Quantum Phase Transition in $K_3D_{1-x}H_x(SO_4)_2$

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Dielectric and thermodynamic properties have been investigated in isotopically mixed crystals $K_3D_{1-x}H_x(SO_4)_2$ with *isolated* hydrogen bonds interconnecting the dimeric SO_4^{2-} units. The critical temperature T_c for the antiferroelectric phase transition decreases with increasing proton concentration (x) and eventually the phase transition vanishes for $x \geq x_c \sim 0.66$. The x-dependent behavior of T_c, the dielectric constant $\epsilon(T)$, and the specific heat jump ΔC at T_c are described by simple transverse Ising Hamiltonian. This indicates a determinative role of the proton tunneling in the phase transition and related properties.

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Protons between two oxygen sites show quantum mechanical tunneling motion as well as thermally activated hopping between the two potential minima. In several organic molecules in a gas phase (or isolated in a matrix), such a tunneling motion has been observed in terms of splittings of specific fluorescence lines or vibrational bands [1]. When such isolated molecular units assemble into a solid phase, a variety of cooperative phenomena are expected to show up. For example, the phase transition and drastic isotope effects observed in KH_2PO_4 (abbreviated as KDP) have been discussed from this viewpoint. However, the hydrogen bonds form an infinite network in this material and the replacement of the proton with the deuteron causes rather unpredictable changes of the local environment, e.g., elongation of the hydrogen bond, besides the suppression of the tunneling motion. In addition, the Pauling "ice rule" does not allow one proton to tunnel independently of the others in the proton potential, so tunneling must be correlated in some way that is not yet well understood. This complicates the interpretation of the phase transition and causes long-term debates on this material [2].

In this Letter, we propose $K_3D_{1-x}H_x(SO_4)_2$ as an ideal system to study the tunneling motion of protons in solid phase free from such complications. We present the variation of the transition temperature T_c, the dielectric constant $\epsilon(T)$, and the specific heat jump ΔC at the transition upon changing the proton concentration x, all of which are well described by the simple transverse Ising Hamiltonian, and indicate that the proton tunneling motion plays a crucial role in the phase transition and related properties.

Crystals of $K_3D_{1-x}H_x(SO_4)_2$ have a simple structure [3]: They are composed of the dimeric SO_4^{2-} units connected by a strong hydrogen bond (SO_4^{2-}-H$\cdots SO_4^{2-}$), as schematically depicted in Fig. 1. Each hydrogen bond in the present system is *isolated* from the others, making a sharp contrast with most of the conventional (anti)ferroelectrics, e.g., KDP with an infinite network of hydrogen bonds. Owing to the isolation of the hydrogen bonds, each proton (deuteron) can move independently of the others in the double-well type proton potential and the interaction between the neighboring protons (deuterons) is considered to be electrostatic in nature (e.g., dipole-dipole interaction). In accord with this expectation, application of hydrostatic pressure slightly increases T_c for the fully deuterated crystal ($x = 0.0$) at a rate of +7 K/GPa [4], perhaps due to the pressure-induced increase in the dipolar interaction strength. This is also in contrast with the large *negative* pressure coefficient of T_c in KDP families, e.g., −46 K/GPa for KDP [5]. Another advantage of targeting the isotopically mixed crystals is that the effective tunneling frequency can be controlled by changing the isotopic composition without changing the lattice parameters [6]. Therefore, we may ascribe the change in the dielectric and thermodynamic properties to the mass-dependent kinetics of protons and

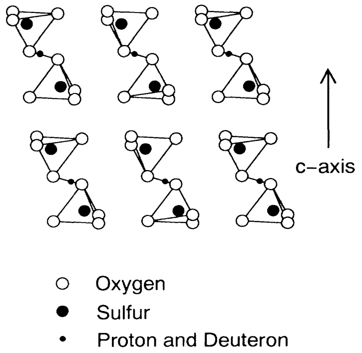

FIG. 1. Schematic structure of $K_3D_{1-x}H_x(SO_4)_2$.

