Quantum Paraelectricity in KD_2PO_4 and KH_2PO_4 under High Pressure

Shoichi Endo
Research Center for Material Science at Extreme Conditions, Osaka University, Toyonaka, Osaka 560-8531, Japan

Kiyoshi Deguchi
Department of Material Science, Shizuoka Institute of Technology, Fukuroi, Shizuoka 437-8555, Japan

Masaharu Tokunaga*
Department of Physics, Graduate School of Science, Hokkaido University, Sapporo 060-0810, Japan

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Phase transition temperatures of hydrogen-bonded ferroelectrics DKDP (KD_2PO_4) and KDP (KH_2PO_4) vanish at pressure p larger than respective critical pressures p_c. The dielectric constants ε_c has been observed to be suppressed with decreasing temperature for $p > p_c$ and analyzed as the quantum paraelectricity by fitting with the Barrett formula in terms of three parameters. The dependences of the three parameters on $p - p_c$ are found to be expressed by almost similar lines, and the phase transition mechanism near p_c is explained from the viewpoint of an anharmonic phonon system in KDP and DKDP.

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Hydrogen-bonded crystals KDP (KH_2PO_4) and DKDP (KD_2PO_4) are well known to display typical order-disorder–type dielectric and thermal behavior associated with their phase transitions at ambient pressure [1]. It has been recently observed in these crystals under high pressure p, however, that the Curie constant C does not decrease in magnitude above a crossover pressure p_0 in spite of the decrease of transition temperature T_c down to 0 at a critical pressure p_c. This experimental result indicates that these crystals undergo a gradual crossover to the displacive type in the mechanism of phase transition around p_0 [2]. The temperature dependence of the dielectric constant ϵ_c along the c axis displays downward deviation from the Curie-Weiss law near $T = 0$ in KDP and DKDP at $p > p_c$ [2–4]. Similar suppressions in dielectric constant have been observed in perovskite-type crystals at ambient pressure. This phenomenon is known as quantum paraelectricity [5], which has been described by the Barrett formula [6]. The suppression in ϵ_c in KDP under high pressure was described by Samara [3] as evidence of the proton tunneling model. The same suppression is also observed in DKDP [2], however, where the tunneling motion of deuterons is believed not to be realized.

The Barrett formula is derived for a lattice vibration system which undergoes a ferroelectric phase transition as follows. Let $Q(\boldsymbol{R})$ be the local coordinate of the ferroelectric mode which describes the phase transition in the $\boldsymbol{R}$th unit cell. The Hamiltonian of this system under an external field E along the ferroelectric axis is given in the form

$$H = \sum_{\boldsymbol{R}} \left\{ \frac{1}{2} m^* \omega_h^2 Q^2(\boldsymbol{R}) + \frac{1}{4} B Q^4(\boldsymbol{R}) - e^* Q(\boldsymbol{R}) E \right\} - \frac{1}{2} \sum_{\boldsymbol{R},\boldsymbol{R}'} e^{*2} J(\boldsymbol{R},\boldsymbol{R}') Q(\boldsymbol{R}) Q(\boldsymbol{R}'),$$

where m^* and e^* stand for the effective mass and the effective charge of an anharmonic oscillator $Q(\boldsymbol{R})$, respectively. The first term describes the summation over Hamiltonians of independent oscillators moving in respective short range adiabatic potentials associated with variations of electronic structures. The harmonic frequency of an oscillator is denoted by ω_h, and the coefficient of the anharmonic term by B. These two terms are derived by expanding the adiabatic potential for $Q(\boldsymbol{R})$ in terms of its power series. The interaction between the oscillators in the $\boldsymbol{R}$ and $\boldsymbol{R}'$ cells is given by $J(\boldsymbol{R},\boldsymbol{R}')$, as introduced in the second term.

The renormalized frequency ω_s of a single oscillator is obtained by renormalizing the anharmonic effect as

$$m^* \omega_s^2 = m^* \omega_h^2 + 3B \langle Q^2(\boldsymbol{R}) \rangle , \tag{2}$$

where $\langle \cdots \rangle$ denotes the thermal average in the harmonic approximation. With the use of the local field $e^* J(0) = \sum_{\boldsymbol{R}} e^* J(\boldsymbol{R})$, the temperature dependence of the dielectric constant is given by

$$\epsilon_c - \epsilon_\infty = \frac{N e^{*2}}{m^* \omega_s^2 - e^{*2} J(0)} , \tag{3}$$

where N stands for the number of unit cells, and ϵ_∞ is the dielectric constant at a high frequency limit.

