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Vanishing of T_c and appearance of quantum paraelectricity in KD_2PO_4 and KH_2PO_4 under high pressure

S Endo¹, K Deguchi² and M Tokunaga³

¹ Research Centre for Materials Science at Extreme Conditions, Osaka University, Toyonaka, Osaka 560-8531, Japan

² Department of Materials Science, Shizuoka Institute of Science and Technology, Fukuroi, Shizuoka 437-8555, Japan

³ Department of Physics Graduate School of Science, Hokkaido University, Sapporo 080-0810, Japan

E-mail: endo@rcem.osaka-u.ac.jp

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Abstract

The temperature dependences of the dielectric constants of the hydrogen-bond ferroelectrics KH_2PO_4 (KDP) and KD_2PO_4 (DKDP) were measured under high hydrostatic pressure. Their ferroelectric transition temperatures T_c monotonically decreased with increasing pressure and the ferroelectric state vanished at p_c : 1.7 GPa for KDP and 6.1 GPa for DKDP. On the other hand, the Curie constant remained finite at p_c , which indicates that the ferroelectric phase transition at high pressure is of displacive type. At pressures around p_c , quantum paraelectricity was observed in KDP and DKDP.

1. Introduction

Mechanisms of ferroelectric transitions are classified into two types: the order–disorder type and the displacive type. In the former, permanent electric dipoles are in incessant reorientational stochastic motion between the two orientations above the transition temperature T_c . They are ordered in one of the two orientations below T_c . In the latter, one of optical lattice vibrational modes becomes unstable at T_c with decreasing temperature. This dependence of the vibrational frequencies on temperature T originates from the anharmonicity in the lattice vibration system.

KH_2PO_4 (KDP) is a ferroelectric with a T_c of about 123 K. Its deuterated isomorph, KD_2PO_4 (DKDP), has a much higher T_c of about 229 K. Such an enormous isotope effect on T_c indicates that proton (deuteron) motion plays the essential role in the ferroelectric transition in KDP and its family, and many years of research have been accumulated. However, the transition mechanism is still controversial [1]. Disordered configurations of protons over two

equilibrium positions above T_c become ordered below T_c [2]. The spontaneous polarization in KDP is, however, attributed to displacements of K, P and O atoms associated with the ordering of the two protons that brings about the distortion of the PO_4 tetrahedra. The reorientation of an H_2PO_4 dipole causes distortion, and is called *quasirotation* [3]. One may argue that ordering of protons brings about the quasirotation of H_2PO_4 . However, as in *the chicken and the egg* controversy, one may conversely argue that the quasirotation brings about the proton ordering [4]. Although the problem of proton tunnelling [5] in KDP is still controversial, it is widely accepted that DKDP behaves as a classical order–disorder-type ferroelectric whose dielectric, optical and thermodynamical properties can be understood without invoking tunnelling [6–8].

An empirical law has been accepted regarding the pressure dependence of T_c in ferroelectrics: $dT_c/dp > 0$ for the order–disorder type; and $dT_c/dp < 0$ for the displacive type. For hydrogen-bond ferroelectrics such as KDP and DKDP, however, $dT_c/dp < 0$ in spite of the order–disorder type of behaviour around ambient pressure. This is one of reasons that hydrogen-bond ferroelectrics are distinguished from those of the typical order–disorder type. Vanishing of T_c in KDP was already reported by Samara [9] above $p_c = 1.7$ GPa. Hikita *et al* [10] also reported the vanishing of T_c above $p_c = 1.48$ GPa in KH_2AsO_4 . Decrease of T_c with pressure in DKDP was reported up to 3.8 GPa by Samara [11], but the vanishing of T_c was not realized due to the insufficient pressure. In this paper, we report the vanishing of T_c in DKDP [12, 13] and the appearance of quantum paraelectricity at low temperatures around p_c in KDP and DKDP.

