

# Study on the Phase Transition of $K_3D_xH_{1-x}(SO_4)_2$ by the Raman Scattering of the Internal $\nu_2$ Mode

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Temperature dependence of the  $\nu_2$  mode in mixed crystals  $K_3D_xH_{1-x}(SO_4)_2$  was studied by Raman scattering from room temperature to 20 K. The  $\nu_2$  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.<sup>1)</sup> 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.<sup>2)</sup> On the other hand, according to the numerical estimation by Totsuji and Matsubara,<sup>3)</sup> 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,<sup>4)</sup> 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 method<sup>5)</sup> 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.<sup>6)</sup> 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.<sup>7)</sup> All spectra were analyzed by the same procedure as in our previous work.<sup>4)</sup>

## §3. Results and Discussion

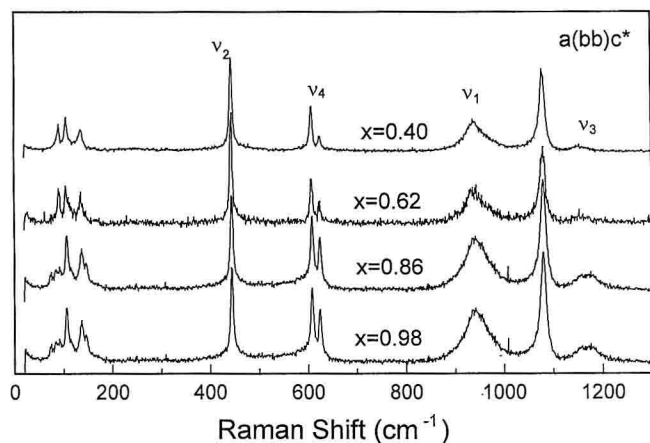
In isotropically mixed crystals, the whole aspect of spectra up to  $1200\text{ cm}^{-1}$  is very similar to those reported in pure compounds. For comparison among various deuteron concentration  $x$ , the Raman spectra in the  $a(bb)c^*$  geometry observed at 295 and 21 K are shown in Figs. 1(a) and 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  $\nu_2$  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  $435\text{ cm}^{-1}$  line increases and that of the  $440\text{ cm}^{-1}$  line decreases, while  $450\text{ cm}^{-1}$  line does not change.

These facts imply that the  $435\text{ cm}^{-1}$  line is the  $\nu_2$  mode of  $DSO_4^-$  and the  $440\text{ cm}^{-1}$  line is that of  $HSO_4^-$ . Since the amount of  $SO_4^{2-}$  ion does not change in mixed crystals, the  $450\text{ cm}^{-1}$  line is the  $\nu_2$  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 $\nu_2$ mode

The temperature dependence of the frequency of the  $\nu_2$  mode for  $x = 0.86$  is given in Fig. 3. Above  $T_c$ , although spectra in Fig. 1 show one  $\nu_2$  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  $D(SO_4^-)_2$ .<sup>8)</sup> The frequencies  $\omega_{0H}$  and  $\omega_{0D}$  are independent of temperature within a present experimental error. Two  $\nu_2$  lines split into three lines in the ordered phase as described above. The splitting of  $\omega_{0H}$  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 reported<sup>2)</sup> 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  $S$ .<sup>9)</sup> 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  $\omega_{0H}$  is the average frequency,  $[\omega(HSO_4^-) + \omega(SO_4^{2-})]/2$ , and  $2\delta$  the splitting at 0 K. We consider

