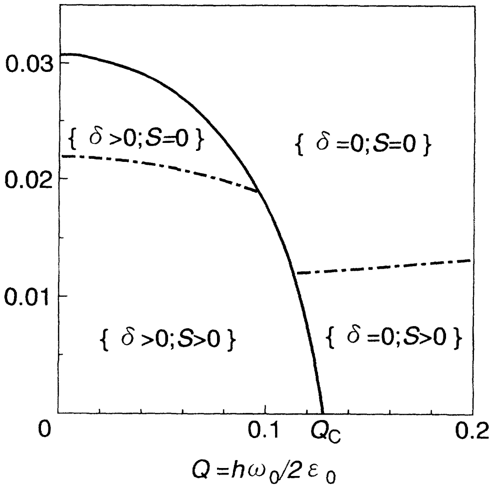

FIG. 1. The phase diagram of t vs Q at $\xi_0=0.25$, $\alpha=0.01$, and $\gamma=0.001$. In the middle narrow region of Q, the ferroelectric transition of the first order appears between the phases $\{\delta>0;S>0\}$ and $\{\delta=0;S=0\}$.

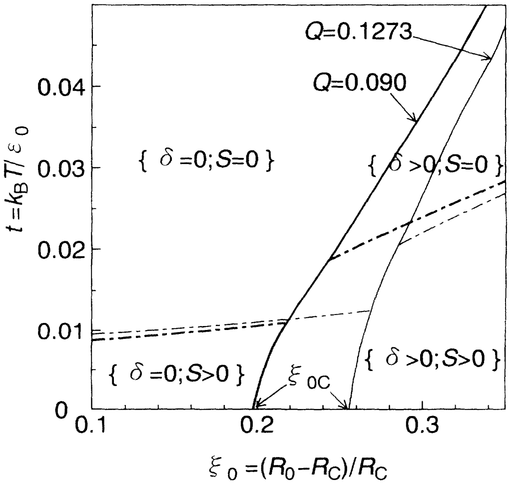

FIG. 2. The phase diagrams of t vs ξ_0 at $\alpha=0.01$ and $\gamma=0.001$. The group of the regions separated by the thick lines shows the phase diagram for $Q=0.090$ and the fine lines for $Q=0.1273$. If Q for proton is $Q_H=0.1273$, then that of deuteron is $Q_D=Q_H/\sqrt{2}=0.090$.

peak of the H(D) ion distribution locates at one of two equilibrium sites in the double-minima-type potential. The vibration energy levels of the H(D) ion lie below the potential barrier, so that the H(D) ion has a small fluctuation as shown in Figs. 3(a) and 3(b) and a high frequency as shown in Figs. 4(a) and 4(b). Consequently, it is expected that high $T_{C\delta}$ is exhibited for sufficiently small Q (or for sufficiently large R_0).

Accordingly as Q increases (or R_0 grows shorter), the peak of the H(D) ion distribution approaches the center of the H(D) bond, the fluctuation becomes large slowly and the frequency becomes low slowly. The $T_{C\delta}$ goes down with the increase in Q (or the shortening of R_0).

Finally, when the Q reaches the certain value Q_C or goes across it (or R_0 reaches the certain value R_{0C} or becomes shorter than it), the peak of the H(D) ion distribution stands on the center of the H(D) bond. The system changes from the asymmetric phase ($\delta > 0$) into the symmetric phase ($\delta = 0$). The H(D) ion has the large fluctuation and the low frequency [corresponding to the case of $Q = 0.1273$ in Figs. 3(a) and 4(a)], because the H(D) ion vibrates about both equilibrium sites in the double-minima-type potential.