The Barrett formula is derived by the quantum statistical mechanical calculation of $\langle Q^2(\boldsymbol{R}) \rangle$ near $T = 0$:

$$\langle Q^2(\boldsymbol{R}) \rangle = \frac{h}{2m^* \omega_h} \coth\left(\frac{h \omega_h}{2kT} \right). \tag{4}$$

By rearranging the result in terms of three parameters M_B, T_{1B}, and T_{0B}, we obtain [6]

$$\epsilon_c - \epsilon_\infty = \frac{M_B}{(T_{1B}/2) \coth(T_{1B}/2T) - T_{0B}} . \tag{5}$$

The parameter T_{1B} is defined from the harmonic frequency

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ω_h of a dielectric unit $e^*Q(\boldsymbol{R})$ as $kT_{1B} \equiv h\omega_h$. The parameter M_B is related to ω_h by the definition

$$M_B = Ne^{*2}\,\frac{m^*\omega_h^2}{3kB}\,, \tag{6}$$

and the parameter T_{0B} is defined by

$$kT_{0B} = [e^{*2}J(0) - m^*\omega_h^2]\,\frac{m^*\omega_h^2}{3B}\,. \tag{7}$$

The transition temperature T_c is defined by the equation obtained by considering the denominator in Eq. (5) to be equal to zero.

If the ferroelectric interaction $J(0)$ originates mainly from long range electrostatic interactions, its magnitude increases with increasing p through the decrease of unit cell volume v as $J(0) \propto v^{-1}$ [7]. The decrease of T_{0B} with increasing p has been explained from the fact that the increase of ω_h^2 is superior to that of $J(0)$. The increase of M_B with increasing p is concluded, if only the increase of ω_h is taken into account. Since the concerned ferroelectric mode interacts with other modes through anharmonic terms in a general theory of lattice vibration, the average in Eq. (4) should be given in the summation over the same expressions given at various frequencies: The parameter T_1 is expressed as $kT_1 = h\omega_{\mathrm{eff}}$ with the use of effective frequency ω_{eff} [5].

Figure 1 shows the results of fitting the formula

$$\epsilon_c - \epsilon_\infty = \frac{M}{(T_1/2)\coth(T_1/2T) - T_0} \tag{8}$$

with temperature dependences of ϵ_c in KDP and DKDP. The local coordinate in this system is considered to be the cooperative motion of two protons (deuterons) and the quasirotation of a PO_4 tetrahedron [8]. The experimental data are well fitted to Eq. (8). The dependences of parameters T_1 and T_0 on p for $p > p_c$ are evaluated in Fig. 2 together with the extrapolated Curie temperature T_e for $p < p_c$. The Curie-Weiss law holds well, and T_e is in accordance with T_c for $p \ll p_c$. The pressure at the intersection of $T_1/2$ and T_0 is defined in this study as the critical pressure p_c where T_c becomes zero. The parameter T_0 decreases and T_1 increases with increasing $p - p_c$. It should be noted that the difference between T_e and T_0, in other words, the quantum effect, becomes noticeable for $p > p_c$. The parameter M remains constant in this high pressure range as though it is extrapolated from the behavior of C for $p < p_c$, as shown in Fig. 3. There exists a significant difference in the magnitude of M between KDP and DKDP.

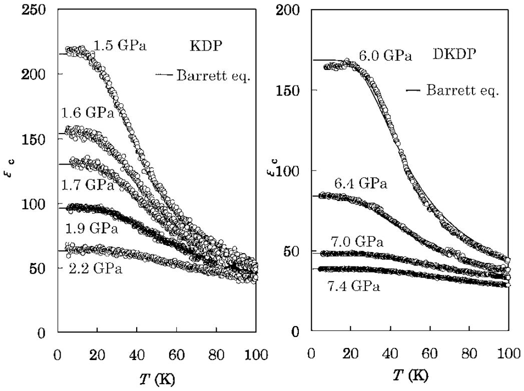

FIG. 1. Fitting the Barrett formula with the experimental dielectric constant ϵ_c for $p > p_c$ in KDP (left) and DKDP (right).