2. Experimental method

Single crystals of KDP and $\text{KH}_{2(1-x)}\text{D}_{2x}\text{PO}_4$ were grown at 45 °C by slowly cooling a saturated aqueous solution, which contained D_2O in the latter case. The sample of DKDP used in the present experiment was 80% deuterated, as estimated from $T_c = 205$ K at ambient pressure using the T_c versus the deuterium content x relation proposed by Samara [14]. Two thin copper wires were attached with silver paste on the gold-plated top and bottom surfaces of the sample disc, the axis of which was parallel to the c -axis of the tetragonal lattice. The typical dimensions of the disc were approximately 1.0 mm diameter and 0.5 mm thickness. The dielectric constants were measured using a YHP4192A impedance analyser.

The sample was compressed by a multianvil apparatus driven by a hydraulic press and was simultaneously cooled down to 4.2 K by immersing the whole anvil assemblage in liquid helium. The experiments were performed under hydrostatic conditions as the sample was sealed with a liquid pressure medium Fluorinert in a Teflon capsule, which was set in a cubic pyrophyllite cell. The pressure was calibrated using the fixed points of Bi and the press load was maintained constant during the cooling and warming processes in the experiment.

3. Experimental results

The temperature dependences of the dielectric constant ϵ_c along the ferroelectric c -axis for KDP and DKDP are given at various pressures in figure 1, where the p -dependence of the geometric electric capacitance was considered by using those of the lattice constants [15]. The temperature where ϵ_c attains a maximum is defined as T_c . There was monotonic decrease with increasing p , as shown in figure 2. Under high pressure ($p > p_c = 1.7$ GPa (KDP) and 6.1 GPa (DKDP)), ϵ_c does not take a maximum as a function of T . It approaches a constant value at zero kelvin. The ferroelectric state vanishes in DKDP at pressure over three times that for KDP; this is another larger isotope effect.

The Curie constants C were evaluated from figure 3 in the case of DKDP by fitting ϵ_c to the Curie–Weiss law, and the dependence of the extrapolated Curie temperature T_0 on p is

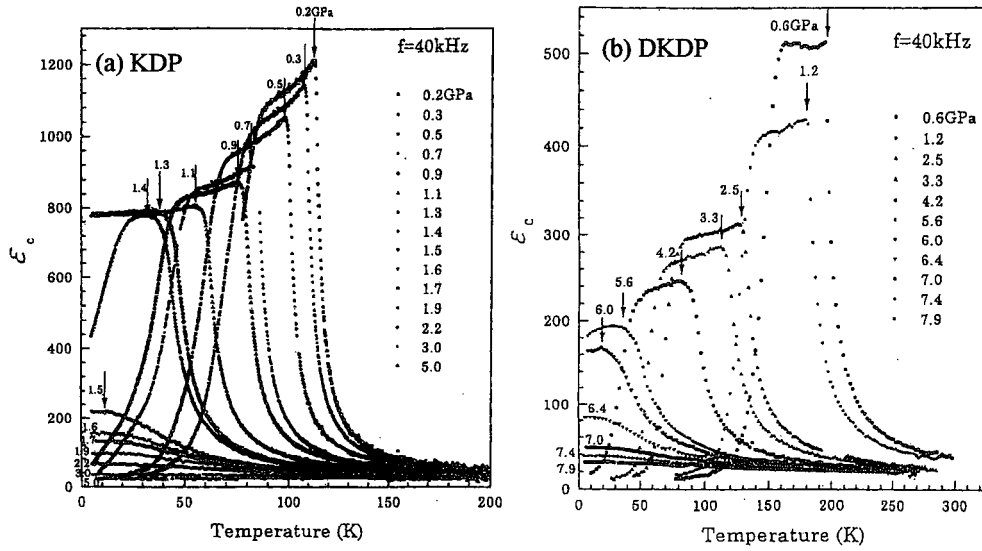


Figure 1. The temperature dependence of the dielectric constant ϵ_c along the c -axis of (a) KDP and (b) DKDP.

