

Study on the Phase Transition of $K_3D_xH_{1-x}(SO_4)_2$ by the Raman Scattering of the Internal ν_2 Mode

Pho KAUNG, Masaru KASAHARA and Toshiro YAGI

Research Institute for Electronic Science, Hokkaido University, Sapporo 060

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Temperature dependence of the ν_2 mode in mixed crystals $K_3D_xH_{1-x}(SO_4)_2$ was studied by Raman scattering from room temperature to 20 K. The ν_2 modes of both HSO_4^- and DSO_4^- ions are observed separately. The frequency shift of HSO_4^- ion, $\omega(HSO_4^-)$, below T_c depends on temperature as $(1 - (T/T_c))^\beta$ with $\beta = 0.25 \pm 0.05$ when it is measured from the frequency at T_c . A discrete change in the frequency of DSO_4^- just below T_c is observed in the mixed crystals and its origin is explained in relation to the interaction among dimers. The temperature dependence of the anomalous broadening of the linewidth above T_c is explained well by a mechanism similar to the motional narrowing effect in NMR.

KEYWORDS: Raman scattering, phase transition, $K_3D(SO_4)_2$, $K_3H(SO_4)_2$, motional narrowing

§1. Introduction

In certain hydrogen bonded ferroelectrics, the drastic increase in the transition temperature T_c with deuteration (isotope effect) is a widely interested phenomenon. An extreme case is that of tripotassium hydrogen disulfate $K_3H(SO_4)_2$ (TKHS) and its deuterated analogue (TKDS), where the hydrogen salt does not show any phase transition down to 4.2 K, while the deuterated one undergoes the antiferroelectric phase transition at 84 K.¹⁾ It was reported that the hydrogen bond in TKHS contracts with lowering temperature to the length where a double minimum potential for a hydrogen changes to a single minimum one.²⁾ On the other hand, according to the numerical estimation by Totsuji and Matsubara,³⁾ the interaction between two hydrogen bonds keeps deuterons at acentric positions in their double minimum potentials. They inferred that non localization of hydrogens is owing to the zero point vibration. In order to understand the phase transition of TKDS, it is useful to change the interaction between D-hydrogen bonds by the mixing of H-hydrogen bonds and to study the dynamics of hydrogens and deuterons.

In a previous paper,⁴⁾ we reported that the Raman line of the internal modes of sulfate ions broadens near T_c and estimated the characteristic time of deuteron motion with the motional narrowing theory upon the assumption that the phase transition is of the order-disorder type. We use the same method for the mixed crystals of TKHS and TKDS in order to obtain the characteristic time of the motion of the hydrogen and deuteron, separately.

§2. Experimental

Single crystals of $K_3D_xH_{1-x}(SO_4)_2$ were grown by the slow evaporation method⁵⁾ from a D_2O/H_2O solution containing 40 wt.% of K_2SO_4 and 24 wt.% of $(D_2SO_4 + H_2SO_4)$. Since T_c was found by the splitting of the internal modes, the concentration x of deuteron was

estimated from the concentration dependence of T_c given in the phase diagram studied by the dielectric measurement.⁶⁾ Crystals with $x = 0.98, 0.86, 0.62$ and 0.40 were studied in this experiment. The experimental setup for Raman scattering was described elsewhere.⁷⁾ All spectra were analyzed by the same procedure as in our previous work.⁴⁾

§3. Results and Discussion

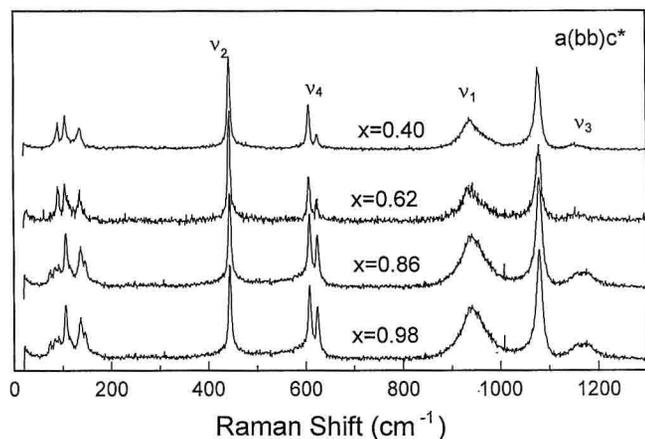
In isotropically mixed crystals, the whole aspect of spectra up to 1200 cm^{-1} is very similar to those reported in pure compounds. For comparison among various deuteron concentration x , the Raman spectra in the $a(bb)c^*$ geometry observed at 295 and 21 K are shown in Figs. 1(a) and 1(b), respectively. Spectra at 295 K do not seem to depend on x . However, the splitting of internal modes at 21 K shows effects of the deuteration as shown in Fig. 2.

