Distributions of excitation energies of protons in hydrogen-bonded crystalline KH₂PO₄: Monte Carlo calculations

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Abstract. Monte Carlo calculations are performed on a model that was proposed in our previous letter to explain a large isotope effect on the transition temperature (T_c) from a ferroelectric phase to a paraelectric phase in KH₂PO₄ (KDP). On the basis of the distribution of the electric dipole moments obtained from these calculations, the distribution of the excitation energies for protons is calculated; it is found that their features are in agreement with the excitation spectra in KDP, observed by inelastic neutron-scattering experiments.

1. Introduction

In the tunnelling model, which had been accepted as the mechanism of the phase transition from a ferroelectric phase to a paraelectric phase in KDP and KD₂PO₄ (DKDP), the phase transition is of a displacive type with a softening of the optical phonon mode [2]. However, recent experiments concerning these materials indicate that the phase transition is of an order–disorder type, and that the mode that had been assigned to the soft mode comprises two components: a polarization-fluctuation mode and a libration mode of PO₄ tetrahedra [3–5]. Therefore, the mechanism of the phase transition in these materials has not yet been clarified, including the physical origin of a large isotope effect on the transition temperature (T_c).

Recently, Kojyo and Onodera [6] proposed a quasi-one-dimensional model for CsH₂PO₄ and CsD₂PO₄, in which a strong coupling between protons (deuterons) and dipole moments is assumed; they showed that the properties of the ferroelectric phase transition in these materials can be explained by their model.

In our previous letter [1] (from now on referred to as I) we calculated the energies and wave functions of both the ground and excited states for a proton in KDP and a deuteron in DKDP by adopting an empirical potential. Based on these quantum-mechanical calculations for protons and deuterons, we proposed a new model for the phase transition in these materials, under the assumption that strong coupling exists between protons and dipole moments, as in the Kojyo–Onodera model.

In this model, a system comprising N distorted PO₄ tetrahedra and $2N$ protons was considered; its energy was written as

$$E_{pot} = \frac{A}{2} \sum_{i=1}^{N} \mu_i^2 + \frac{1}{2} \sum_{ij}^{N} D_{ij} \mu_i \mu_j - \sum_{(ij)}^{2N} E_{ij}^0 \tag{1}$$

with

$$E_{ij}^0 = \left[h^2 + I^2 K^2 (\mu_i + \mu_j)^2 \right]^{1/2} - h. \tag{2}$$

The first term in (1) is the elastic energy due to a mechanical deformation of the tetrahedra; the second term is 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 neighbouring tetrahedra (i and j). This expression was derived under the following assumptions: (1) the distortion of tetrahedron i is proportional to its electric dipole moment μ_i; (2) all dipole moments of the tetrahedra lie along the c axis in a KDP (DKDP) crystal; and (3) the interaction between a proton and the dipole moments can be expressed as $K(\mu_i + \mu_j)x$, where μ_i and μ_j are the dipole moments of two tetrahedra (i and j) connected by the proton, x is the position of the proton in the direction of the oxygen–hydrogen–oxygen bond (O–O bond) and K is a constant.

Since $-\infty < \mu_i < +\infty$ for all i, the average $\langle X \rangle$ of a physical quantity (X) in thermal equilibrium should be calculated using the relation

$$\langle X \rangle = \int d\mu_1 \ldots \int d\mu_N \left[X \exp(-E_{pot}/k_B T) \right] \Big/ \int d\mu_1 \ldots \int d\mu_N \exp(-E_{pot}/k_B T) \tag{3}$$

if X depends on only the dipole moments $\{\mu_i\}$. We assumed here that the classical approximation is valid for the motion of the dipoles. Since it is difficult to perform such calculations analytically, we adopted in I the assumption of permanent dipoles, that is, $\mu_i = \mu_s S_i (S_i = 1$ or -1 for all i), where μ_s is a saturated dipole moment. Under this assumption, E_{pot} can be rewritten as an Ising-type expression. Upon applying the mean-field approximation to this expression we found that this model gives a consistent account of the isotope effect on T_c.