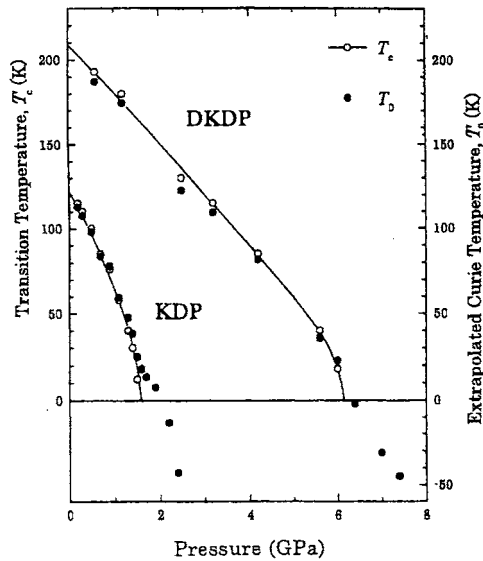


Figure 2. Pressure dependences of the transition temperature T_c and T_0 for KDP and DKDP. The lines are guides to the eye to T_c .

shown in figure 2. The dependence of C on p is shown in figure 4. The Curie constant C of KDP is almost constant, whereas that of DKDP initially decreases in parallel to T_c , but is saturated to 2.4×10^3 K above $p_0 \sim 4$ GPa. The effective dipole moments μ_{eff} have been evaluated using the relation $k_B C = N \mu_{eff}^2$, where N denotes the density of dipoles derived from the dependences of the lattice constants on p [15]. The dependence of μ_{eff} on p also reveals a saturation value similar to that in C .

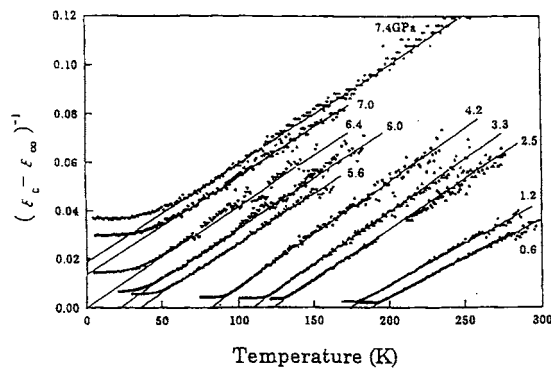


Figure 3. Curie-Weiss fits to $(\epsilon - \epsilon_c)^{-1}$ at various pressures in DKDP. The value of ϵ_∞ is 11 ± 2 , from least-squares fits. The straight lines in the figure are calculated ones.

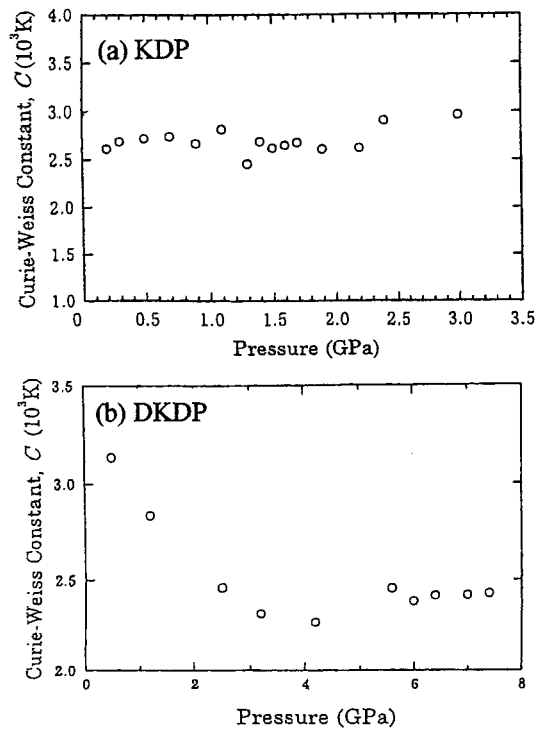


Figure 4. The pressure dependence of the Curie constant C for (a) KDP and (b) DKDP.