Figure 2 shows the ν_2 mode spectra in the ordered phase for various values of x in $K_3D_xH_{1-x}(SO_4)_2$ crystals. With increasing x , the intensity of the 435 cm^{-1} line increases and that of the 440 cm^{-1} line decreases, while 450 cm^{-1} line does not change.

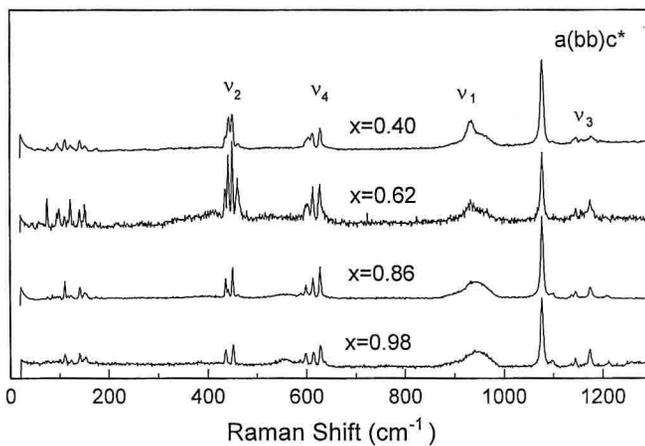
These facts imply that the 435 cm^{-1} line is the ν_2 mode of DSO_4^- and the 440 cm^{-1} line is that of HSO_4^- . Since the amount of SO_4^{2-} ion does not change in mixed crystals, the 450 cm^{-1} line is the ν_2 mode of SO_4^{2-} . Therefore, what one should note is that the distinct lines of HSO_4^- and DSO_4^- can be detected separately from a specimen of the mixed crystal in the ordered phase. This means that we can study the relation between the motion of hydrogens and deuterons in the mixed crystals.

3.1 The temperature dependence of the frequency of the ν_2 mode

The temperature dependence of the frequency of the ν_2 mode for $x = 0.86$ is given in Fig. 3. Above T_c , although spectra in Fig. 1 show one ν_2 line, Lorentzian fit gives



(a)



(b)

Fig. 1. Raman spectra of mixed crystals $K_3D_xH_{1-x}(SO_4)_2$ observed in the $a(bb)c^*$ geometry at (a) 295 and (b) 21 K, for $x = 0.40, 0.62, 0.86$ and 0.98 .

two lines corresponding to $H(SO_4^-)_2$ and $D(SO_4^-)_2$.⁸⁾ The frequencies ω_{0H} and ω_{0D} are independent of temperature within a present experimental error. Two ν_2 lines split into three lines in the ordered phase as described above. The splitting of ω_{0H} into $\omega(HSO_4^-)$ and $\omega(SO_4^{2-})$ and the line broadening mentioned later imply that a hydrogen in the mixed crystal moves in a double minimum potential in the disordered phase and stays at an acentric site in the ordered phase, although the potential for a hydrogen of TKHS is reported²⁾ to be single minimum below 100 K.

It was shown that the splitting of spectra of the nuclear magnetic resonance in the ordered phase for the order-disorder phase transition is proportional to the long range order parameter S .⁹⁾ Upon the assumption that the same consideration can be applied to the Raman scattering, the temperature dependence of the Raman frequency in the ordered phase is explained as follows. We define frequencies at 0 K as

$$\omega(HSO_4^-)_{T=0} = \omega_{0H} - \delta \quad (1)$$

$$\omega(SO_4^{2-})_{T=0} = \omega_{0H} + \delta. \quad (2)$$

where ω_{0H} is the average frequency, $[\omega(HSO_4^-) + \omega(SO_4^{2-})]/2$, and 2δ the splitting at 0 K. We consider

