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Electric dipole waves and vibration motion of protons in hydrogen-bonded crystalline KH_2PO_4 at low temperatures

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Abstract. On the basis of a model that was proposed to explain a large isotope effect on the temperature (T_c) of the transition from a ferroelectric phase to a paraelectric phase in KH_2PO_4 (KDP), the motion of electric dipole moments is examined in the framework of the harmonic approximation; it is concluded that, in the ferroelectric phase, there are electric dipole waves, by which the vibration motion of a proton is induced along the direction of an oxygen–hydrogen–oxygen (O–O) bond. Scattering of thermal neutrons induced by this motion of protons (deuterons) is also examined.

1. Introduction

In our previous letter [1] we calculated the energies and wave functions of the ground and excited states for a proton in KDP and a deuteron in KD_2PO_4 (DKDP) by adopting an empirical potential, under the assumption that a strong coupling exists between protons (deuterons) and dipole moments induced by distortion of PO_4 tetrahedra. On the basis of these quantum-mechanical calculations for protons and deuterons, we proposed a new model for the phase transition from a ferroelectric phase to a paraelectric phase. From examinations of this model [1, 2], we found the following features: (1) the phase transition is of an order–disorder type with a large isotope effect on the transition temperature; (2) the isotope effect is due to changes of a potential shape for a proton induced by ordering of the dipole moments, but not the tunnelling motion of protons; (3) distributions of the dipole moments have a broad peak even in the ferroelectric phase, and accordingly the excitation energies for the proton motion in the direction along an O–O bond have so wide a distribution that observations of a peak corresponding to the excitation of this mode are practically impossible [2]. These features seem to agree with those of observations for these materials [3–6].

Most of the theoretical studies [7–10] concerning the mechanism of the ferroelectric phase transition in KDP are based on the assumption introduced by Slater [11] and refined by Takagi [12]: the static and dynamic properties of this system are described by the configuration energy determined by proton configurations around a PO_4 tetrahedron. In our model, however, such interactions between protons are not considered explicitly. The correlation between protons appears as a result of the strong coupling between protons and distortion of PO_4 tetrahedra. Since the Slater–Takagi model is widely accepted, it is necessary to examine the reliability of our model in detail, although it gives a consistent account of isotope effects on the transition temperature and the saturated dipole moment.

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In this paper, the motion of dipole moments in our model is examined in the framework of the harmonic approximation to reveal dynamic properties of protons and dipole moments in the ferroelectric phase. Our plan is as follows. The main features of our model are described in section 2. In section 3, it is shown that there are electric dipole waves with dispersion, in the ferroelectric phase. On the basis of this result, quantization of the electric dipole waves is performed. Scattering of thermal neutrons by the vibration motion of protons induced by the electric dipole waves is examined in section 4. In section 5, some aspects of our results are discussed, including a comparison with scattering functions of neutrons obtained in section 4 and recent neutron-scattering experiments. The purpose of the present paper is to show that it gives a consistent account of some properties of the ferroelectric phase in KDP and DKDP, as specific evidence for the usefulness of our model.

2. Model

Let us consider a system comprising N distorted PO_4 tetrahedra and $2N$ protons, under the assumption that (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) there is an interaction between a proton and dipole moments expressed as $K(\mu_i+\mu_j)x$, where μ_i and μ_j are dipole moments of two tetrahedra (i and j) connected by the proton, x is a displacement of the proton in the direction along the O–O bond, measured from the centre of this bond, and K is a coupling constant.

Protons are expected to follow the motion of dipole moments because of the smallness of the proton mass. The adiabatic approximation that separates the motion of fast protons from that of slow dipole moments should, therefore, be valid for a description of the present system. In this approximation, the wave function of the system is written as

$$\Psi(r_1,\ldots,r_{2N},\mu_1,\ldots,\mu_N)=\chi(\{\mu_i\})\prod_{n=1}^{2N}\psi(r_n;\{\mu_i\}) \tag{1}$$

where $\chi(\{\mu_i\})$ is the wave function of the dipole moments and $\psi(r_n;\{\mu_i\})$ is the ground-state wave function of proton n.

The adiabatic potential of the system may be expressed as a function of N dipole moments. We wrote it as [1, 2]

$$E_{\text{pot}}=\frac{A}{2}\sum_{i=1}^{N}\mu_i^2+\frac{B}{4}\sum_{\langle ij\rangle}^{2N}\mu_i\mu_j-\sum_{\langle ij\rangle}^{2N}E_{ij}^0. \tag{2}$$

Here, the first term is the elastic energy due to a mechanical deformation of the tetrahedra; the second term is the interaction energy between dipoles taking account of only the nearest-neighbour interaction; 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).

Knowledge of $-E_{ij}^0$ and $\psi(r_n;\{\mu_j\})$ is obtained from quantum-mechanical calculations for protons (deuterons) in KDP (DKDP). In the previous letter [1], we assumed that a potential with double minima along the direction of an O–O bond acts on a proton. In this case, the interaction between the proton and dipole moments induces a drastic change of the potential acting on the proton. Accordingly, the wave function and energy of the ground state for the proton (deuteron) strongly depend on $\mu_i+\mu_j$. In figure 1, profiles of the ground-state

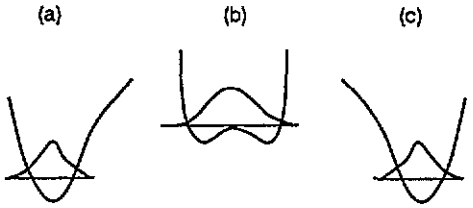

Figure 1. Schematic profiles of the potential and wave functions of a proton along the direction of an O–O bond (a) at $\mu_i + \mu_j = 2\mu_s$, (b) at $\mu_i + \mu_j = 0$ and (c) at $\mu_i + \mu_j = -2\mu_s$.

wave function of the proton along the direction of the O–O bond are shown with those of the potential acting on the proton, schematically.