4. Discussion

4.1. Vanishing T_c with finite C

Let the electric polarizability be α for a dielectric unit. As the following discussion also holds for macroscopic polarization, a dielectric unit can be assigned as an assembly of dipoles in a

small region. The dielectric constant ε_c is given in terms of α by

$$\varepsilon_c = 1 + \frac{\alpha/v}{\varepsilon_0(1 - (\alpha/v)L)}, \quad (1)$$

where L indicates the local electric field that depends on the crystal structure, v is the volume of the dielectric unit, and ε_0 is the dielectric constant of vacuum. Since we are interested in the dependence of a macroscopic quantity ε_c on T under high pressure, it would be appropriate to examine the experimental results on the simplest basis. Thus, we introduce a difference in α only in the dependence on T between reorientational stochastic motion and anharmonic oscillation. Motion of the dielectric unit means quasirotational motion of D_2PO_4 dipoles in DKDP.

In the order–disorder-type ferroelectrics, C has a simple relation with T_c :

$$C \approx (\varepsilon_\infty + 2)T_c, \quad (2)$$

where ε_∞ indicates the high-frequency dielectric constant independent of T . This relation is derived from the assumption of a Curie's law $\alpha_d = \alpha_e + (a/T)$ for the stochastic motion of a dielectric unit with a constant a and polarizability α_e independent of T . Substituting α_d for α in equation (1), and rearranging it as

$$\varepsilon_c = \varepsilon_\infty + \frac{C}{T - T_c}, \quad (3)$$

we obtain C and T_c as

$$\begin{aligned} k_B C &= \frac{a/v}{\varepsilon_0(1 - L(\alpha_e/v))^2}, \\ k_B T_c &= \frac{L(a/v)}{1 - L(\alpha_e/v)}. \end{aligned} \quad (4)$$

The dependence of L on p can be neglected within the variation of lattice constants in this range of p [15]. Relation (2) is derived from equation (4) by substituting the Lorentz field $(3\varepsilon_0)^{-1}$ for L in the case of macroscopic polarization as the dielectric unit [16]. The polarizability α_e is related to ε_∞ through the Clausius–Mossotti relation:

$$\frac{\varepsilon_\infty - 1}{\varepsilon_\infty + 2} = \frac{\alpha_e/v}{3\varepsilon_0}. \quad (5)$$

In most order–disorder-type ferroelectrics including DKDP, C and T_c obey relation (2) [16]. The parallel decreases in magnitude of T_c and C observed in DKDP for $p < p_0$ are attributed to that of $\mu_{eff}^2 \propto a$. As mentioned in section 1, the mechanism of the reorientational motion of D_2PO_4 dipoles and the factor that determines the magnitude of μ_{eff} have not been established. Hydrogen bonds gradually decrease in length in this range of p , as shown by Nemes *et al* [17]. The decrease in magnitude of μ_{eff} with increasing p may be related to this decrease.

With increasing p for $p > p_0$, T_c tends to zero, but C for DKDP is saturated to approximately 2.4×10^3 K. In the case of KDP, C is almost independent of p within the pressure region examined, including p_c . The relation (2) no longer holds at those pressures. This magnitude of C still corresponds to μ_{eff} for typical order–disorder-type ferroelectrics. As long as the order–disorder-type mechanism is valid, the vanishing of T_c with such a large value of C suggests that a disordered state with non-zero entropy holds down to $T = 0$ in contradiction to the third law of thermodynamics. As mentioned in section 1, DKDP exhibits order–disorder-type behaviour at ambient p . The vanishing of T_c with finite C with increasing p for DKDP suggests a crossover to displacive-type behaviour of the phase transition mechanism, as discussed below.

On the other hand, the Curie–Weiss law for displacive-type ferroelectrics can be considered as follows [18]. The dependences of the lattice vibrational frequencies on T are derived from anharmonic terms in the potential energy for the anharmonic oscillation of a dielectric unit. The frequency ω , corresponding to the lowest-energy mode, is given by $\omega^2 = \omega_0^2 + bk_B T$ with a constant b . The linear dependence on T originates from mean square displacements of the dielectric unit. The ionic polarizability α_i is proportional to the inverse of ω^2 ; $\alpha_i = S/\omega^2$ with a constant S . The constant S is related to the oscillator strength f through $S = e^2 f/m$ with the effective charge e and the effective mass m , which do not depend on p , of the dielectric unit. Substituting α_i for α in equation (1), we derive the Curie–Weiss law

$$\varepsilon_c - 1 = \frac{1}{\varepsilon_0} \frac{S/v}{\omega_0^2 + bk_B T - (S/v)L} = \frac{C}{T - T_c}, \quad (6)$$

with C and T_c given by

$$\begin{aligned} k_B C &= (S/v)/(\varepsilon_0 b), \\ k_B T_c &= ((S/v)L - \omega_0^2)/b. \end{aligned} \quad (7)$$