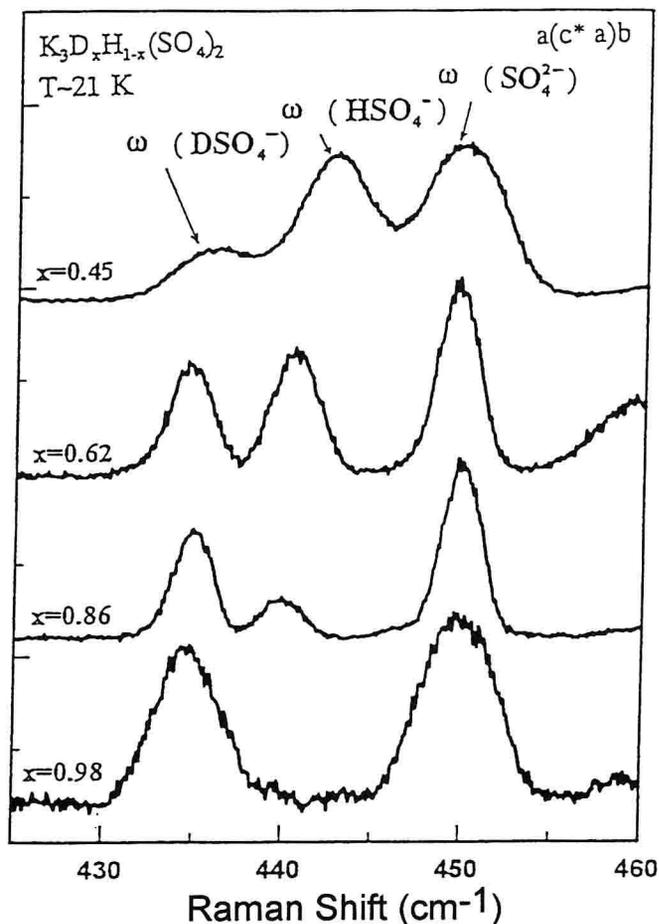


Fig. 2. Raman spectra of the ν_2 modes of $K_3D_xH_{1-x}(SO_4)_2$ in the $a(c^*a)b$ geometry at 21 K for $x = 0.40, 0.62, 0.86$ and 0.98 . Each line is assigned by x dependence of the intensity.

a sulfate ion, HSO_4^- , at 0 K. As temperature increases, HSO_4^- changes to SO_4^{2-} and then back to HSO_4^- from time to time because of the motion of the hydrogen in the O-H-O bond due to the thermal excitation. We define the probabilities to find the ions HSO_4^- and SO_4^{2-} as p_+ and p_- respectively and, then, the long range order parameter S is proportional to $p_+ - p_-$. According to the motional narrowing theory, a single line is observed when the characteristic time τ_c of the hydrogen motion is shorter than the inverse of δ , that is, $\tau_c\delta < 1$ and two lines are observed in case of $\tau_c\delta > 1$. When $\tau_c \sim 1$, each line becomes so broad. Because no crossover from $\tau_c\delta < 1$ to $\tau_c\delta > 1$ is found even near T_c in the present study, we consider that $\tau_c\delta < 1$ holds for both the hydrogen and the deuteron over the whole temperature range studied. Thus, $\omega(HSO_4^-)$ is the frequency averaged over two states with different probabilities;

$$\begin{aligned} \omega(HSO_4^-) &= p_+\omega(HSO_4^-)_{T=0} + p_-\omega(SO_4^{2-})_{T=0} \\ &= \omega_{0H} - (p_+ - p_-) \cdot \delta = \omega_{0H} - S \cdot \delta. \quad (3) \end{aligned}$$

That is, the frequency in the ordered phase is proportional to S when it is measured from ω_{0H} . The similar consideration can be applied to the frequency of the ion which is SO_4^{2-} at 0 K. One should notice that the splitting in the ordered phase is not caused by the slowing down of the hydrogen motion but by the ions becoming