Under the assumption of permanent dipoles, however, it is expected that there are a considerable number of states with $\mu_i + \mu_j = 0$ in a paraelectric phase, since antiparallel alignments of neighbouring dipoles occur. As shown in figure 2 in I, the excitation energies $(\Delta E_x, \Delta E_y$ and $\Delta E_z)$ at $|\mu_i + \mu_j| = 2\mu_s$ are 0.16, 0.12 and 0.16 eV, respectively, whereas $\Delta E_x = 0.09$, $\Delta E_y = 0.13$ and $\Delta E_z = 0.17$ eV at $|\mu_i + \mu_j| = 0$. Here, ΔE_x is the excitation energy for the motion of a proton in the direction along an O–O bond, and ΔE_y and ΔE_z are those in the directions perpendicular to the O–O bond direction. Therefore, a peak corresponding to ΔE_x at $\mu_i + \mu_j = 0$ is expected to appear in the excitation spectra in a paraelectric phase. Nevertheless, no such peak has yet been observed in an inelastic neutron-scattering experiment [7]. This indicates that more rigorous calculations are required to confirm the reliability of our model for KDP.

In this paper, the Monte Carlo method is used to calculate thermal average of physical quantities in our model using (3). The purpose of this paper is to examine the properties of the excitation spectra of protons in our model by using a treatment beyond the assumption of permanent dipoles.

2. The determination of the parameters and the calculation method

To perform a treatment beyond the assumption of permanent dipoles, we take into account only the nearest-neighbour interaction for the direct interaction between dipole moments (the second term in (1)), i.e.,

$$\frac{1}{2} \sum_{i,j=1}^{N} D_{ij} \mu_i \mu_j = \frac{B}{4} \sum_{(ij)}^{2N} \mu_i \mu_j \tag{4}$$

where $\sum$ on the right-hand side denotes the summation over pairs of neighbouring tetrahedra. This approximation was adopted in order to simplify the calculations. Note

that the number of parameters becomes only five upon adopting this approximation. Three of these parameters (h, I and K) were obtained from the quantum-mechanical calculations in I: h and I were determined so as to reproduce the $K(\mu_i + \mu_j)$ dependence of the ground-state energy $-E_{ij}^0$ obtained, whereas, taking account of the observation of the excitation energies, K was chosen as $2\mu_s K d = 1.5$ eV, where d is the distance of an O–O bond. These values are as follows: $h^H = 0.110$ eV, $h^D = 0.058$ eV ($= 0.53 h^H$), $I = 0.22$ Å, and $IK = 0.6 h^H / \mu_s^H$. Here, h^H and h^D are h in KDP and DKDP, respectively, and μ_s^H is a saturated dipole moment in KDP. In the present calculation, the isotope effect of I is disregarded because of its smallness.

Knowledge concerning the remaining parameters (A and B) is required in order to proceed with our calculations. We now examine the behaviour of the system $T = 0$ K. If $\mu_i = \mu_s$ holds for all tetrahedra, E_{pot} can be written as

$$E_{pot} = N\left\{ \tfrac{1}{2}(A + B)\mu_s^2 - 2\left(\left[h^2 + \left(2IK\mu_s \right)^2 \right]^{1/2} - h \right) \right\}. \tag{5}$$

Since μ_s is determined by the relation $\partial E_{pot}/\partial \mu_s = 0$, we obtain the following relation between the parameters:

$$B = 2(2IK)^2 / \left[h^2 + \left(2IK\mu_s \right)^2 \right]^{1/2} - A. \tag{6}$$

On the other hand, if the dipoles of neighbouring tetrahedra align so as to be antiparallel, E_{pot} is as follows:

$$E_{pot} = \tfrac{1}{2} N(A - B)\mu_s^2. \tag{7}$$

This means that the condition under which a ferroelectric phase becomes stable is $A > B$. In both KDP and DKDP the ferroelectric phase is observed at low temperatures. Accordingly, we obtain

$$A > (2IK)^2 / \left[h^2 + \left(2IK\mu_s \right)^2 \right]^{1/2}. \tag{8}$$

We thus use A and B, which satisfy relations (6) and (8).