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deuterons.

Considering these features, we describe the present system in terms of the following Hamiltonian [7,8]:

$$H = -\sum_{i} \Omega_i \sigma_i^x - \sum_{\langle ij \rangle} J_{ij} \sigma_i^z \sigma_j^z, \tag{1}$$

where the pseudospin variable $\boldsymbol{\sigma}_i$ represents the two-state dynamics of the proton (or the deuteron) occupying the ith site. The z component σ^z takes the value $+1$ or -1 according to the two minima of the potential formed by the outer oxygen atoms (or the SO_4^{2-} ions). The tunneling motion is described by the σ_i^x term with the tunneling frequency Ω_i that takes either of the two values Ω_H or Ω_D. Since the geometrical difference between the hydrogenerated and deuterated compounds is extremely small [6], the dipolar interaction J_{ij} between the neighboring sites is assumed to be independent of the species of the paired atoms and is put to be J. The use of a single parameter J is valid as far as the present system is concerned, because the dipolar interaction strength is rather pressure and hence structure insensitive [4] and is considered not to vary much with the isotopic substitution.

Isotopically mixed crystals of $K_3D_{1-x}H_x(SO_4)_2$ were synthesized by slow recrystallization from a stoichiometric H_2O/D_2O solution, which contains K_2SO_4 and an excess of H_2SO_4/D_2SO_4. The crystals obtained were pseudohexagonal plates with well-developed c faces, and typical sizes of the samples were 0.5 mm in thickness and 2×2 mm^2 in area. To determine the proton concentration (x) of each crystal, we performed the proton-NMR measurements of D_2O solution of the mixed crystals and carefully monitored the intensity of the signal for HDO species. The integrated intensity linearly increases with the proton concentration of the starting solvent, indicating that the x value of the crystal is identical to that of the solvent. Temperature dependence of the dielectric constant ϵ (c component) was measured using an *LCR* meter at frequency of 10 kHz. The reproducibility of the overall ϵ-T profile was fairly good, though the absolute values of ϵ were scattered in respective runs within the uncertainty of 20% due to the difficulty in precise determination of area of the small electrode. The heat capacity was measured by a conventional adiabatic heat method with use of calibrated Ge thermometers.

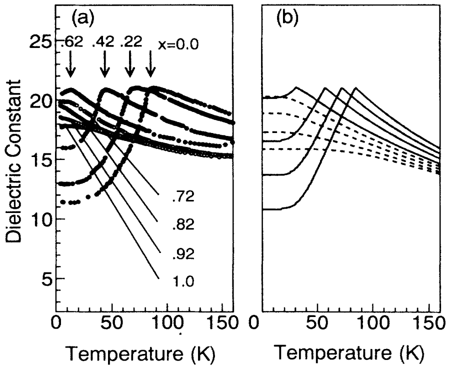

FIG. 2. Temperature dependence of the dielectric constant for $K_3D_{1-x}H_x(SO_4)_2$ with various x values: (a) Experimental results and (b) calculated ones based on the transverse Ising model with the parameters Ω_H=167 K, Ω_D=52 K, and Jz = 95 K. Downward arrows indicate the critical temperatures for the dielectric phase transition.