We also found that the ground-state energy is expressed as

$$E_{ij}^0 = [h^2 + I^2K^2(\mu_i + \mu_j)^2]^{1/2} - h \tag{3}$$

with $h^H = 0.110$ eV, $h^D = 0.058$ eV ($= 0.53h^H$) and $IK = 0.6h^H/\mu_s^H$, where h^H and h^D are h in KDP and DKDP, respectively, and μ_s^H is a saturated dipole moment in KDP. We note here that the isotope effect of IK is disregarded because of its smallness [2].

Furthermore, it was found from the behaviour of the system at $T = 0$ K that the relations

$$A + B = 2\frac{(2IK)^2}{\sqrt{h^2 + (2IK\mu_s)^2}} \tag{4}$$

$$A > \frac{(2IK)^2}{[h^2 + (2IK\mu_s)^2]^{1/2}} \tag{5}$$

and

$$(h^H)^2 + (2IK\mu_s^H)^2 = (h^D)^2 + (2IK\mu_s^D)^2 \tag{6}$$

hold [2]. Here, μ_s^D is μ_s in DKDP.

By substituting the values of h^H, h^D and IK into equation (6), $\mu_s^D = 1.2\mu_s^H$ is obtained. This value for μ_s^D is in good agreement with the observed value [13].

In the adiabatic approximation, the state of the system is described as the motion of a system point on the adiabatic potential surface. Upon applying the classical approximation to the motion of dipole moments, the motion of the system point is represented by a set of the following equations:

$$M\frac{d^2\mu_i}{dt^2} = -\frac{\partial E_{pot}}{\partial \mu_i} \qquad (i = 1, \ldots, N) \tag{7}$$

where M is an effective mass with a dipole moment. We emphasize here that the motion of protons in the ground state is completely determined by the motion of the system point, under this approximation.

3. Electric dipole waves in the ferroelectric phase

In the ferroelectric phase, it is expected that most dipole moments lie in the same direction and deviations of these values from the saturated value μ_s are small. A force acting on μ_i, $-\partial E_{pot}/\partial \mu_i$, may, therefore, be expressed as $\sum_j f_{ij}\Delta\mu_j$ using $\Delta\mu_j = \mu_j - \mu_s$. Upon applying this linear approximation, the equation of motion for the dipole moments is rewritten to that of $\Delta\mu_j$, i.e.,

$$M\frac{d^2\Delta\mu_i}{dt^2} = \sum_j f_{ij}\Delta\mu_j \tag{8}$$

where $f_{ij} = f_0$ for $i = j$; $f_{ij} = f_1$ when i and j are neighbours; and $f_{ij} = 0$ otherwise.

For f_0 and f_1, the following expressions are obtained from equation (3):

$$f_0 = A - \frac{4(IK)^2}{\sqrt{h^2 + (2IK\mu_s)^2}}\left[1 - \frac{(2IK)^2}{h^2 + (2IK\mu_s)^2}\right] \tag{9}$$

and

$$f_1 = \frac{B}{4} - \frac{(IK)^2}{\sqrt{h^2 + (2IK\mu_s)^2}}\left[1 - \frac{(2IK)^2}{h^2 + (2IK\mu_s)^2}\right]. \tag{10}$$

The parameters in our model are summarized in table 1, including A and B determined so as to reproduce the transition temperature T_c in KDP.

Table 1. Values of h, IK, A, B, f_0 and f_1 used in our calculations. Here, $h^H = 0.11$ eV and $\mu_s^H = 4.8 \times 10^{-22}$ μC cm. The transition temperatures, T_c, obtained using these values are also denoted.

	h/h^H	$IK\mu_s^H/h^H$	$A(\mu_s^H)^2/h^H$	$B(\mu_s^H)^2/h^H$	$f_0(\mu_s^H)^2/h^H$	$f_1(\mu_s^H)^2/h^H$	T_c (K)
KDP	1.0	0.6	0.96	0.88	0.58	0.13	120
DKDP	0.53	0.6	0.96	0.88	0.86	0.19	310

3.1. Dipole waves

It is convenient to specify positions of dipole moments by a set of lattice vectors $\boldsymbol{R}_l$ that locate each cell of the crystal. When we choose a unit cell as in figure 2, each cell contains four PO_4 tetrahedra, whose positions are specified by $\boldsymbol{R}_l + \boldsymbol{t}_p$ $(p = 1, \ldots, 4)$. Using these symbols, solutions of equation (8) can be represented as

$$\Delta\mu_{l,p} = \sqrt{\frac{4}{N}}\sum_k \xi_p(k)\exp[-\mathrm{i}(\omega t + \boldsymbol{k}\cdot\boldsymbol{R}_l)] \tag{11}$$

where ω is a frequency, $\boldsymbol{k}$ a wave number vector and $N/4$ the number of unit cells in the lattice.