The length d of an O–O bond is larger in DKDP than in KDP by about 1%. The modest change of d gives an important effect on T_c, as shown in I. This is due to the fact that h strongly depends on d since the depth and the form of the potential field acting on a proton (a deuteron) is sensitive to d.

On the other hand, A and B are parameters describing the strength of the mechanical deformation energy of the tetrahedra and that of the direct interaction between neighbouring dipoles, respectively. Therefore, the changes of d and the mass should have no influence on A and B, i.e., A and B are expected to be identical in both KDP and DKDP. From this we obtain

$$\left(h^H \right)^2 + \left(2IK\mu_s^H \right)^2 = \left(h^D \right)^2 + \left(2IK\mu_s^D \right)^2 \tag{9}$$

using (6), where μ_s^D is μ_s in DKDP. Substituting the values of h^H, h^D and IK into (9), we obtain $\mu_s^D = 1.2\mu_s^H$. This isotope effect on μ_s agrees well with the observations [8].

Monte Carlo calculations were performed on a KDP lattice with $N (= 4000)$ tetrahedra imposing a periodic boundary condition, by using the Metropolis important sampling method [9]. In the calculations, μ_i were chosen at random from values between $-6\mu_s$ and $+6\mu_s$; the average was calculated from data of $\sim$1000–2000 Monte Carlo steps obtained after the first 1000 Monte Carlo steps.

3. Results

We now discuss some of the results of our Monte Carlo calculations. Figure 1 gives the temperature dependences of the thermal average of dipoles. From this figure we can see that
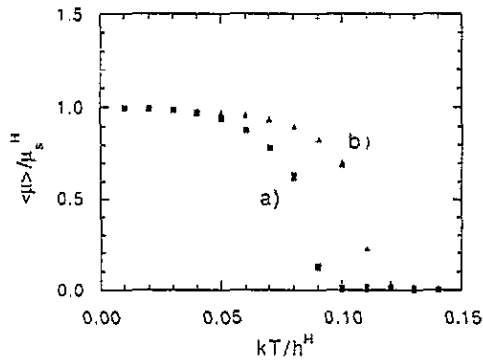
Figure 1. Temperature dependences of the thermal average of dipole moments in KDP obtained by assuming (a) $A = 0.96h^H/(\mu_s^H)^2$ and (b) $A = 1.0h^H/(\mu_s^H)^2$.
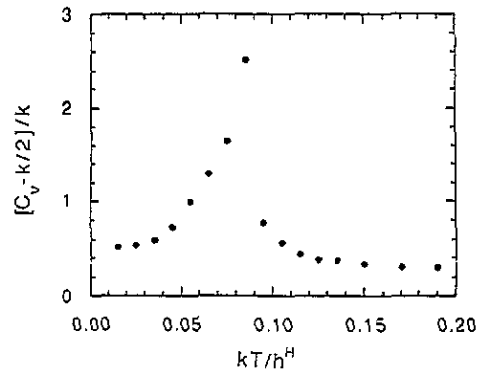
Figure 2. Temperature dependences of the specific heat due to the motion of dipole moments in KDP obtained by assuming $A = 0.96h^H/(\mu_s^H)^2$.

there is a phase transition from a ferroelectric phase to a paraelectric phase; the transition temperatures (T_c) are 120 K for $A = 0.96h^H/(\mu_s^H)^2$ and 140 K for $A = 1.0h^H/(\mu_s^H)^2$ when $h = h^H$ is used. If $h = h^D(= 0.53h^H)$ is adopted, T_c is 310 K for $A = 0.96h^H/(\mu_s^H)^2$ and 360 K for $A = 1.0h^H/(\mu_s^H)^2$. Here, $h^H = 0.11$ eV and $\mu_s^H = 4.8 \times 10^{-22}$ μC cm. Note that the observed values of T_c are 122 K in KDP and 230 K in DKDP.