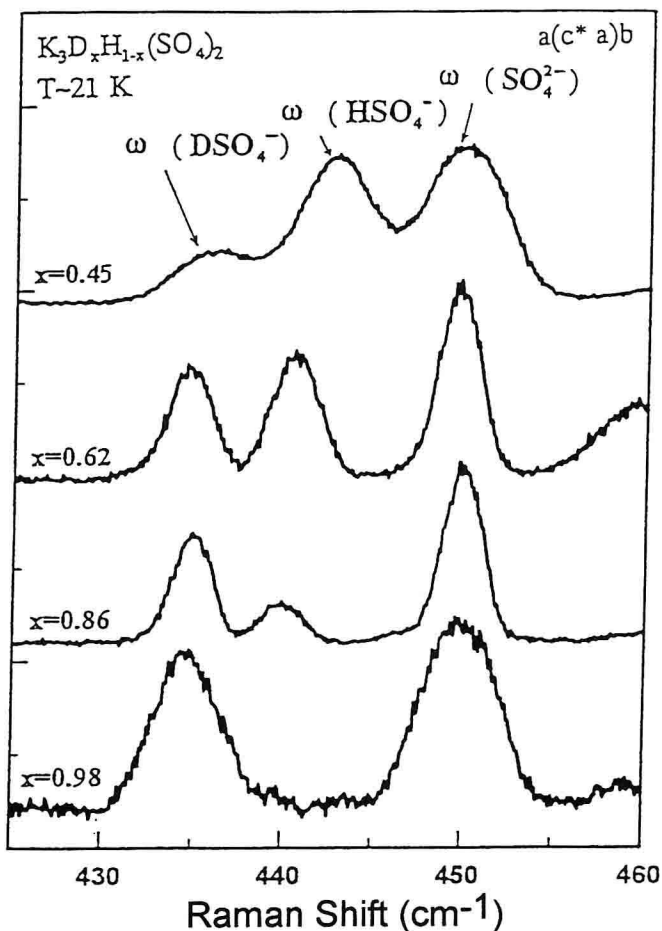


Fig. 2. Raman spectra of the  $\nu_2$  modes of  $K_3D_xH_{1-x}(SO_4)_2$  in the  $a(c^*a)b$  geometry at 21 K for  $x = 0.40, 0.62, 0.86$  and  $0.98$ . Each line is assigned by  $x$  dependence of the intensity.

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  $\tau_c$  of the hydrogen motion is shorter than the inverse of  $\delta$ , 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  $\omega_{0H}$ . 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



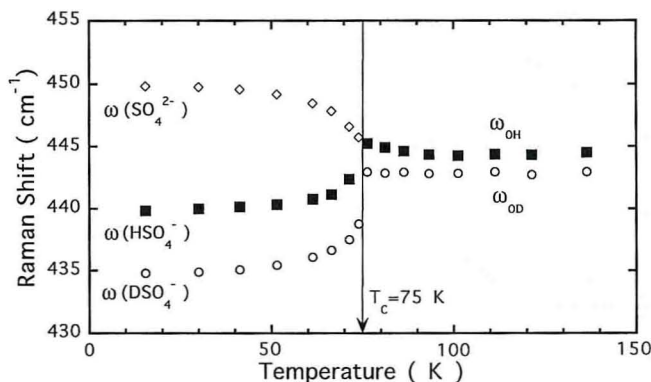
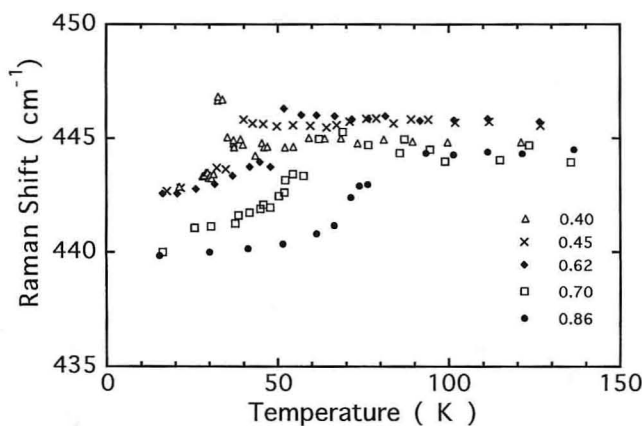


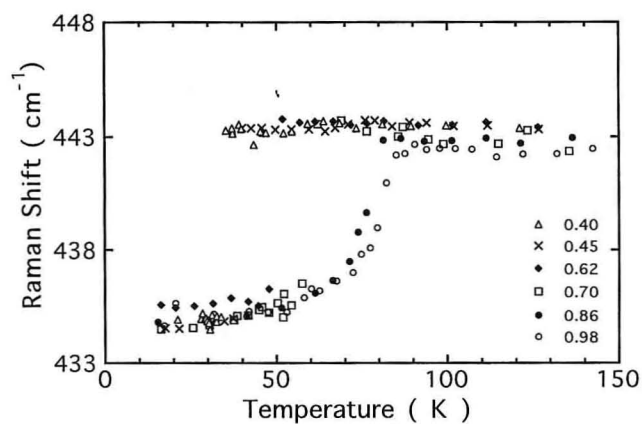
Fig. 3. The temperature dependence of  $\omega_{OH}$ ,  $\omega_{OD}$ ,  $\omega(HSO_4^-)$ ,  $\omega(DSO_4^-)$  and  $\omega(SO_4^{2-})$  of the  $\nu_2$  mode in the mixed crystal of  $x = 0.86$ .