Substituting them into equation (8), we obtain a set of linear homogeneous equations. The condition with which these equations possess non-trivial solutions is

$$\begin{vmatrix} f_0 - M\omega^2 & (1+e^{-ik_a a})f_1 & 0 & (1+e^{-ik_b b})e^{-ik_c c}f_1 \\ (1+e^{ik_a a})f_1 & f_0 - M\omega^2 & (1+e^{-ik_b b})f_1 & 0 \\ 0 & (1+e^{ik_b b})f_1 & f_0 - M\omega^2 & (1+e^{ik_a a})f_1 \\ (1+e^{ik_b b})e^{ik_c c}f_1 & 0 & (1+e^{-ik_a a})f_1 & f_0 - M\omega^2 \end{vmatrix} = 0 \tag{12}$$

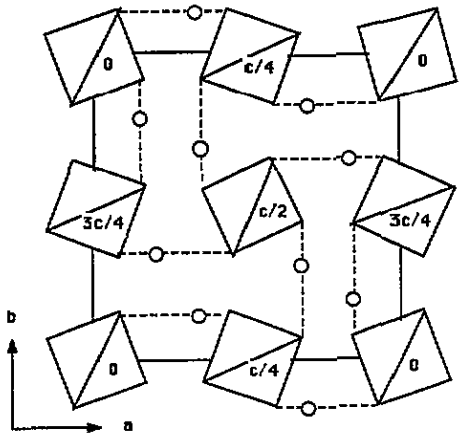

Figure 2. The projection of the unit cell used in the calculation on the a–b plane. There are four PO_4 tetrahedra (□) and eight protons (○) in the cell. For simplicity, it is assumed that all O–O bonds are parallel to the a axis or the b axis. In the figure, the heights of the centres of PO_4 tetrahedra are also denoted.

where a is a lattice constant of the a axis, k_a is a wave number in the direction of the a axis and so on.

From the condition, four eigenfrequencies are obtained:

$$\left(\frac{\omega_1}{\omega_0}\right)^2 = 1 - 2\frac{f_1}{f_0}\sqrt{1 + \frac{\cos k_a a + \cos k_b b}{2} + \sqrt{\frac{1+\cos k_c c}{2}(1+\cos k_a a)(1+\cos k_b b)}} \tag{13}$$

$$\left(\frac{\omega_2}{\omega_0}\right)^2 = 1 - 2\frac{f_1}{f_0}\sqrt{1 + \frac{\cos k_a a + \cos k_b b}{2} - \sqrt{\frac{1+\cos k_c c}{2}(1+\cos k_a a)(1+\cos k_b b)}} \tag{14}$$

$$\left(\frac{\omega_3}{\omega_0}\right)^2 = 1 + 2\frac{f_1}{f_0}\sqrt{1 + \frac{\cos k_a a + \cos k_b b}{2} - \sqrt{\frac{1+\cos k_c c}{2}(1+\cos k_a a)(1+\cos k_b b)}} \tag{15}$$

and

$$\left(\frac{\omega_4}{\omega_0}\right)^2 = 1 + 2\frac{f_1}{f_0}\sqrt{1 + \frac{\cos k_a a + \cos k_b b}{2} + \sqrt{\frac{1+\cos k_c c}{2}(1+\cos k_a a)(1+\cos k_b b)}} \tag{16}$$

where $\omega_0 = \sqrt{f_0/M}$ is used.

When using values for f_0 and f_1 from table 1, we find that all frequencies ($\omega_1, \omega_2, \omega_3$ and ω_4) have real values in the Brillouin zone. This means that the stable electric dipole waves with four branches exist in both KDP and DKDP.

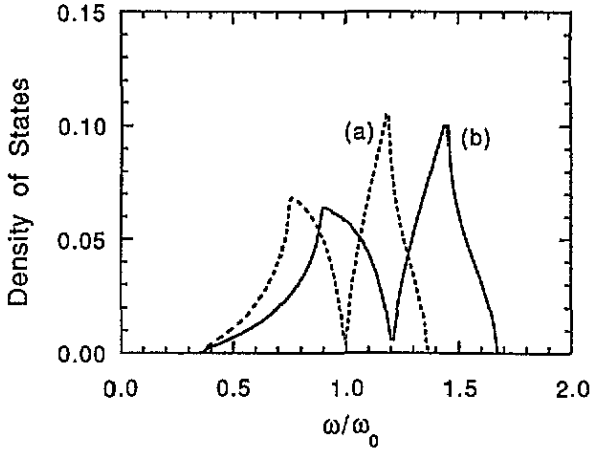

Figure 3. The density of states of the dipole waves (a) in KDP and (b) in DKDP.

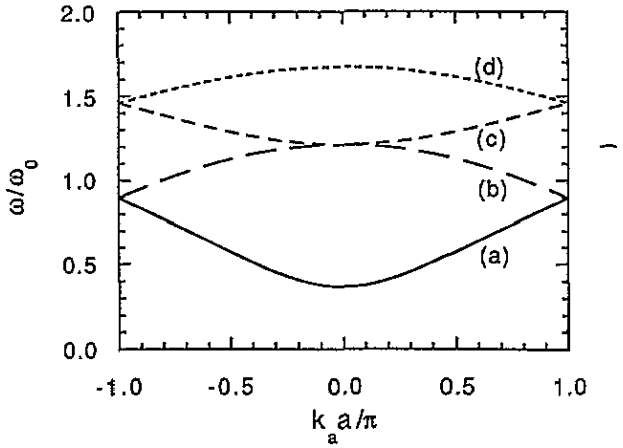

Figure 4. The dispersion relations of the dipole waves in DKDP for wave vectors parallel to the a axis. (a) $\omega_1(k_a)$, (b) $\omega_2(k_a)$, (c) $\omega_3(k_a)$, and (d) $\omega_4(k_a)$.

In figure 3, the density of states for the dipole waves is shown. As seen in this figure, it has two peaks. These peak positions show an isotope effect: the peak positions in DKDP are at frequencies about 1.2 times higher than those of KDP.

In order to clarify features of the dispersion of the dipole waves, as an example, the dispersion relation in the direction of the a axis in DKDP is shown in figure 4.

3.2. Quantization of the dipole waves

In the framework of the linear approximation, the motion of dipole moments could be regarded as for a set of harmonic oscillators. The quantization of the dipole waves may, therefore, be processed exactly in the same manner as for photons and phonons.