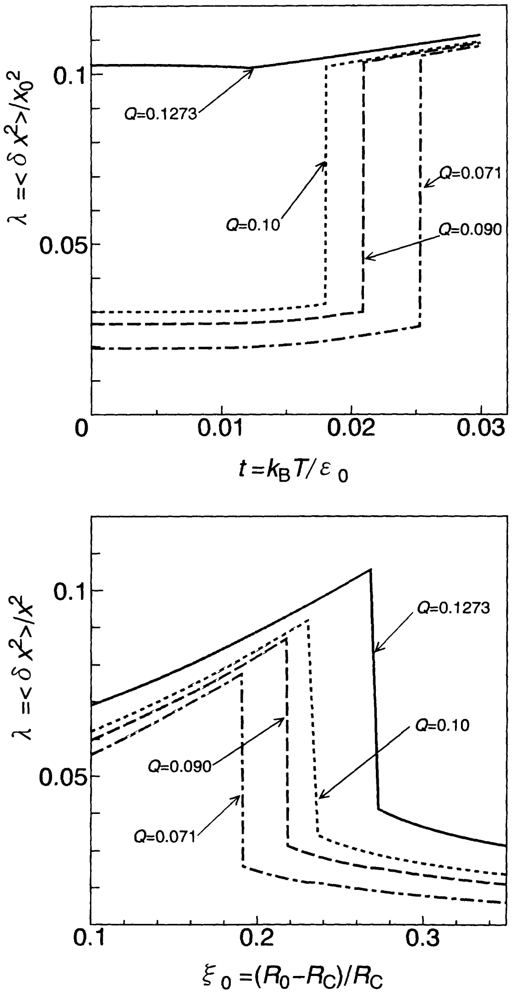

FIG. 3. (a) The temperature dependences of the fluctuations λ's of the H(D) ion for various values of Q at $\xi_0 = 0.25$, $\alpha = 0.01$, and $\gamma = 0.001$. When the $Q_H = 0.1273$ (or $= 0.10$), the $Q_D = 0.090$ (or $= 0.071$). The nonzero values of λ's at absolute zero temperature arise from the zero-point vibrations of the H(D) ion. The large gap in the curve λ appears at $T = T_{C\delta}$. (b) The dependences of the fluctuations λ's of the H(D) ion on the R_0 for the various values of Q at $t = 0.01$, $\alpha = 0.01$, and $\gamma = 0.001$. The large gap in curve λ appears at $R_0 = R_{0C}$ (or $\xi_0 = \xi_{0C}$).

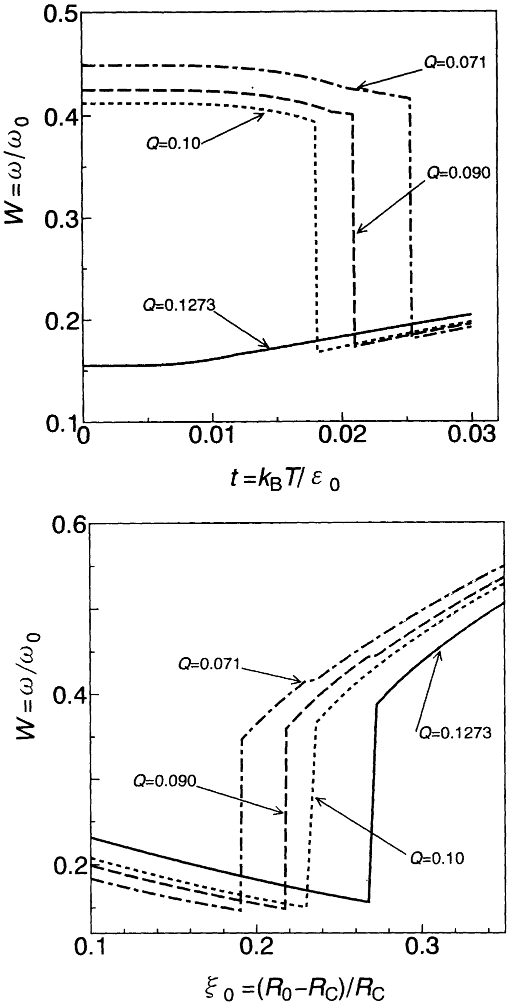

FIG. 4. (a) The temperature dependences of the frequencies ω's of the H(D) ion for various values of Q at $\xi_0 = 0.25$, $\alpha = 0.01$, and $\gamma = 0.001$. (b) The dependences of the frequencies ω's of the H(D) ion on the R_0 for various values of Q at $\xi_0 = 0.25$, $\alpha = 0.01$, and $\gamma = 0.001$.