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)

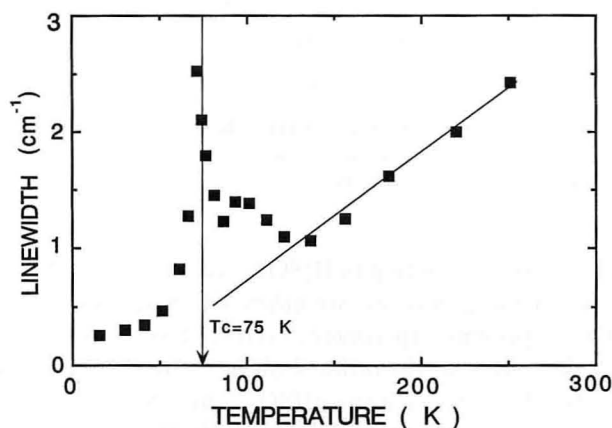
Fig. 4. The temperature dependence of (a)  $\omega_{OH}$  and  $\omega(HSO_4^-)$  and (b)  $\omega_{OD}$  and  $\omega(DSO_4^-)$ .

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  $\omega_{OD}$ . This point will be discussed later.

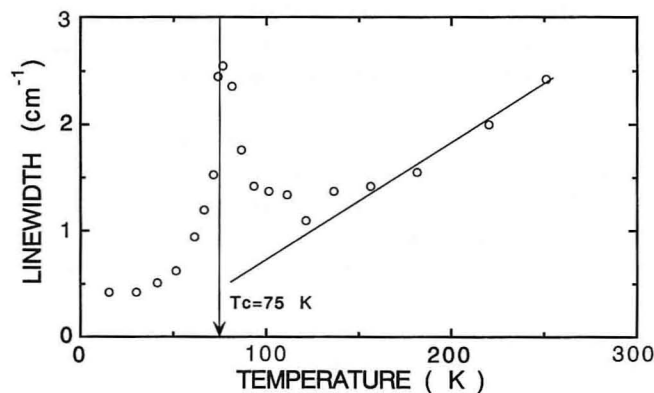
Three  $\nu_2$  modes in the ordered phase are reduced to two lines at  $T_c$  as shown in Fig. 3. This indicates that hydrogen or deuterium spends the same average time at each site of the double minimum potential in the disordered phase. It does not stay on any site for a period long enough to give 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  $\nu_2$  line centered at  $\omega_{OH}$  ( $\omega_{OD}$ ).

### 3.2 Anomalous broadening of the $\nu_2$ 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  $\Delta$  is found near  $T_c$  as a deviation from the solid line. Here,  $\Delta$  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)  $\omega_{OH}$  and  $\omega(HSO_4^-)$  peaks and (b)  $\omega_{OD}$  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  $\tau_c$ , we analyze the anomalous line broadening by the application of the motional narrowing theory developed in the nuclear magnetic resonance.<sup>10)</sup> 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  $\Delta$  is proportional to  $\tau_c$  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  $\tau_c$  for mixed crystals. The inverse of  $\tau_c$  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  $\tau_c$  is expressed as