When using boson operators, $a_\nu^\dagger(\boldsymbol{k})$ and $a_\nu(\boldsymbol{k})$, called creation and annihilation operators, respectively, the Hamiltonian of the dipole waves is

$$H = \sum_{\nu=1}^{4} \sum_{k} \hbar\omega_\nu(k)[a_\nu^\dagger(k)a_\nu(k) + \tfrac{1}{2}] \tag{17}$$

and $\Delta\mu_{l,p}$ is expressed as

$$\Delta\mu_{l,p} = \left(\frac{\hbar}{NM}\right)^{1/2} \sum_{\nu,k} \frac{1}{\sqrt{2\omega_\nu(k)}} [g_p^\nu(k)e^{ik\cdot R_l}a_\nu(k) + g_p^{\nu*}(k)e^{-ik\cdot R_l}a_\nu^\dagger(k)] \tag{18}$$

where $g_p^\nu(k)$ is an eigenvector for eigenfrequency $\omega_\nu(k)$ obtained from equation (12) and $g_p^{\nu*}(k)$ is the complex conjugate of $g_p^\nu(k)$.

Note that there are the following relations:

$$\sum_{p=1}^{4} g_p^{\nu*}(k)g_p^{\nu'}(k) = \delta_{\nu,\nu'} \tag{19}$$

$$\sum_{\nu=1}^{4} g_p^{\nu*}(k)g_{p'}^{\nu}(k) = \delta_{p,p'} \tag{20}$$

and

$$g_p^\nu(-k) = g_p^{\nu*}(k) \tag{21}$$

for the eigenvectors and

$$[a_\nu(k), a_{\nu'}^\dagger(k')] = \delta_{\nu\nu'}\delta(k - k') \tag{22}$$

$$[a_\nu(k), a_{\nu'}(k')] = [a_\nu^\dagger(k), a_{\nu'}^\dagger(k')] = 0 \tag{23}$$

$$a_\nu(k)|n_\nu(k)\rangle = \sqrt{n_\nu(k)}|n_\nu(k) - 1\rangle \tag{24}$$

and

$$a_\nu^\dagger(k)|n_\nu(k)\rangle = \sqrt{n_\nu(k) + 1}|n_\nu(k) + 1\rangle \tag{25}$$

for the boson operators.

It is easy to calculate the thermal average of the square of fluctuations of dipoles, defined by

$$\langle\Delta\mu^2\rangle_T = \frac{1}{N}\left\langle \sum_{p=1}^{4} \sum_{l} \Delta\mu(R_l, p)^2 \right\rangle_T \tag{26}$$

from equation (18) by using equations (19)–(25). Here the thermal average $\langle\ldots\rangle_T$ is given by

$$\langle\ldots\rangle_T = \sum_i P_i\langle\chi_i|\ldots|\chi_i\rangle \tag{27}$$

where P_i is the probability distribution function for state i.

The result obtained is as follows:

$$\langle \Delta\mu^2 \rangle_T = \frac{\hbar}{NM} \sum_{\nu=1}^{4} \sum_{k} \frac{n_\nu(k) + \frac{1}{2}}{\omega_\nu(k)} \tag{28}$$

with

$$n_\nu(k) = \frac{1}{e^{\hbar\omega_\nu(k)/k_B T} - 1}. \tag{29}$$

At $T = 0$ K, therefore, the magnitude of the quantum fluctuations of dipole moments is evaluated by

$$\sqrt{\langle \Delta\mu^2 \rangle_{T=0}} = \left[\frac{\hbar\omega_0}{f_0} \frac{1}{N} \sum_{\nu=1}^{4} \sum_{k} \frac{\omega_0}{2\omega_\nu(k)} \right]^{1/2} \tag{30}$$

where $\omega_0 = \sqrt{f_0/M}$. To estimate $\sqrt{\langle \Delta\mu^2 \rangle_{T=0}}$, knowledge of ω_0 is required. This value will be estimated in section 5.

4. Scattering of thermal neutrons by the motion of protons due to the dipole waves

The scattering intensity of thermal neutrons by protons can be obtained from the scattering function defined by

$$S_{\text{inc}}(q, \omega) = \sum_{l,\alpha} M_{l,\alpha;l,\alpha}(q\omega) \tag{31}$$

for incoherent scattering and

$$S_{\text{coh}}(q, \omega) = \sum_{l,\alpha} \sum_{l',\alpha'} M_{l,\alpha;l',\alpha'}(q, \omega) \tag{32}$$

for coherent scattering, with

$$M_{l,\alpha;l',\alpha'}(q, \omega) = \sum_{i} P_i \sum_{f} \langle i | e^{-iq\cdot r_{l,\alpha}} | f \rangle \langle f | e^{iq\cdot r_{l',\alpha'}} | i \rangle \delta[\omega + (E_i - E_f)/\hbar]. \tag{33}$$

Here $|i\rangle$ and $|f\rangle$, respectively, are the initial and final states of the system; $r_{l,\alpha}$ is a position vector of a proton; and E_i and E_f, respectively, are energies of the initial and final states. Since we adopted here the unit cell shown in figure 2, each cell contains eight protons, whose position vectors $r_{l,\alpha}$ ($\alpha = 1, \ldots, 8$) are related to lattice vector R_l by

$$r_{l,\alpha} = R_l + s_\alpha + u_{l,\alpha} \tag{34}$$

where s_α is a position vector of the centre of an O–O bond measured from the origin of unit cell l.