We also calculated the specific heat (c_V) from E_{pot} using the relation $c_V = \partial E_{pot}/N\partial T + \frac{1}{2}k_B$. The result is shown in figure 2. It was found from this calculation that there is a peak of c_V near to T_c, due to an entropy change induced by the phase transition, and that its entropy change is about $k_B \ln 2$ per hydrogen atom. This means that the phase transition in our model is of the order–disorder type. We note here that c_V at low temperatures is k_B. This is due to the fact that the motion of dipoles is restricted to one dimension and the classical approximation is adopted for the dipoles.
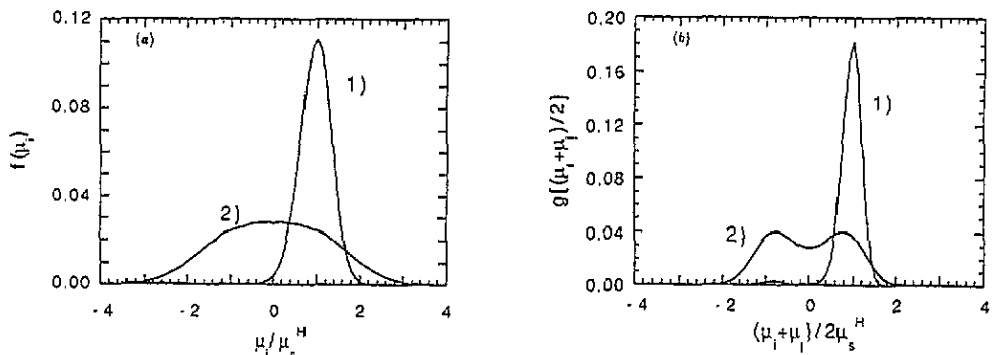

Figure 3. Calculated distributions of the dipole moments: (a) $f(\mu_i)$ at (1) $T = 60$ K and (2) $T = 190$ K; (b) $g[\frac{1}{2}(\mu_i + \mu_j)]$ at (1) $T = 60$ K and (2) $T = 190$ K. In these calculations, $A = 0.96h^H/(\mu_s^H)^2$ and $h = 0.11$ eV are assumed.

Figure 3 shows two kinds of distribution of the dipole moments obtained from our Monte Carlo calculations using $A = 0.96h^H/(\mu_s^H)^2$ and $h = h^H(= 0.11$ eV): a distribution of μ_i, $f(\mu_i)$, and a distribution of a sum of two neighbouring dipole moments, $g[\frac{1}{2}(\mu_i + \mu_j)]$. At $T < T_c$, both of the distributions (f and g) have a peak at μ_s^H, due to an ordering of the dipoles. We emphasize here that the width of g is of the order of μ_s^H, even at $T = 60$ K. At $T > T_c$, f has a broad peak at $\mu_i = 0$, whereas g has two broad peaks at

about $\pm 0.8 \mu_s^H$. This remarkable difference between f and g indicates that there is a strong correlation between neighbouring dipoles, even in the paraelectric phase. Similar features are also found for f and g obtained from calculations using $h = h^D (= 0.058$ eV).

Since the excitation energies of a proton depend on the sum of two neighbouring dipoles in our model, the result of g obtained here is expected to have a serious influence on the excitation spectra of protons. By using the present result for $g[\frac{1}{2}(\mu_i + \mu_j)]$ and the dependence of the excitation energies on $\mu_i + \mu_j$ obtained in our previous letter, we calculated the distributions of the excitation energies from the ground state to the excited states. The result is shown in figure 4. In the calculations, we assumed that the broadening of the energy levels due to other sources, such as lattice vibration, may be expressed by a Gaussian distribution with a standard deviation proportional to $k_B T$.
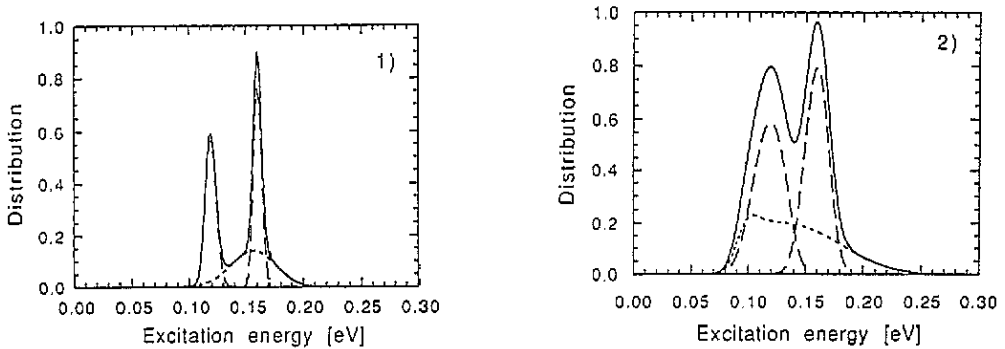