C. Ferroelectric transitions

As is also seen in Figs. 1 and 2, in the symmetric phase ($\delta = 0$), the ferroelectric transition temperature T_{CS} increases accordingly as Q increases (or R_0 grows longer). Contrary to this, in the asymmetric phase ($\delta > 0$), T_{CS} decreases accordingly as Q increases but increases accordingly as R_0 extends. The T_{CS} in the asymmetric phase is considerably high compared with that in the symmetric one. Especially, as is seen in Fig. 2, the result that a linear relation holds between T_{CS} and R_0, whether the system is in the symmetric or the asymmetric phase, suggests an appearance of correlation between the O-O distance and the ferroelectric transition temperature. This fact is interpreted as follows.

For the symmetric phase ($\delta=0$), as is clear from Eq. (26), parameter η depends only on the fluctuation λ (the parameters γ and α are fixed) and increases with λ, furthermore λ increases accordingly with an increase in Q (or an extension to R_0) as shown in Figs. 3(a) and 3(b). Consequently, the η increases accordingly as Q increases (or R_0 extends) in the symmetric phase. An increase in η yields a larger distortion of the PO_4 ion (or larger dipole moment of $K\text{-}PO_4$).

On the other hand, for the antisymmetric phase ($\delta>0$), the fluctuation λ is sufficiently small, the parameter η depends remarkably on δ rather than λ, and decreases with δ. δ shortens with the increase in Q (or the shortening of R_0) as is clarified by the fact that the $T_{C\delta}$ goes down accordingly as Q increases. Consequently η decreases accordingly as Q increases or R_0 shortens.

In Fig. 5(a), the order parameter S of the ferroelectric transition is plotted as a function of temperature T, and in Fig. 5(b), as a function of R_0. In addition, Figs. 6(a) and 6(b) show the dipole moments $\mu(=\eta S)$ of $K\text{-}PO_4$ corresponding to Figs. 6(a) and 6(b), respectively.