To evaluate the scattering function of neutrons, knowledge of a matrix element $\langle i | e^{-iq\cdot r_{l,\alpha}} | f \rangle$ is required. In the adiabatic approximation, the matrix element is expressed as

$$\langle i | e^{-iq\cdot r_{l,\alpha}} | f \rangle = e^{-iq\cdot(R_l + s_\alpha)} \langle \chi_i | I_{l,\alpha} | \chi_f \rangle \tag{35}$$

with

$$I_{l,\alpha} = \int \psi^*_{l,\alpha} e^{-iq\cdot u_{l,\alpha}} \psi_{l,\alpha} \, d^3u_{l,\alpha} \tag{36}$$

where $|\chi_i\rangle$ ($|\chi_f\rangle$) is the initial (final) state of the dipole moments and $\psi_{l,\alpha}$ is the ground-state wave function of proton (l, α).

A proton in the ferroelectric phase is localized in a single potential valley deepened by the interaction between the proton and dipole moments (see figure 1). By using the coordinate axes shown in figure 5, therefore, the ground state wave function $\psi_{l,\alpha}$ is approximated as

$$\psi_{l,\alpha} = \psi^x_{l,\alpha} \psi^y_{l,\alpha} \psi^z_{l,\alpha} \tag{37}$$

with

$$\psi^x_{l,\alpha} = \left(\frac{m\omega_x}{\pi\hbar}\right)^{1/4} \exp\left[-\frac{m\omega_x}{2\hbar}(x_{l,\alpha} - x^0_{l,\alpha})^2\right] \tag{38}$$

$$\psi^y_{l,\alpha} = \left(\frac{m\omega_y}{\pi\hbar}\right)^{1/4} \exp\left[-\frac{m\omega_y}{2\hbar} y^2_{l,\alpha}\right] \tag{39}$$

and

$$\psi^z_{l,\alpha} = \left(\frac{m\omega_z}{\pi\hbar}\right)^{1/4} \exp\left[-\frac{m\omega_z}{2\hbar} z^2_{l,\alpha}\right] \tag{40}$$

where m is the proton mass, ω_x an angular frequency of the proton in the x direction, and so on. We assumed here that the wave function has its maximum value at $(x^0_{l,\alpha}, 0, 0)$.

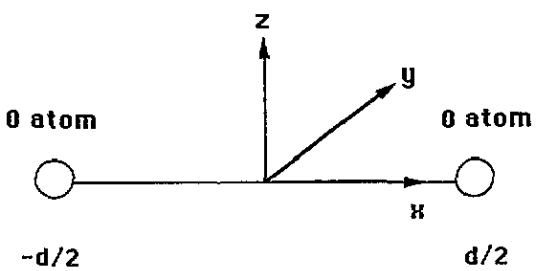

Figure 5. The coordinate axes used for describing the wave function of a proton.

We can calculate $I_{l,\alpha}$ from equation (36) using this wave function. The result is as follows:

$$I_{l,\alpha} = e^{-(\hbar/4m\omega_x)(q\cdot x_\alpha)^2} e^{-i(q\cdot x_\alpha)x^0_{l,\alpha}} e^{-(\hbar/4m\omega_y)(q\cdot y_\alpha)^2} e^{-(\hbar/4m\omega_z)(q\cdot z_\alpha)^2} \tag{41}$$

where x_α, y_α, and z_α are unit vectors defined by

$$u_{l,\alpha} = x_{l,\alpha} x_\alpha + y_{l,\alpha} y_\alpha + z_{l,\alpha} z_\alpha. \tag{42}$$

In our model, the wave function in the O–O direction, $\psi^x_{l,\alpha}$, strongly depends on a sum of dipole moments with two PO_4 tetrahedra connected by the proton, $\mu_i + \mu_j$, as described in section 2. Both ω_x and $x^0_{l,\alpha}$, therefore, depend on $\mu_i + \mu_j$. Considering the smallness of $\Delta\mu_i$ $(= \mu_i - \mu_s)$ in the ferroelectric phase, we assume these dependences as follows:

$$x^0_{l,\alpha} = x^0_\alpha(1 + d_{l,\alpha}) \tag{43}$$

and

$$\omega_x = \omega^0_x(1 + Cd_{l,\alpha}) \tag{44}$$

using $d_{l,\alpha}$ defined by

$$d_{l,\alpha} = \frac{\Delta\mu_i + \Delta\mu_j}{2\mu_s} \tag{45}$$

where x^0_α and ω^0_x, respectively, denote $x^0_{l,\alpha}$ and ω_x at $\mu_i + \mu_j = 2\mu_s$ and C is a constant. The dependence of the excitation energies of a proton on $\mu_i + \mu_j$ (see the previous letter [1]) indicates that C is of the order of unity.

When using equations (42), (43), and (44), $I_{l,\alpha}$ is rewritten as

$$I_{l,\alpha} = e^{-\eta_\alpha} e^{-i(q\cdot x_\alpha)x^0_\alpha} e^{-iw_\alpha d_{l,\alpha}} \tag{46}$$

with

$$\eta_\alpha = \frac{\hbar(q\cdot x_\alpha)^2}{4m\omega^0_x} + \frac{\hbar(q\cdot y_\alpha)^2}{4m\omega_y} + \frac{\hbar(q\cdot z_\alpha)^2}{4m\omega_z} \tag{47}$$

and

$$w_\alpha = (q\cdot x_\alpha)x^0_\alpha(1 - i(q\cdot x_\alpha)\gamma a^2/x^0_\alpha) \tag{48}$$

where γ is defined by

$$\gamma = \frac{\hbar C}{4m\omega^0_x a^2}. \tag{49}$$

For $M_{l,\alpha;l',\alpha'}(q,\omega)$ defined by equation (32), therefore, we obtain

$$M_{l,\alpha;l',\alpha'}(q,\omega) = G_{l,\alpha;l',\alpha'}\sum_i P_i \sum_f \langle\chi_i|e^{-iw_\alpha d_{l,\alpha}}|\chi_f\rangle\langle\chi_f|e^{iw^*_{\alpha'}d_{l',\alpha'}}|\chi_i\rangle\delta[\omega + (E_i - E_f)/\hbar] \tag{50}$$

with

$$G_{l,\alpha;l',\alpha'} = e^{-(\eta_\alpha+\eta_{\alpha'})}e^{-iq\cdot(R_l - R_{l'} + s_\alpha - s_{\alpha'})}e^{-i[(q\cdot x_\alpha)x^0_\alpha - (q\cdot x_{\alpha'})x^0_{\alpha'}]} \tag{51}$$

where w^*_α is the complex conjugate of w_α.