In this derivation, we disregarded the optical dielectric constant ε_∞ for simplicity.

The frequency ω_0 originates from the short-range force, and $(S/v)L$ from the electrostatic long-range force. The softening of the lowest mode is due to the decreasing mean square displacements ($\propto T$) in the denominator of equation (6). The decrease of T_c with increasing p in this type of ferroelectric is attributed to the dominant increase of ω_0^2 in comparison with the negligibly small increase of v^{-1} in equation (7) [19]. On the basis of equation (7), we can explain the finding that C does not tend to zero even if T_c does with increasing p . A more fundamental approach was given as the displacive limit in the self-consistent phonon theory [20]. An experimental example was clearly obtained for a prototypical displacive-type ferroelectric SbSI [19], where C remains finite even if T_c becomes zero. The present experimental result of vanishing T_c with finite C suggests that the phase transition mechanism in DKDP turns into a displacive-type one for $p > p_0$, and DKDP as well as KDP are considered to undergo displacive-type phase transitions at $p_0 > p > p_c$.

4.2. Disordered dipolar configurations above T_c or at $p > p_c$

On the basis of the vanishing of T_c with finite C obtained from measurements of ε_c under high pressure, we have concluded that there is a crossover into a displacive-type behaviour in the phase transition mechanism of DKDP for $p > p_0$, and observed no transition for $p > p_c$ in DKDP and KDP. Disordered configurations of permanent dipoles are excluded above T_c in a ‘naive’ displacive-type ferroelectric. Some experimental facts have been reported for $p > p_c > p_0$ for other hydrogen-bond crystals that cannot be explained by the ‘naive’ displacive-type mechanism. The distortion of H_2PO_4 radicals associated with the origin of permanent dipoles [5] was observed in KDP at room temperature for $p > p_c$ [21]. Disordered configurations of protons on hydrogen bonds were observed even if T_c tends to zero under high pressures [22]. On the basis of distortion of squaric acid molecules $\text{H}_2\text{C}_4\text{O}_4$ from a square observed for $p > p_c$, quantum fluctuations of $\text{H}_2\text{C}_4\text{O}_4$ molecules between the two respective configurations were proposed [23]. These results indicate that disordered configurations of permanent dipoles hold down to 0 K contrary to the third law of thermodynamics for $p > p_c$. Disordered configurations of dipoles were observed above and near T_c in perovskite crystals which undergo displacive-type phase transitions [24]. Those observed in hydrogen-bond crystals can be attributed to such order–disorder-type behaviours as those observed in perovskite ferroelectrics. Although the magnitude of saturated C suggests disordered dipolar configurations, no supporting experimental results have been reported for DKDP for