First, we present results of the x dependence of T_c for the antiferroelectric (AFE)-to-paraelectric (PE) phase transition as well as the temperature variation of ϵ. Figure 2(a) shows the ϵ-T curve for $K_3D_{1-x}H_x(SO_4)_2$ with varying x. Profiles of the ϵ-T curves for $K_3D(SO_4)_2$ ($x = 0.0$) and $K_3H(SO_4)_2$ ($x = 1.0$) crystals agree with the previously reported ones [9]. T_c was determined by the inflection point of the ϵ-T curve, and is indicated by a downward arrow. The x dependence of T_c is plotted by closed circles in Fig. 3. Except for the lower temperature region ($\leq$30 K), the phase boundary is approximately represented by a nearly straight line, as indicated by an eye-guiding dotted line. As T_c approaches zero temperature, the slope becomes steeper and eventually the phase transition vanishes at $x_c \sim 0.66\pm0.04$. In other words, the protons (deuterons) cannot show any long-range order above x_c even at zero temperature due to the cooperative tunneling motion of the protons, which can be regarded as the simplest example of the quantum phase transition. Similar x-T phase diagrams have been reported in the isotopically mixed crystals of other analogous compounds, $Rb_3D_{1-x}H_x(SO_4)_2$ ($x_c \sim 0.78$) and $Rb_3D_{1-x}H_x(SeO_4)_2$ ($x_c \sim 0.96$) [10].

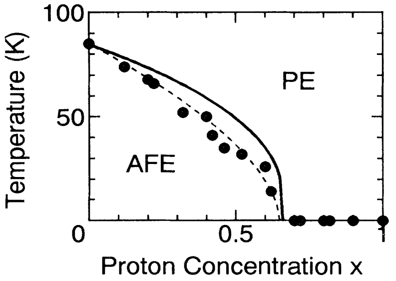

FIG. 3. Proton concentration (x) dependence of the critical temperature for $K_3D_{1-x}H_x(SO_4)_2$. Solid curve is a calculated result based on the transverse Ising model with the parameters Ω_H=167 K, Ω_D=52 K, and Jz = 95 K. Dotted line is merely a guide to the eye. AFE and PE mean antiferroelectric and paraelectric phase transition, respectively.

Now, let us return to the ϵ-T curve shown in Fig. 2(a). In the fully deuterated compound (x = 0.0), ϵ critically increases on approaching T_c (=85 K) from the low temperature side and then gradually decreases above T_c, which is typical of the AFE phase transition. T_c rapidly decreases with increasing x and eventually the phase transition disappears above x_c: For the $x \geq 0.70$ sample, there is no trace of the phase transition and ϵ monotonously increases with decreasing temperature. Even in the proton-rich samples that show no phase transition ($x \geq 0.70$), x-dependent behavior is observed: At $x = 0.82$, ϵ increases steeply with decreasing temperature, while the low-temperature enhancement of ϵ is remarkably suppressed at $x = 0.92$ and 1.0. In particular, the dielectric constant becomes almost temperature independent below ~40 K at $x = 1.0$. Such a suppression is ascribed to the active tunneling motion of protons between the two potential minima, which disturbs the response of the protons to the external electric field, as will be demonstrated by the model calculation (described below).

We employ the simple mean field approximation [8] to the Hamiltonian in Eq. (1), and obtained the following self-consistent equation for the molecular field [11] $\Gamma = (-1)^i Jz\langle\sigma_i^z\rangle$ with z being the number of nearest neighbor sites,

$$\Gamma = Jz\left(x\frac{\Gamma}{\sqrt{\Omega_{\mathrm{H}}^2+\Gamma^2}}\tanh\beta\sqrt{\Omega_{\mathrm{H}}^2+\Gamma^2} + (1-x)\frac{\Gamma}{\sqrt{\Omega_{\mathrm{D}}^2+\Gamma^2}}\tanh\beta\sqrt{\Omega_{\mathrm{D}}^2+\Gamma^2}\right). \quad (2)$$