Table 2. Position vectors s_α, unit vectors x_α and the relation between $C_\alpha^\nu(k)$ and $g_p^\nu(k)$. Here, $C_\alpha^\nu(k)$ is expressed in units of $[(\omega_0/2\omega_\nu)\hbar\omega_0/Nf_0(\mu_s^H)^2]^{1/2}$.

α	s_α	x_α	$C_\alpha^\nu(k)$
1	$(a/4, 0, c/8)$	$(1, 0, 0)$	$g_1^\nu + g_2^\nu$
2	$(3a/4, 0, c/8)$	$(1, 0, 0)$	$g_1^\nu e^{ik_a a} + g_2^\nu$
3	$(a/4, b/2, 5c/8)$	$(1, 0, 0)$	$g_3^\nu + g_4^\nu$
4	$(3a/4, b/2, 5c/8)$	$(1, 0, 0)$	$g_3^\nu + g_4^\nu e^{ik_a a}$
5	$(a/2, b/4, 3c/8)$	$(0, 1, 0)$	$g_2^\nu + g_3^\nu$
6	$(a/2, 3b/4, 3c/8)$	$(0, 1, 0)$	$g_3^\nu e^{ik_b b} + g_4^\nu$
7	$(0, b/4, 7c/8)$	$(0, 1, 0)$	$g_1^\nu e^{ik_c c} + g_4^\nu$
8	$(0, 3b/4, 7c/8)$	$(0, 1, 0)$	$g_1^\nu e^{i(k_b b + k_c c)} + g_4^\nu$

If we write changes of dipole moments with two PO_4 tetrahedra connected by proton (l, α) as $\Delta\mu(R_n, p)$ and $\Delta\mu(R_{n'}, p')$, from equation (18), $d_{l,\alpha}$ is expressed as

$$d_{l,\alpha} = \sum_{\nu,k} [C_\alpha^\nu(k) e^{ik\cdot R_l} a_\nu(k) + C_\alpha^{\nu*}(k) e^{-ik\cdot R_l} a^{\nu\dagger}(k)] \tag{52}$$

where

$$C_\alpha^\nu(k) = \sqrt{\frac{\hbar}{2NM\omega_\nu(k)\mu_s^2}} [g_p^\nu(k) e^{ik\cdot(R_n - R_l)} + g_{p'}^\nu(k) e^{ik\cdot(R_{n'} - R_l)}]. \tag{53}$$

Note that $C_\alpha^\nu(k)$ is independent of l since $R_n - R_l$ and $R_{n'} - R_l$ are determined only by α. The relation between $C_\alpha^\nu(k)$ and g_p^ν is listed in table 2 with s_α and x_α, respectively, defined by equations (34) and (42).

We note here that $q\gamma a^2/x_\alpha^0 \sim 0.1$ for $qa = \pi$, since $\hbar\omega_x^0 \sim 0.1$ eV, $a \sim 7.5$ Å, $x_\alpha^0 \sim 0.2$ Å, and $C \sim 1$ for KDP and DKDP. This means that, in KDP (DKDP), a dominant contribution to the scattering function comes from a displacement of the proton position induced by changes of dipole moments, and not a deformation of the shape of the proton wave function described by ω_x. We, therefore, adopt the following approximation for w_α below:

$$w_\alpha = (q \cdot x_\alpha) x_\alpha^0. \tag{54}$$

Under this approximation, calculations of $M_{l,\alpha;l',\alpha'}(q, \omega)$ are processed in exactly the same manner as for scattering of thermal neutrons by phonons [14]. The result is as follows:

$$M_{l,\alpha;l',\alpha'}(q, \omega) = G_{l,\alpha;l',\alpha'} e^{-2W_{\alpha,\alpha'}} [\delta(\omega) + V_{l,\alpha;l',\alpha'}] \tag{55}$$

where

$$W_{\alpha,\alpha'} = \tfrac{1}{4} \sum_{k,\nu} [w_\alpha^2 |C_\alpha^\nu(k)|^2 + w_{\alpha'}^2 |C_{\alpha'}^\nu(k)|^2][2n_\nu(k) + 1] \tag{56}$$

and

$$V_{l,\alpha;l',\alpha'} = w_\alpha w_{\alpha'} \sum_{k,\nu} [C_\alpha^\nu(k) C_{\alpha'}^{\nu*}(k) e^{ik\cdot(R_l - R_{l'})} (n_\nu(k) + 1)\delta(\omega - \omega_\nu)$$
$$+ C_\alpha^{\nu*}(k) C_{\alpha'}^\nu(k) e^{-ik\cdot(R_l - R_{l'})} n_\nu(k)\delta(\omega + \omega_\nu)]. \tag{57}$$

The term with $\delta(\omega)$ comes from the elastic scattering and the other terms describe scattering with emission or absorption of a single energy quantum of the dipole waves.