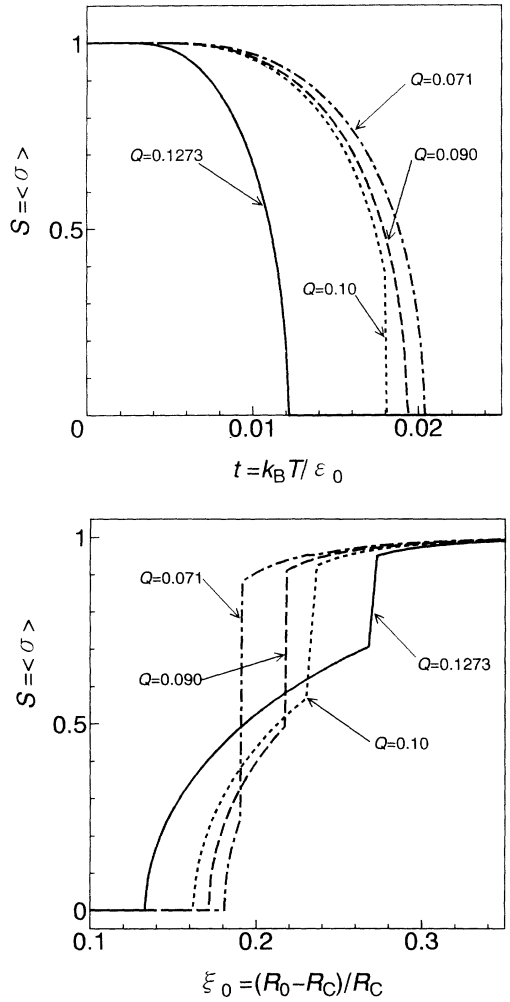

FIG. 5. (a) The temperature dependences of order parameter S for various values of Q at $\xi_0=0.25$, $\alpha=0.01$, and $\gamma=0.001$. In the case of $Q=0.071$ or 0.090, the H(D) bond stands on the asymmetric ($\delta>0$) and the system undergoes the ferroelectric transition of a second order at $T=T_{CS}$ lying below $T_{C\delta}$. In the case of $Q=0.10$, the system undergoes the ferroelectric transition of the first order at $T=T_{C\delta}$ accompanying the symmetric transition of the first order. In the case of $Q=0.1273$, the H(D) bond is the symmetric ($\delta=0$) and the system undergoes the ferroelectric transition of the second order at $T=T_{CS}$ similarly to the case of $Q=0.071$ (or 0.090). (b) The dependences of the order parameters S on R_0 for various values of Q at $t=0.01$, $\alpha=0.01$, and $\gamma=0.001$. The order parameter S increases with R_0. The gap in the curve S appears at the symmetric transition point between $\delta=0$ and $\delta>0$.

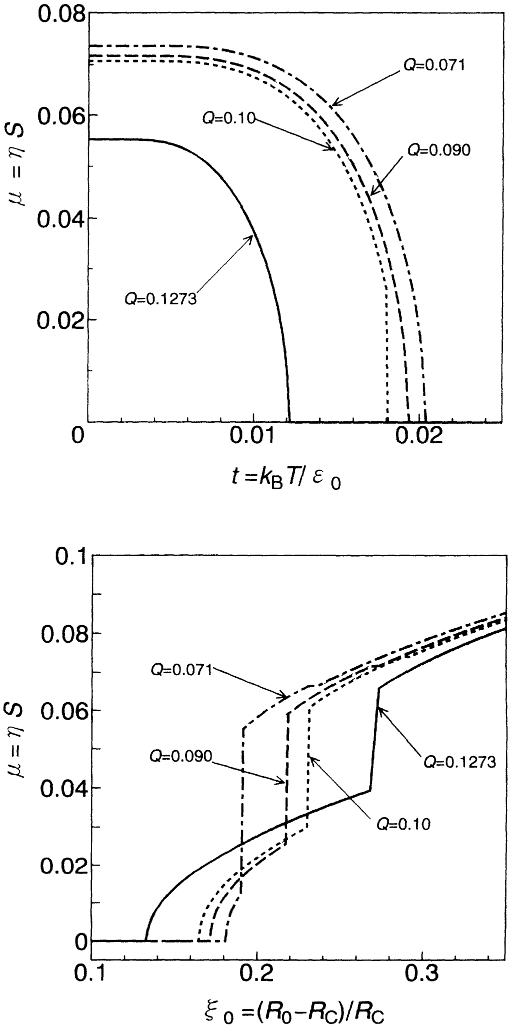

FIG. 6. (a) The temperature dependences of the dipole moment $\mu(=\eta S)$ of $K\text{-}PO_4$ ion for various values of Q at $\xi_0=0.25$, $\alpha=0.01$, and $\gamma=0.001$. (b) The dependences of the dipole moment μ on R_0 for various values of Q at $t=0.01$, $\alpha=0.01$, and $\gamma=0.001$.

D. Isotope effects

Let us define Q_H as the quantum-effect magnitude of proton, then that of deuteron Q_D, given as $Q_H/\sqrt{2}$ [see Eqs. (19) and (20)], is smaller than Q_H. Now, as an example, we consider the case of $Q_H=0.1273$ (therefore, $Q_D=0.090$) in Fig. 1, in which the hydrogen bond is the symmetric ($\delta_H=0$) but the deuterium bond the asymmetric ($\delta_D>0$).