From Eq. (2) the transition temperature T_c is readily obtained by taking the limit $\Gamma \to 0$. The dielectric constant $\epsilon(T)$ is also given by

$$\epsilon(T) = \epsilon_B + \mu^2 N\frac{\overline{\chi_0}(T)}{1+Jz\overline{\chi_0}(T)}, \quad (3)$$

where $\overline{\chi_0}(T) = x\chi_0^{(\mathrm{H})} + (1-x)\chi_0^{(\mathrm{D})}$ with $\chi_0^{\mathrm{H(D)}}$ being the polarizability of a single proton (deuteron) tunneling between the two minima in the presence of the molecular field Γ and N (μ) is the density (magnitude) of the dipoles. The polarizability is defined as $\chi_0^{\mathrm{H(D)}} = (\Omega_{\mathrm{H(D)}}^2/\tilde{\Omega}_{\mathrm{H(D)}}^3)\tanh\beta\tilde{\Omega}_{\mathrm{H(D)}} + (\beta\Gamma^2/\tilde{\Omega}_{\mathrm{H(D)}}^2)\mathrm{sech}^2\beta\tilde{\Omega}_{\mathrm{H(D)}}$, where $\tilde{\Omega}_{\mathrm{H(D)}} \equiv \sqrt{\Omega_{\mathrm{H(D)}}^2+\Gamma^2}$. The parameters appearing in the model Hamiltonian Eq. (1), Ω_{H}, Ω_{D}, and Jz, are determined so as to reproduce the values of T_c (=85 K) at $x = 0.0$ and x_c (~0.66), and profiles of the ϵ-T curves at $x = 0.0$, 0.22, 0.42, and 0.62 [closed circles in Fig. 2(a)]: The best-fit results are Ω_{H}=167 K, Ω_{D}=52 K, and $Jz = 95$ K. In the fitting procedure, the background value of ϵ is determined to be ϵ_B ~2.2, which corresponds to the minimum value of the vertical axis of Fig. 2(a). In Fig. 2(b) are shown the calculated $\epsilon(T)$ curves using Eq. (3) for various x corresponding to the experimental data in Fig. 2(a): Solid and dotted curves are for $x \leq x_c$ and $x \geq x_c$, respectively. Overall agreement between the theory [Fig. 2(b)] and experiment [Fig. 2(a)] is satisfactory. The same parameters also reproduce the x-dependent features of T_c, as indicated by a solid curve in Fig. 3. Here, a systematic deviation of the calculated curve toward the higher-temperature region is seen, which is perhaps due to a drawback of the molecular-field approximation: This approximation neglects effects of the fluctuation and therefore tends to overestimate T_c.

Thus the global features of the phase diagram and the dielectric constant $\epsilon(T)$ are described by the tunneling model of Eq. (1). However, there are adjustable parameters and the applicability of the tunneling model is not uniquely dictated. When the phase transition is suppressed by the quantum fluctuations rather than by the thermal agitations, the entropy of the system remains small even in the PE phase. In the limit of zero-temperature quantum phase transition between the two ground states, the entropy is zero in both the AFE and PE phases. Therefore, the thermodynamic quantity is expected to give a clue to the relative importance of the quantum fluctuation. Especially in the mean field theory of the Ising model (classical limit), the jump in the specific heat ΔC at the transition is predicted to be $\frac{3}{2}k_B$, independent of the coupling constant J and hence T_c. Therefore, the absolute value of ΔC as well as its x dependence gives important information.

The inset of Fig. 4 shows contributions of the proton (deuteron) correlation to the specific heat per dimer unit (i.e., per one proton or deuteron), that is, the remainder of the raw specific data after subtracting that of $K_3H(SO_4)_2$; open and closed circles are for $x = 0.0$ and $x = 0.42$, respectively. At $x = 0.0$ (open circles), the remainder component ($\tilde{C}$) of the specific heat gradually increases up to around $\frac{3}{2}k_B$ (the value in the order-disorder limit) on approaching T_c from the low-temperature side and then suddenly drops at T_c. [A similar behavior for $\tilde{C}$ has been also observed in the isomorphic compound $Rb_3D(SeO_4)_2$ [12].] The anomaly of $\tilde{C}$ at T_c is observed to decrease in magnitude with increasing x, as seen in the