By taking the sum over lattice vectors, we have the following expressions:

$$S_{\rm inc}(q,\omega)=\sum_{\alpha}G_{0,\alpha;0,\alpha}{\rm e}^{-2W_{\alpha,\alpha}}w_{\alpha}^{2}\sum_{k,\nu}|C_{\alpha}^{\nu}(k)|^{2}[(n_{\nu}(k)+1)\delta(\omega-\omega_{\nu})+n_{\nu}(k)\delta(\omega+\omega_{\nu})] \tag{58}$$

for the incoherent inelastic scattering and

$$S_{\rm coh}(q,\omega)=\sum_{\alpha}\sum_{\alpha'}G_{0,\alpha;0,\alpha'}{\rm e}^{-2W_{\alpha,\alpha'}}w_{\alpha}w_{\alpha'}\sum_{\nu}C_{\alpha}^{\nu}(q)C_{\alpha'}^{\nu*}(q)$$
$$\times[(n_{\nu}(q)+1)\delta(\omega-\omega_{\nu})+n_{\nu}(q)\delta(\omega+\omega_{\nu})] \tag{59}$$

for the coherent inelastic scattering.

We emphasize here that the scattering functions are proportional to $w_{\alpha}w_{\alpha'}$ for inelastic scattering processes with absorption or emission of a single energy quantum of the dipole waves. This means that these processes make no contribution to the inelastic scattering functions with scattering vector, q, parallel to the c axis, when all O–O bonds are perpendicular to the c axis.

5. Discussion

We found that there are electric dipole waves with dispersion in both KDP and DKDP, by which the motion of protons is induced, as a result of the strong coupling between protons and dipole moments. Furthermore, it was concluded that this motion of protons is detected by experiments of inelastic neutron scattering using scattering vector, q, perpendicular to the c axis. Thus it is necessary to examine in detail the scattering functions obtained and to make a comparison between them and experimental results to judge the reliability of the present result. Since inelastic scattering processes with loss of energy by a neutron to a crystal are observed under ordinary experimental circumstances, we will discuss below scattering with emission of a single energy quantum of the dipole waves.

For simplicity, we consider here scattering of thermal neutrons for q parallel to the a axis. In this case, the scattering function for the incoherent scattering is as follows:

$$S_{\rm inc}(q,\omega)=4(q\Delta)^{2}{\rm e}^{-q^{2}U}\sum_{k,\nu}|C_{\alpha}^{\nu}(k)|^{2}[n_{\nu}+1]\delta(\omega-\omega_{\nu}) \tag{60}$$

with

$$U=2\hbar/4m\omega_{x}^{0}+\Delta^{2}\sum_{k,\nu}|C_{\alpha}^{\nu}(k)|^{2}[2n_{\nu}+1] \tag{61}$$

where $q=|q|$ and $\Delta(=|x_{\alpha}^{0}|)$ is 0.18 Å for KDP and 0.22 Å for DKDP, respectively. Here, we used the fact that both $\sum_{k,\nu}|C_{\alpha}^{\nu}(k)|^{2}[2n_{\nu}+1]$ and $\sum_{k,\nu}|C_{\alpha}^{\nu}(k)|^{2}[n_{\nu}+1]\delta(\omega-\omega_{\nu})$ do not depend on α. For the incoherent inelastic scattering, using some fixed value of q, therefore, the ω dependence of the scattering intensity is determined by $\sum_{k,\nu}|C_{\alpha}^{\nu}(k)|^{2}[n_{\nu}+1]\delta(\omega-\omega_{\nu})$.

In figure 6, these values at $T=0$ and $T=0.4\hbar\omega_{0}/k_{\rm B}$ are shown for KDP. As seen in this figure, profiles of the scattering function have a dip at ω_{0} like the density of states

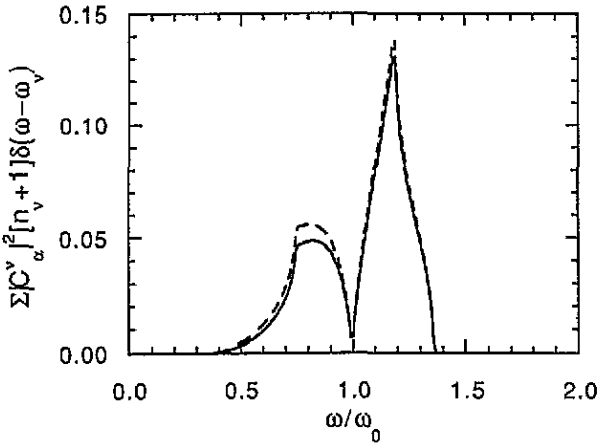

Figure 6. The ω dependence of the scattering function for the incoherent scattering in KDP. The results at $T = 0$ and at $T = 0.4\hbar\omega_0/k_B$ are shown by solid and broken lines, respectively. Note here that $0.4\hbar\omega_0/k_B \sim 110$ K, if we assume $\hbar\omega_0 = 25$ meV (see section 5).

for the dipole waves. Note that the height of the peak at $\omega = 1.2\omega_0$ increases little with increasing temperature.

The temperature dependence of equation (60) also appears from that of U. This gives rise to the decrease of the scattering intensity with increasing temperature.

It is important to recognize here that the temperature dependence of the incoherent inelastic scattering function is not determined by only the Bose distribution function n_ν in equation (60). One of the other factors that determine the temperature dependence is the population of protons in the ground state. The population decreases with increasing temperature, due to the excitation of protons to excited states. This effect decreases the scattering intensity with increasing temperature.

Another factor is that the linear approximation adopted here is inadequate at high temperatures. Especially at temperatures near or above T_c, deviations of dipole moments from μ_s become large and a considerable number of dipoles flip to the opposite direction. This means that the lifetime of a dipole wave becomes short and the transfer of a proton (deuteron) between two sites occurs frequently.

These two factors give rise to a decrease of the height and a broadening of the peaks of the scattering function with increasing temperatures. At sufficiently high temperatures above T_c, especially, the peaks should disappear. We emphasize here that the peaks disappear when q is parallel to the c axis.