The p dependences of the three parameters provide us with useful information to discuss qualitatively the dependences of microscopic parameters on p if compared with their definitions derived from the Hamiltonian given in Eq. (1) as follows. The decrease of T_0 with increasing p is in accordance with the prediction of T_{0B} derived from that of ω_h in Eq. (5). Since the Barrett formula is well fitted with the experimental results, T_1 is considered to be described by ω_{eff}, which will become hard with increasing p, in general. The fact that M remains constant is, however, inconsistent with the fact that only ω_h increases with increasing p. Therefore, it is natural to conclude that not only the coefficient of the second-order term $m^*\omega_h^2$ but also that of the fourth-order term B increases with increasing p, since both quantities are derived from the same adiabatic potential for $Q(\boldsymbol{R})$ in the Barrett formula.

In order to compare the dependences of the three parameters on p in KDP and DKDP, they are given as functions of $p - p_c$ in Fig. 4. No difference in magnitude of T_0 and T_1 between KDP and DKDP suggests that the dependence of the phase transition mechanism on p near $p \sim p_c$ should be explained from the same point of view. As far as the quantum paraelectricity under high pressure is concerned, the mechanism of phase transition in these crystals is considered to be as that of an anharmonic phonon system.

The same mathematical form is derived for ϵ_c in the proton tunneling model [9], where the dependence of the soft

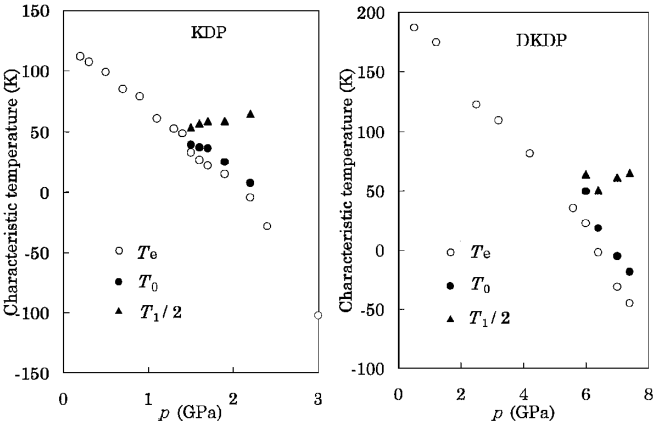

FIG. 2. Dependences of T_0 (solid circles) and T_1 (closed triangles) at $p < p_c$ together with extrapolated Curie temperature (open circles) on pressure p at $p < p_c$ in KDP (left) and DKDP (right).

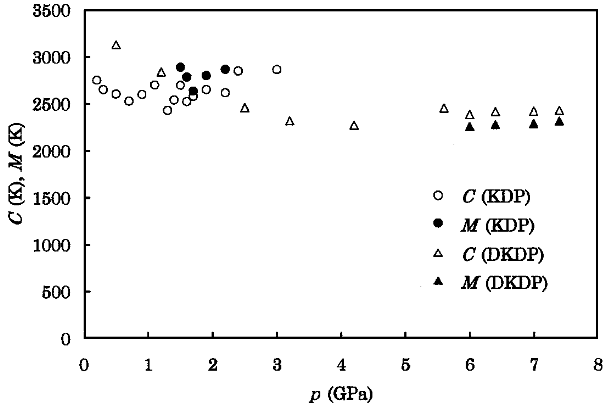

FIG. 3. Dependences of C (open symbols) and M (solid symbols) on pressure p in KDP (circles) and DKDP (triangles).

ferroelectric mode frequency on temperature originates from the distribution of tunneling protons over two levels separated by the tunneling frequency $2\Omega_t$. The dielectric constant ϵ_c is arranged in the same form as Eq. (5) with the dielectric constant ϵ_0 independent of proton motions:

$$\epsilon_c - \epsilon_\infty = \frac{M_t}{\Omega_t \coth(\Omega_t/kT) - T_{0t}}. \tag{9}$$

The suppression of ϵ_c in KDP has been explained by this equation as evidence of the tunneling proton model [3]. The tunneling frequency $2\Omega_t$ plays the role of kT_1. The parameters M_t and T_{0t} are given by

$$kM_t = N\mu_t^2, \qquad kT_{0t} = \mu_t^2 J(0), \tag{10}$$

where the effective dipole moment associated with the motion of a proton between two minima is given by μ_t, and the summation of effective interactions among protons (deuterons) by $\mu_t^2 J(0)$. From Eq. (9), T_c is given by

$$T_c = T_{0t}\frac{q}{\tanh^{-1} q} \qquad \left(q \equiv \frac{\Omega_t}{kT_{0t}}\right). \tag{11}$$