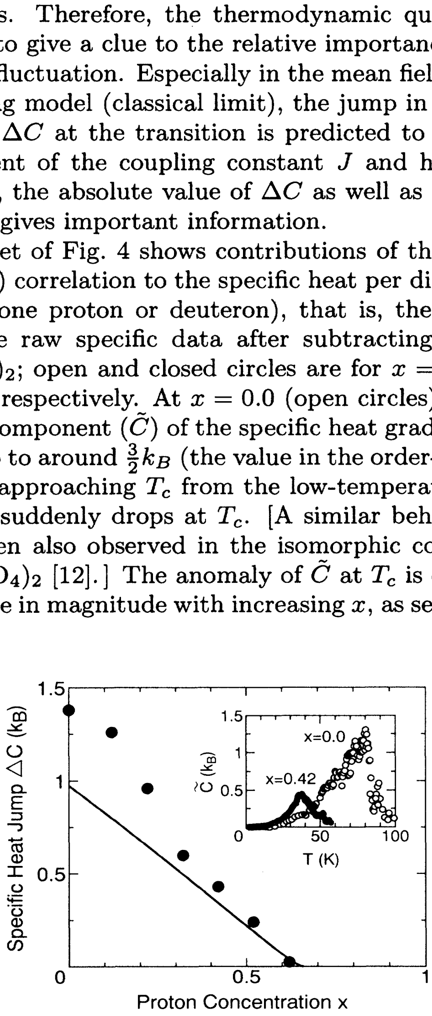

FIG. 4. Proton concentration (x) dependence of the specific heat jump ΔC at T_c for $K_3D_{1-x}H_x(SO_4)_2$. The solid line is a calculated result based on the transverse Ising model with the parameters Ω_{H}=167 K, Ω_{D}=52 K, and $Jz = 95$ K. The inset shows contributions of the proton (deuteron) correlation to the specific heat ($\tilde{C}$) per dimer unit.

inset for the $x = 0.42$ sample (closed circles). We defined the maximum value of the remainder component $\tilde{C}$ as the specific heat jump (ΔC), and plotted it in Fig. 4 against x. One may notice that ΔC continuously decreases with increasing x, or equivalently with decreasing T_c. Such a reduction in ΔC is ascribed to the enhanced tunneling motion of the protons (deuterons). As indicated by a solid line in Fig. 4, we can semiquantitatively reproduce the reduction in ΔC by the transverse Ising Hamiltonian Eq. (1) with the same parameters given above [13].

Although the present system is a mixed crystal with random distribution of protons and deuterons, the qualitative features of the physical quantities described above are similar to those of the virtual crystal with the uniform effective tunneling frequency $\Omega(x)$ that increases with x. For this virtual crystal, the collective modes (pseudo-spin-wave-like modes) are expected to exist and soften toward T_c [7]. This is analogous to the displacive phase transition, where a specific phonon mode softens and finally condenses at $T = T_c$. Therefore, the classical-to-quantum crossover of the phase transition discussed above may be interpreted also in terms of the crossover from the order-disorder to displacive type. Another implication is that the collective modes may be detected, e.g., by neutron scattering, though the wave vector **q** is not well defined in the present system.

In summary, we have deduced the dielectric phase diagram and relating dielectric and thermodynamic properties of $K_3D_{1-x}H_x(SO_4)_2$ as a function of proton concentration (x). With increasing x, we could effectively increase the tunneling frequency of the protons or deuterons. It was observed that the increase of the correlated tunneling motion drives the dielectric phase transition from the classical to quantum nature and finally suppresses the phase transition itself. Lastly, we mention that the importance of the quantum fluctuation has manifested itself in other systems, e.g., the anomalous dielectric (paraelectric) properties of $SrTiO_3$ and $KTaO_3$ near zero temperature [14] and also in squaric acid ($H_2C_4O_4$) under high pressures [15]. We hope that comparison among these systems and the present one clears up the role of quantum effects in the dielectrics.

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