In this case, Fig. 5(a) shows that the ferroelectric transition temperature T_{CS} rose rapidly by substituting hydrogen atoms for deuterium atoms and Fig. 6(a) shows that the dipole moment $\mu(=\eta S)$ at zero temperature increased rapidly on deuteration. This fact suggests that remarkable isotope effects are exhibited on the ferroelectric transition temperature and the dipole moment in KDP-type crystals. The example above (the case of $Q_H=0.1273$, $Q_D=0.090$) displays that the geometric isotope effect is also exhibited remarkably.

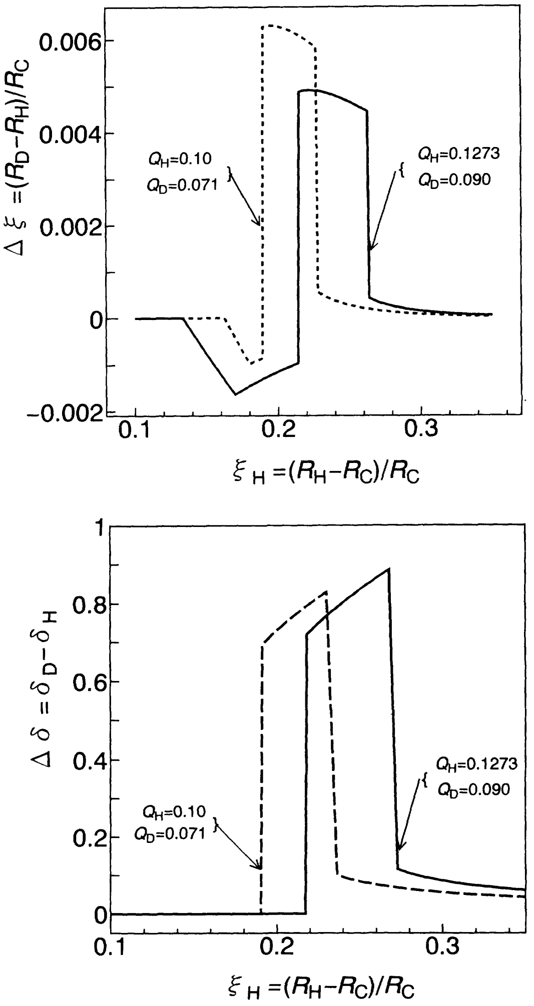

FIG. 7. (a) The expansions $\Delta\xi$ of the hydrogen-bonded distance R_H on deuteration for $Q_H=0.1273$ ($Q_D=0.090$) and $Q_H=0.10$ ($Q_D=0.071$) at $t=0.01$, $\alpha=0.01$, and $\gamma=0.001$. (b) The expansions $\Delta\delta$ of δ_H on deuteration for $Q_H=0.1273$ ($Q_D=0.090$) and $Q_H=0.10$ ($Q_D=0.071$) at $t=0.01$, $\alpha=0.01$, and $\gamma=0.001$.

In Fig. 7(a), the expansion of $\Delta\xi[=(R_D-R_H)/R_C]$ on deuteration is plotted against R_H, the various values of which give the hydrogen-bonded distances of KDP-type materials. It is seen in Fig. 7(b) that the difference $\Delta\delta(=\delta_D-\delta_H)$ on deuteration also expands remarkably in the same range of R_H that the expansion of $\Delta\xi$ appears remarkably, where δ_H denotes the distance between the two equilibrium sites of a proton on the hydrogen bond and δ_D that of a deuteron on the deuterium bond. These results for the geometric isotope effects agree qualitatively with those obtained in the previous paper.