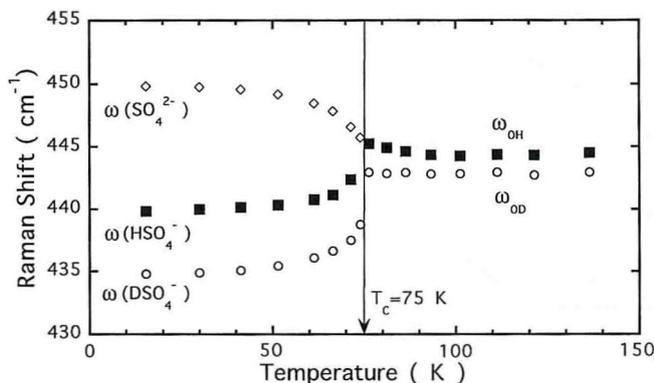
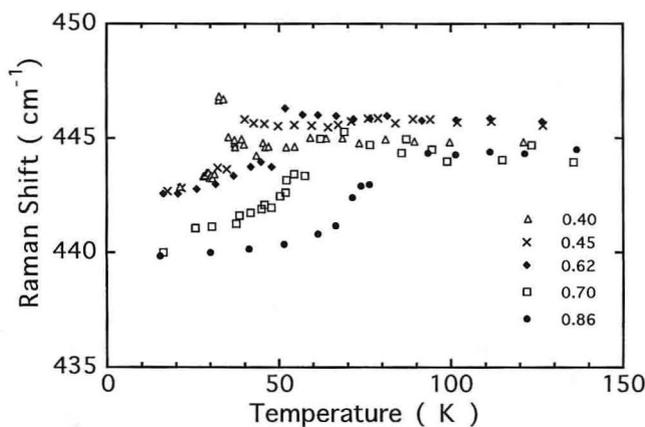


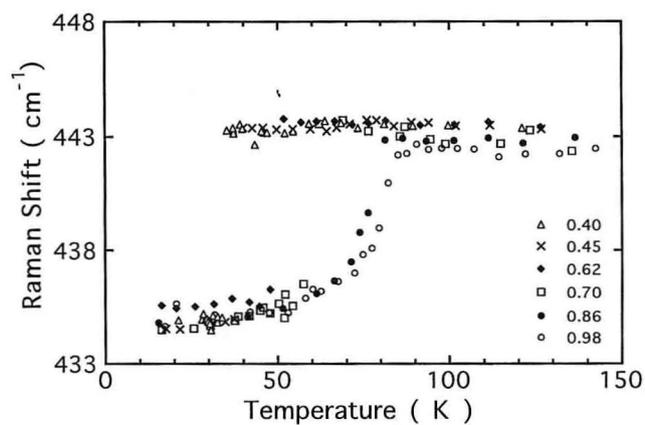
Fig. 3. The temperature dependence of ω_{OH} , ω_{OD} , $\omega(HSO_4^-)$, $\omega(DSO_4^-)$ and $\omega(SO_4^{2-})$ of the ν_2 mode in the mixed crystal of $x = 0.86$.

inequivalent due to the localization of the hydrogen.

The Raman frequency shifts of $\omega(HSO_4^-)$ are plotted against temperature in Fig. 4(a) for all concentrations studied here, $x = 0.40, 0.45, 0.62, 0.70$ and 0.86 . The frequency difference $\omega_{OH} - \omega(HSO_4^-)$ of each concentration shows a common temperature dependence as $(1 - (T/T_c))^\beta$ with $\beta = 0.25 \pm 0.05$. In contrast to this, the frequency shifts of $\omega(DSO_4^-)$ shows the temperature dependence quite different from that of HSO_4^- especially



(a)



(b)

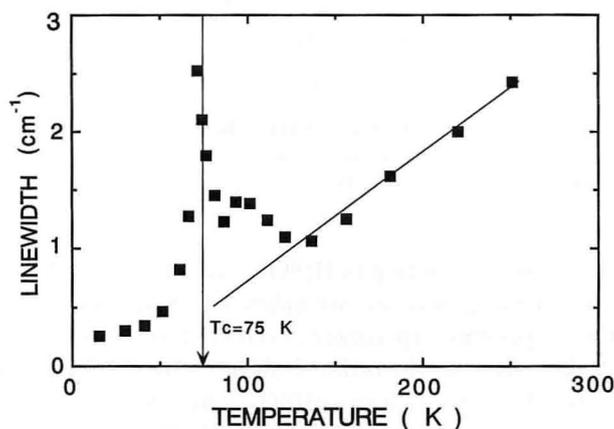
Fig. 4. The temperature dependence of (a) ω_{OH} and $\omega(HSO_4^-)$ and (b) ω_{OD} and $\omega(DSO_4^-)$.

for a low x (Fig. 4(b)). The temperature dependence of $\omega(DSO_4^-)$ below T_c is well expressed by a single curve for all concentrations after a drastic decrease from ω_{OD} . This point will be discussed later.