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

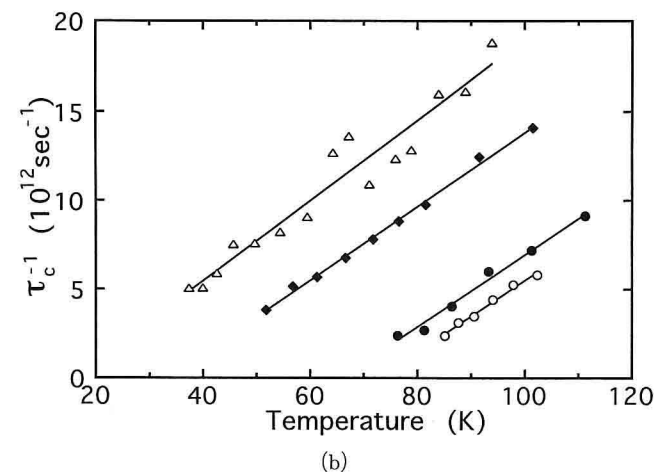
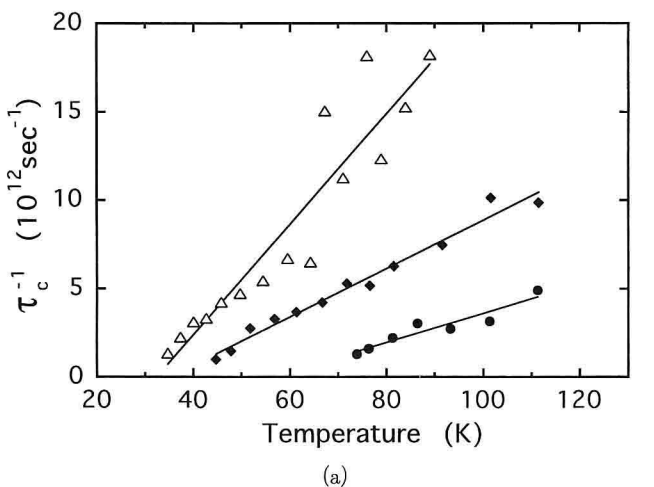


Fig. 6. The inverse of  $\tau_c$  of (a) the hydrogen and (b) the deuteron motions in the hydrogen bond. (o:  $x = 0.98$ ,  $\bullet$ :  $0.86$ ,  $\blacklozenge$ :  $0.62$  and  $\Delta$ :  $0.40$ .) Solid lines are the least square fits.

where  $\tau_0^{-1}$  is the characteristic time of a hydrogen (deuteron) in an isolated hydrogen bond. The extrapolated  $\tau_c$  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  $\tau_0^{-1}$  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  $\tau_c^{-1}$  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,  $\tau_c$  of H and D at 5 K above  $T_c$  are plotted against the concentration  $x$ . Both  $\tau_c$  decrease with decreasing  $x$  and seem to be zero around  $x = 0.10$ . The shorter  $\tau_c$  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  $\tau_c$  means that the hydrogen (deuteron) moves in a single minimum potential and no phase transition is found. Thus, the concentration dependence of  $\tau_c$  is essentially consistent with the dielectric measurement.<sup>6)</sup> As shown in Fig. 7, we obtained rather a unusual result that  $\tau_c$  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.<sup>11)</sup> The present Raman scattering study gives the bond length characteristic for the mixed crystals.

Totsuji and Matsubara<sup>4)</sup> inferred that the zero point vibration of hydrogens seriously influences the ordering

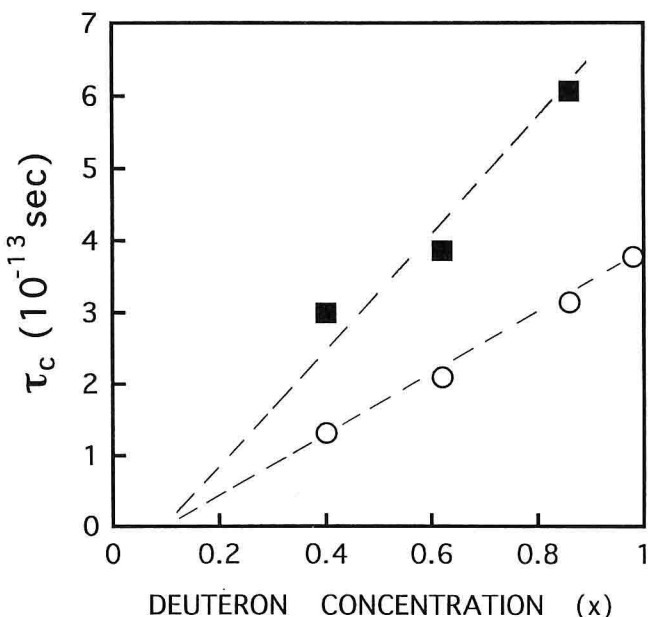


Fig. 7. The concentration dependence of  $\tau_c$  at  $T_c + 5 \text{ K}$ . ( $\blacksquare$ :  $\tau_c$  of the hydrogen,  $\circ$ : those of the deuteron.) The dashed lines are guides for eyes.



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  $\tau_c$  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  $\text{DSO}_4^-$  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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