One can see from Fig. 7(a) [or 7(b)] that a curve $\Delta\xi$ vs R_H (or $\Delta\delta$ vs R_H) produces three regions; the shorter, the middle, and the longer distances of the hydrogen bond. In the region of the shorter R_H, the contraction of the hydrogen-bond distance on deuteration appears. In this region, both hydrogen and deuterium bonds are symmetric ones ($\delta_H=\delta_D=0$), so that the parameter η increases with Q as mentioned above. As a result, the order parameter S (the distortion of the PO_4 ion) for the hydrogen bond becomes larger than that for the deuterium bond since $Q_H>Q_D$, and the hydrogen-bonded distance becomes longer than the deuterium-bonded distance in this region. In the region of the middle R_H, in which the hydrogen bond is the symmetric ($\delta_H=0$) but the deuterium bond is the asymmetric (δ_D), the η (or S) for the deuterium bond is much larger than that of the hydrogen bond. In this region, R_D becomes considerably longer than R_H and δ_D also become longer than δ_H and the geometric isotope effects are exhibited remarkably on R_H and δ_H. In the region of the longer R_H, in which both hydrogen and deuterium bonds are asymmetric ones ($\delta_H>0,\delta_D>0$), the geometric isotope effect is hardly seen.

This fact suggests that for KDP-type materials such that the remarkable isotope effects concerning T_{CS} and μ appear, the geometric isotope effects is also exhibited remarkably in KDP-type materials constructed with a suitable distance of the hydrogen bond.

IV. DISCUSSION

The geometric isotope effects on the hydrogen-bonded distance and the distance between the two equilibrium sites of proton and the isotope effects concerning the ferroelectric transition temperature and the dipole moment of K-PO_4 have been explained by a theoretical form. This form is constructed by assuming the relation between the O-O distance and the distortion of the PO_4 ion. In order to simplify the calculations, we carried out the simple double-minima-type potential instead of the double-Morse potential. However, we expect that our results will not be very different, in principle, from those obtained by the double-Morse potential.

It is revealed in this paper that the origin of these isotope effects is due to a difference in δ between the hydrogen and deuterium bonds. It should be noted that the difference arises not from the tunneling motion of proton (or deuteron) but from the quantum-mechanical fluctuations such as the zero-point vibration of proton (or deuteron).

Especially, it is noticed these isotope effects are exhibited remarkably on the KDP-type materials in which the hydrogen-bonded distance is a suitable distance such that the hydrogen bond stands on the symmetric bond ($\delta_H=0$) and the deuterium bond on deuteration stands on the asymmetric bond ($\delta_D>0$).

---

[1] R. Blinc and B. Zeks, in *Soft Modes in Ferroelectrics and Antiferroelectrics,* edited by E. P. Wohlfarth (North-Holland, Amsterdam, 1974).

[2] M. E. Lines and A. M. Grass, in *Principles and Applications of Ferroelectric and Related Materials* (Clarendon, Oxford, 1977).

[3] G. A. Samara, Ferroelectrics **20**, 87 (1978).

[4] R. Blinc, B. Zeks, J. F. Sanpaio, A. S. T. Pires, and F. C. Sa-Bareto, Phys. Rev. B **20**, 1991 (1979).

[5] M. Ichikawa, Acta Crystallogr. B **34**, 2074 (1978).

[6] M. Ichikawa, Chem. Phys. Lett. **79**, 583 (1981).

[7] M. Ichikawa, N. Motida, and N. Yamada, Phys. Rev. B **36**, 874 (1987).

[8] M. Ichikawa, J. Phys. Soc. Jpn. **56**, 3748 (1987).

[9] M. Ichikawa and K. Motida, J. Phys. Soc. Jpn. **56**, 3750 (1987).

[10] R. J. Nelmes, J. Phys. C **21**, L881 (1988).

[11] H. Sugimoto and S. Ikeda, Phys. Rev. Lett. **67**, 1306 (1991).

[12] G. A. Samara, Ferroelectrics **5**, 25 (1973).

[13] S. Tanaka, Phys. Rev. B **42**, 10 488 (1990).