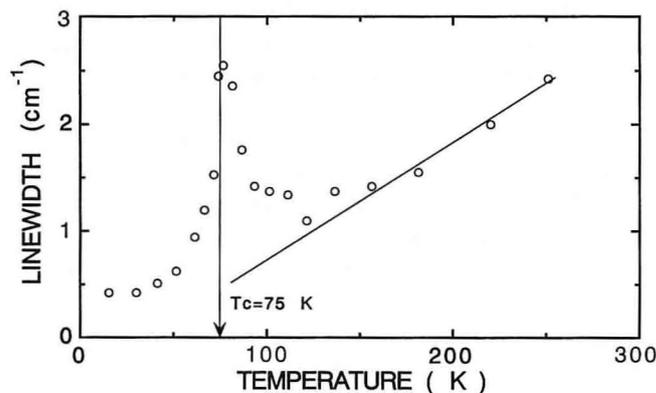
Three ν_2 modes in the ordered phase are reduced to two lines at T_c as shown in Fig. 3. This indicates that hydrogen or deuterium spends the same average time at each site of the double minimum potential in the disordered phase. It does not stay on any site for a period long enough to give a Raman line corresponding to its particular sulfate site. Equal staying time and the rapid change between HSO_4^- (DSO_4^-) and SO_4^{2-} and *vice versa* make two sites equivalent spectroscopically and give only a single motional averaged ν_2 line centered at ω_{OH} (ω_{OD}).

3.2 Anomalous broadening of the ν_2 line near T_c

The temperature dependences of the linewidth for $x = 0.86$ are shown in Figs. 5(a) and 5(b). In addition to the usual temperature dependence of the linewidth indicated by a solid line in each figure, the anomalous line broadening Δ is found near T_c as a deviation from the solid line. Here, Δ is defined as the difference between the observed width and the solid line which is hypothetical one observable if the crystal does not undergo the phase transition. The hypothetical linewidth is assumed, for simplicity, to depend on temperature linearly



(a)



(b)

Fig. 5. The temperature dependence of the linewidth of (a) ω_{OH} and $\omega(HSO_4^-)$ peaks and (b) ω_{OD} and $\omega(DSO_4^-)$ peaks of the mixed crystal of $x = 0.86$. Solid lines are the hypothetical ones observable if the crystal does not undergo the phase transition.

as shown in Figs. 5(a) and 5(b). Because the frequency of a single sulfate ion changes stochastically between two frequencies, $\omega(HSO_4^-)$ and $\omega(SO_4^{2-})$ with a characteristic time τ_c , we analyze the anomalous line broadening by the application of the motional narrowing theory developed in the nuclear magnetic resonance.¹⁰⁾ According to the theory, a line shape is expressed as

$$I(\omega) = \frac{\tau_c \delta^2}{[(\omega - \omega_{0H})^2 + (\tau_c \delta^2 / 2)^2]} \quad (4)$$

for $\tau_c \delta \ll 1$ using the notation in eqs. (1) and (2). Then, the linewidth Δ is proportional to τ_c as

$$\Delta = \tau_c \delta^2 / 2. \quad (5)$$

Hence, the anomalous broadening of the linewidth indicates that the deuteron or hydrogen motion slows down near T_c .

Figures 6(a) and 6(b) show the temperature dependence of the inverse of τ_c for mixed crystals. The inverse of τ_c of all crystals depends on temperature with almost the same gradients for D-related ions, whereas those for H-related ones increase with decreasing x . The temperature dependence of τ_c is expressed as

$$\tau_c^{-1} = (\tau_0 T)^{-1} (T - T_0) \propto \exp(-U/kT) \cdot (T - T_0), \quad (6)$$