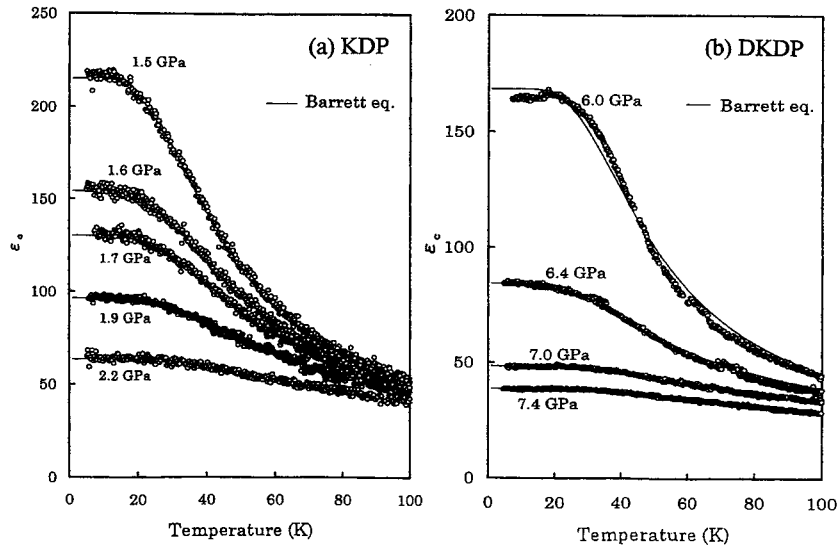


Figure 5. Fitting the Barrett formula with the experimental dielectric constant for $p > p_c$: (a) KDP and (b) DKDP.

$p > p_c > p_0$. Experimental studies examining the possibility of disordered configurations are now in progress for DKDP.

4.3. Appearance of quantum paraelectricity

Figure 5 shows the temperature dependence of ϵ_c at pressures around p_c of KDP and DKDP. As seen in figures 3 and 5, the dielectric constants at high pressures $p > p_c$ are suppressed with decreasing temperature down to zero and exhibit a deviation from the Curie–Weiss law [12, 13]. The suppression in the dielectric constant of KDP under high pressure was first described by Samara [11, 25] as evidence of the proton tunnelling model. However, the same suppression was also observed in DKDP in which the tunnelling motion of the deuteron is believed not to be realized.

In some perovskite-type crystals, similar suppressions have been observed at ambient pressure. This phenomenon is known as quantum paraelectricity [26], and has been described by the Barrett formula [18] based on an anharmonic lattice vibration system. The Barrett formula for the dielectric constant is written as

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

The parameter T_1 is defined from the harmonic frequency ω_h of a dielectric unit as $k_B T_1 = h\omega_h$. In this formula, the suppression of the dielectric constant at low temperatures is realized by the zero-point motion of ω_h -vibration.

The full lines in figure 5 represent the results of fitting equation (8). The characteristic feature of the dielectric constant at lower temperatures around p_c is well described by the Barrett formula, which strongly suggests the appearance of quantum paraelectricity in KDP and DKDP under high pressure. Quantum paraelectricity is consistent with the conclusion that the phase transition in KDP and DKDP at high pressure is of displacive type.

The experimental values of the parameters in equation (8) are shown in figure 6 against pressure. It is interesting to note that the values of T_1 and T_0 are almost the same for KDP

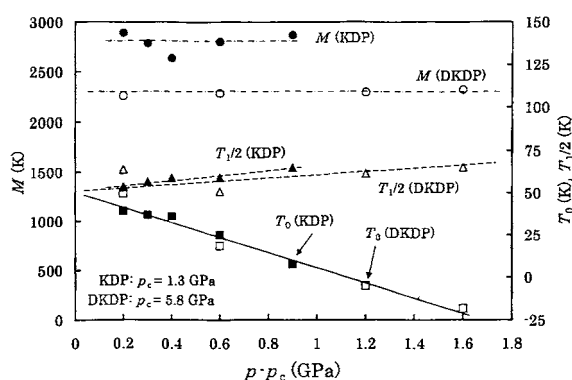


Figure 6. Dependences of the three parameters of the Barrett formula on $(p - p_c)$ in KDP (closed) and DKDP (open).

and DKDP at the same $p - p_c$. As far as quantum paraelectricity is concerned, there is no significant difference between KDP and DKDP.

It should be mentioned that the same mathematical form as that of equation (8) is derived for the $\epsilon_c - T$ relation in the proton tunnelling model [5]. In this model, the parameter T_1 in equation (8) is replaced by $2\Omega_t/k_B$, using the tunnelling frequency Ω_t . However, the value of T_1 given in figure 6 is too small to explain the enormous isotope effect on T_c of $\text{KH}_{2(1-x)}\text{D}_{2x}\text{PO}_4$ in the framework of the naive tunnelling model. The details of this problem will be discussed elsewhere.

Acknowledgments

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