Figure 4. Calculated distributions of the excitation energies for a proton at (1) $T = 60$ K and (2) $T = 190$ K. The distributions for ΔE_x and for both ΔE_y and ΔE_z are denoted by short-dashed and long-dashed curves, respectively. The full curve indicates the total distribution. In these calculations, $A = 0.96 h^H / (\mu_s^H)^2$ and $h = 0.11$ eV are assumed.

One of the striking features of the result is that ΔE_x distributes over a wide energy range. Although such a broadening of the distribution of ΔE_x is remarkable in the paraelectric phase, it is also considerable at temperatures lower than T_c. Another is that the distributions of ΔE_y and ΔE_z have sharp peaks at 0.12 and 0.16 eV, respectively, in both the paraelectric and ferroelectric phases, in contrast with the distribution of ΔE_x. These properties are independent of the transition temperature.

These features are due to the $\mu_i + \mu_j$ dependence of the excitation energies: ΔE_x strongly depends on $\mu_i + \mu_j$, whereas both ΔE_y and ΔE_z are almost independent of $\mu_i + \mu_j$ (see figure 2 in I); therefore, only ΔE_x distributes over a wide energy range, when the distribution of $\mu_i + \mu_j$ has a remarkable broadening, as obtained here.

We emphasize here that the total distribution defined by summing these three distributions has only two peaks in both the ferroelectric and paraelectric phases; therefore, no peak corresponding to ΔE_x at $\mu_i + \mu_j = 0$ is observed in the excitation spectra of protons. This feature of the total distribution is in good agreement with the excitation spectra in KDP crystals observed by inelastic neutron scattering experiments, except for the 0.028 eV peak [7]. This agreement strongly indicates that the broadening of the distribution of ΔE_x due to the mechanism described here is realized in KDP.

4. Discussion

We note here that the broadening of the distribution of ΔE_x at 60 K is considerable. This peak broadening is caused by the fact that thermal fluctuations of $\mu_i + \mu_j$ are

large. In a system with such large fluctuations in ordered phases, quantum fluctuations are expected to be large in the low-temperature region where quantum effects become dominant. Accordingly, distributions of ΔE_x should be broad, even at very low temperatures. This indicates that observations of the peak of ΔE_x are difficult under ordinary conditions, even if the peak position of ΔE_x does not coincide with that of ΔE_y or ΔE_z. The present result that excitation spectra have only two peaks in both the paraelectric and ferroelectric phases, therefore, seems to be a common property in hydrogen-bonded crystals with remarkable isotope effects on T_c. In fact, excitation spectra with two large peaks are also observed in RbH_2PO_4 (RDP) [10]. In order to confirm this inference, however, more detailed studies are required, including experimental efforts.

Finally, we make the following remarks concerning the validity of the present calculation.

(i) Finite-size effects appear in Monte Carlo calculations [9]. Accordingly, the estimates of the transition temperatures should be viewed with care. Errors of the transition temperatures, however, have no influence on the present conclusions for the distributions of the excitation energies of protons, since the features of the distributions obtained here are not dependent on the transition temperature.

(ii) The long-range part of the direct interaction between the dipole moments was disregarded in our calculations for simplicity. A long-range interaction, however, plays some role for the behaviour of some physical quantities near to the transition point. Consequently, the critical properties obtained here could be described incorrectly. Nevertheless, we believe that this approximation is good enough for the present purpose, since the states of a proton and the distributions of dipoles are mainly determined by the short-range interactions.

In summary, Monte Carlo calculations were performed on a model proposed in I to explain the ferroelectric phase transition in KDP. It was found that our model gives a consistent account of the excitation spectra of the protons in KDP observed by inelastic neutron scattering. This result strongly indicates that the model is valid and that treatment beyond the assumption of permanent dipoles is essential to understand the properties of hydrogen-bonded crystals.

Acknowledgments

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