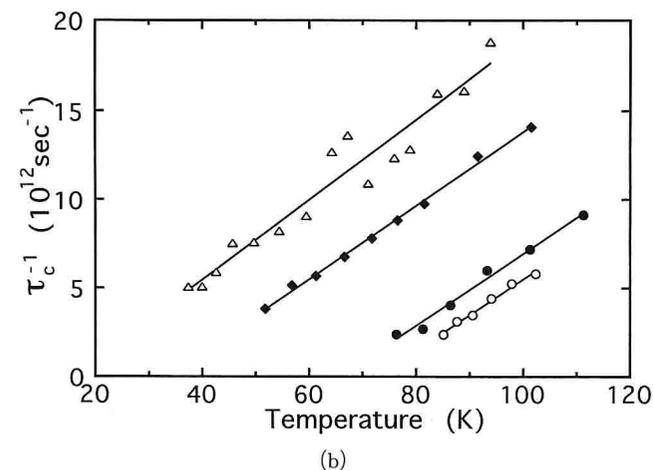
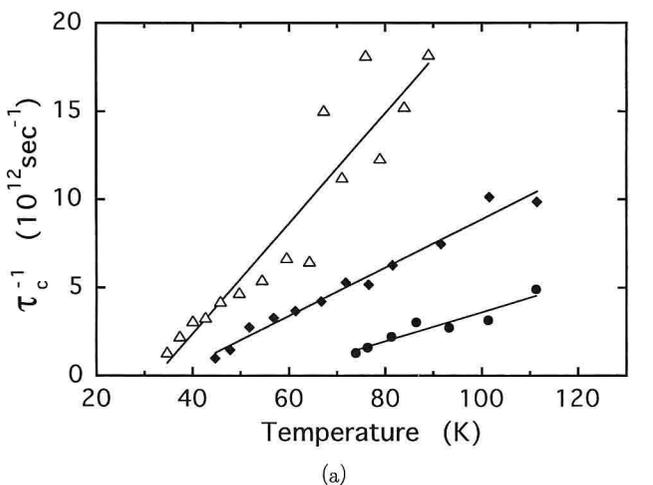


Fig. 6. The inverse of τ_c of (a) the hydrogen and (b) the deuteron motions in the hydrogen bond. (o: $x = 0.98$, \bullet : 0.86 , \blacklozenge : 0.62 and Δ : 0.40 .) Solid lines are the least square fits.

where τ_0^{-1} is the characteristic time of a hydrogen (deuteron) in an isolated hydrogen bond. The extrapolated τ_c is considered to diverse at T_0 which depends on x and about 10–20 K below T_c . Right hand term of eq. (6) is given by taking account of the relation that τ_0^{-1} is proportional to $T^{-1} \cdot \exp(-U/kT)$, where U is the barrier height of the double minimum potential. As shown in Figs. 6(a) and 6(b), the present result indicates that U does not depend on x for D-related hydrogen bond, whereas U for H-related hydrogen bond decreases with decreasing x . One can also see from Figs. 6(a) and 6(b) that a linear relation of τ_c^{-1} against temperature holds over a wide temperature range. This means that the length of the hydrogen bond changes with temperature so that the factor U/T in eq. (6) is constant against T .

In Fig. 7, τ_c of H and D at 5 K above T_c are plotted against the concentration x . Both τ_c decrease with decreasing x and seem to be zero around $x = 0.10$. The shorter τ_c of H with decreasing x implies the lower barrier in the double minimum potential and, in turn, corresponds to a lower T_c . The zero value of τ_c means that the hydrogen (deuteron) moves in a single minimum potential and no phase transition is found. Thus, the concentration dependence of τ_c is essentially consistent with the dielectric measurement.⁶⁾ As shown in Fig. 7, we obtained rather a unusual result that τ_c for H is slightly longer than that for D over the whole concentration range. It should be concluded that the distance between two sites for H is longer than that for D in mixed crystals. This conclusion is quite important because the X-ray study of the pure TKHS and pure TKDS gave the result $R_{HH} = 0.65 \text{ \AA}$ and $R_{DD} = 0.66 \text{ \AA}$ at room temperature.¹¹⁾ The present Raman scattering study gives the bond length characteristic for the mixed crystals.