In an experiment on the incoherent inelastic scattering for KDP performed by Shibata and Ikeda [6], a single peak has been observed at 28 meV, in addition to peaks corresponding to the excitation of protons to excited states. They found that the peak at 28 meV has the following features: (1) the peak intensity becomes small gradually when the temperature increases and vanishes at high temperatures above T_c and (2) there is no observation of this peak for q parallel to the c axis. These properties agree well with those of the peak at $\omega = 1.2\omega_0$. Accordingly, it is reasonable to consider that the observed peak at 28 meV corresponds to the peak at $\hbar\omega = 1.2\hbar\omega_0$. If it does, we may take $\hbar\omega_0 \sim 25$ meV.

From the value for $\hbar\omega_0$ and equation (30), quantum fluctuations of dipole moments may be estimated: $\sqrt{\langle\Delta\mu^2\rangle} = 0.46\mu_s^H$ for KDP and $\sqrt{\langle\Delta\mu^2\rangle} = 0.35\mu_s^H$ for DKDP. These values indicate that both KDP and DKDP are systems with large quantum fluctuations of dipole

moments. Thus we conclude that the broadening of the distribution of the excitation energy for the motion of protons along the O–O bond direction is considerable even at $T = 0$ K, as predicted in our previous paper [2].

Next we will discuss the coherent scattering. For q parallel to the a axis, using U defined by equation (61), the coherent inelastic scattering function is written as

$$S_{\mathrm{coh}}(q,\omega) = q^2 \mathrm{e}^{-q^2U} \sum_{\alpha=1}^{4} \sum_{\alpha'=1}^{4} x_\alpha^0 x_{\alpha'}^0 \mathrm{e}^{-\mathrm{i}q(s_\alpha - s_{\alpha'})} \mathrm{e}^{-\mathrm{i}q(x_\alpha^0 - x_{\alpha'}^0)} \sum_{\nu=1}^{4} C_\alpha^\nu(q) C_{\alpha'}^{\nu *}(q)[2n_\nu + 1]\delta(\omega - \omega_\nu). \tag{62}$$

This function depends on the configuration of protons (deuterons) strongly. We calculated the incoherent scattering function numerically for two periodic configurations of protons (deuterons) shown in table 3. From these calculations, we found that only $S_{\mathrm{coh}}(q, \omega_1(q))$ has a significant scattering intensity for configuration a, whereas for configuration b, only $S_{\mathrm{coh}}(q, \omega_3(q))$ is non-vanishing.

Table 3. Configurations of deuterons considered in the text, a and b. We assumed that a displacement of a deuteron measured from the centre of the O–O bond, x_α^0, is Δ, $-\Delta$, or 0. Here, Δ is 0.18 Å for KDP and 0.22 Å for DKDP.

x_α^0	a	b
x_1^0	Δ	Δ
x_2^0	$-\Delta$	$-\Delta$
x_3^0	$-\Delta$	Δ
x_4^0	Δ	$-\Delta$
x_5^0	Δ	0
x_6^0	$-\Delta$	0
x_7^0	$-\Delta$	0
x_8^0	Δ	0

Configuration a satisfies the ice rule, in which all PO_4 tetrahedra have two protons (deuterons) on their nearest-neighbour positions. At $T = 0$ K, this configuration should be realized in both KDP and DKDP, because of the symmetry of the crystal. On the other hand, at temperatures near T_c, configuration b is also expected to be realized in some local regions, since the number of dipoles that flip to the opposite direction increases with increasing temperature. This means that, at least, both of the dispersion relations, $\omega_1(q)$ and $\omega_3(q)$, are observed in coherent inelastic scattering experiments at high temperatures near T_c.

Recently, for DKDP, Todate *et al* [15] performed experiments on the coherent inelastic scattering in ferroelectric phases at temperatures near T_c. In these experiments, they observed a dispersion relation with a minimum energy of $\sim$ 10 meV at the Γ point and a maximum energy of $\sim$ 20 meV at the zone boundary. This dispersion relation is similar to one obtained for configuration a in our calculations when $\hbar\omega_0 = 25$ meV is used. They also observed another dispersion relation with a minimum energy of $\sim$ 25 meV at the Γ point and a maximum energy of $\sim$ 30 meV at the zone boundary. The feature of this dispersion relation is also similar to one for configuration b. In spite of such agreement, at present, it is not clear whether or not the observed dispersion relations are those of the dipole waves obtained here. In order to confirm our inference, more detailed studies are required, including experiments at low temperatures.

Finally, we make remarks as to the validity of the present calculation. In our calculations, only the nearest-neighbour interaction for the direct interaction between dipole moments is taken into account, for simplicity. This approximation seems to be inadequate for calculations of some quantities. For example, the density of states of the dipole waves decomposes to four peaks, when the dipole interaction with next-nearest neighbours cannot be disregarded. Thus we must admit that there is a possibility that the peak structure obtained here is incorrect. It is, therefore, necessary to perform more detailed calculations including the long-range part of the direct interaction between dipole moments to obtain qualitative agreement with the structure of peaks measured by inelastic scattering experiments. Nevertheless, we believe that the present calculation is enough to conclude the existence of the dipole waves in KDP and DKDP and to confirm the reliability of our model because many of the properties discussed here are expected to be unchanged by the long-range interaction.

6. Conclusion

We showed that our model, proposed to explain the ferroelectric phase transition in KDP, predicts that stable dipole waves exist in a ferroelectric phase and quantum fluctuations of the dipole moments are considerable. We also found that the motion of protons induced by the dipole waves makes an important contribution to the neutron scattering. From the comparison of the scattering functions obtained here with experiments on inelastic neutron scattering, we conclude that our model gives a consistent account of properties of the ferroelectric phase in KDP and DKDP. This conclusion is regarded as specific evidence that our model is useful to describe the physics of KDP crystals.

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