In the naive tunneling model, T_{0t} is considered to be the same in KDP and DKDP, and the decrease of T_c in KDP is attributed to the tunneling frequency Ω_t far larger than that in DKDP. The application of p has been considered to correspond to the partial substitution of D by H in DKDP, since Ω_t would be increased by the reduction of the hydrogen-bonded length, and, thus, the increase of the overlap integral between proton wave functions in a double well. Figure 4 suggests that DKDP and KDP are nearly equal in the magnitudes of $2\Omega_t (= kT_1)$ and $\mu_t^2 J(0)$ $(= kT_0)$ at the same $p - p_c$. The transition temperature T_c deviates from T_e to vanish owing to the quantum effect T_1 at $p \geq p_c$, but T_c is nearly equal to T_e at $p < p_c$ where $T_1/2$ is smaller than T_0.

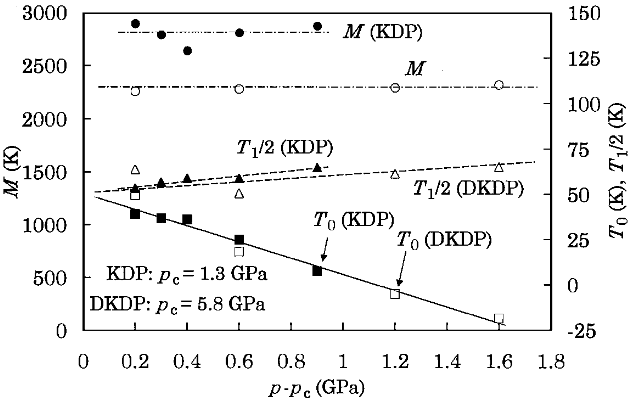

FIG. 4. Dependences of the three parameters on $(p - p_c)$ in KDP (solid symbols) and DKDP (open symbols).

Figure 4 indicates that the maximum value of $\Omega_t = T_1/2$ is less than 65 K. The tunneling frequency $2\Omega_t$ becomes smaller as p decreases down to ambient pressure, where T_c is 213 K in DKDP, and 123 K in KDP. Even if we set $\Omega_t = 0$ (which means $T_{0t} = 213$ K) in DKDP in Eq. (11), $\Omega_t < 65$ K cannot explain the decrease of T_c in KDP without taking into account the marked decrease of T_{0t} down to about 123 K. The tunneling frequency Ω_t far smaller than T_{0t} cannot explain the decrease of T_c in KDP. This fact was already pointed out at the early stage in the study of the tunneling model [10]. The decrease of T_e in KDP at $p < p_c$ should be explained on the basis of quantum effects other than tunneling [11]. From these discussions on the basis of the magnitude of Ω_t, it is concluded that the naive tunneling proton model should be improved so as to overcome these inconsistencies with the present experimental results.

After recent spectroscopic and calorimetric studies on the molecular crystal $C_{13}H_6BrOOH$ (BHP) with hydrogen bonds within molecules, evidence of $2\Omega_t$ was found in BHP where no phase transition is observed down to 0 K, and an order-disorder–type phase transition is observed at 34 K in the deuterated crystal [12] at ambient pressure. This result implies that tunneling motion of protons exists in hydrogen-bonded crystals where no phase transition is observed down to $T = 0$. The magnitude of $2\Omega_t$ determined by Matsuo *et al.* [12] is similar to T_1 in Fig. 4. Thus, we cannot exclude the possibility of tunneling protons realized in KDP at $p > p_c$, though the decrease of T_c should be attributed to the decrease of T_{0t} at $p < p_c$ as mentioned in relation to Fig. 2 contrary to the naive tunneling model. The possibility of tunneling deuterons in DKDP is also suggested along these lines, however, judging from the magnitude of T_1 at $p > p_c$. It is impossible only from a dielectric study, however, to conclude whether T_1 is due to Ω_t or ω_{eff} in KDP and DKDP for $p > p_c$.

In conclusion, the suppression of a dielectric constant near $T = 0$ realized under high pressure in KDP and DKDP has been analyzed in terms of the Barrett formula, and is understood as the quantum paraelectricity. The p dependences of the parameters used to fit the Barrett formula are evaluated, and the origin of the p dependences has been attributed to the increase of the adiabatic potential for the ferroelectric displacement under high pressure, from the microscopic point of view. From these results, the phase transition mechanism in KDP and DKDP is concluded to be of the displacive type as far as the temperature variation under high pressure is concerned, in contrast to the dielectric and thermal behavior of the order-disorder type at ambient pressure.

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*Electronic address: tokunaga@statphys.sci.hokudai.ac.jp

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