Totsuji and Matsubara⁴⁾ inferred that the zero point vibration of hydrogens seriously influences the ordering

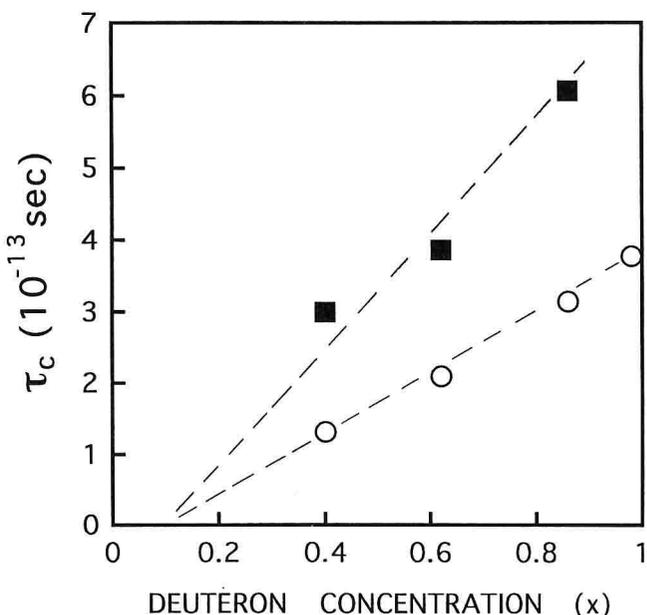


Fig. 7. The concentration dependence of τ_c at $T_c + 5 \text{ K}$. (\blacksquare : τ_c of the hydrogen, \circ : those of the deuteron.) The dashed lines are guides for eyes.

of its neighboring hydrogens. Thus, it is reasonable to assume that a hydrogen disturbs the ordering of its surrounding deuterons via the inter-bond interaction. Figure 7 indicates the increase of τ_c of hydrogens with increase of the concentration. This means the increase of U in the hydrogen bonds corresponding to the elongation of the bond length caused by the interaction with the deuteron bonds. In this enlarged bonds, hydrogen becomes to be able to take one of two minimum positions in the potential, that is, hydrogens are possible to localize in the bond with lowering temperature in the mixed crystals in contrast to the case of the pure crystal for $x = 0$. In this sense, we can say that the hydrogen bonds are "softer" than the deuteron bonds. This soft hydrogen bond screens the interaction between the deuteron bonds for low concentration of deuterons. So deuterons do not localize in their bonds even if temperature is lowered than T_c of pure TKDS ($x = 1.0$). Thus the Raman frequency shift of $\omega(\text{HSO}_4^-)$ shows a continuous change at the phase transition as shown in Fig. 4(a). Once a hydrogen localized in the bond, the bond has a dipole moment which produces the electric field to the nearest deuteron bonds. The field triggers an abrupt ordering of deuteron in the bond as shown in Fig. 4(b), where the frequencies of DSO_4^- ions lie on a single curve for all mixed crystals, because all of the deuterons inter-

act with each other producing a cooperative interaction as expected for the pure TKDS. The present paper is the first study to elucidate experimentally the existence of the interaction among hydrogen bonds in the zero dimensional hydrogen bonded system.

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- 1) K. Gesi: J. Phys. Soc. Jpn. **48** (1980) 886.
 - 2) Y. Noda, H. Kasatani, Y. Watanabe and H. Terauchi: J. Phys. Soc. Jpn. **61** (1992) 905.
 - 3) C. Totsuji and T. Matsubara: Solid State Commun. **89** (1994) 677.
 - 4) M. Kasahara, P. Kaung and T. Yagi: J. Phys. Soc. Jpn. **63** (1994) 441.
 - 5) G. S. Parry and L. Glaser: Z. Kristallogr. **113** (1960) 57.
 - 6) Y. Moritomo, Y. Tokura, N. Nagaoka, T. Suzuki and K. Kumagai: Phys. Rev. Lett. **71** (1993) 17.
 - 7) M. Kasahara, P. Kaung and T. Yagi: J. Phys. Soc. Jpn. **61** (1992) 3432.
 - 8) We interpreted in ref. 4 that the two lines in the disordered phase is resulted from the disappearance of the double degeneracy of the ν_2 mode caused by lowering of DSO_4^- ion symmetry. However, the present study reveals that two lines are assigned to the two kinds of ions, HSO_4^- and DSO_4^- .
 - 9) M. Kasahara: J. Phys. Soc. Jpn. **44** (1978) 537.
 - 10) A. Abragam: *The Principles of Nuclear Magnetism* (Oxford, Clarendon, 1961) Chap. X.
 - 11) Y. Noda and H. Kasatani: J. Phys. Soc. Jpn. **60** (1991) 13.
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