

RAMAN SCATTERING OF $K_3D_xH_{1-x}(SO_4)_2$ SINGLE CRYSTALS

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In mixed crystal of $K_3H(SO_4)_2$ and $K_3D(SO_4)_2$, the internal modes of HSO_4^- , DSO_4^- and SO_4^{2-} were separately observed. In the ordered phase, the splittings between $\omega(HSO_4^-)$ and $\omega(SO_4^{2-})$, and $\omega(DSO_4^-)$ and $\omega(SO_4^{2-})$ depend on temperature as $(T_c - T)^\beta$ with $\beta = 0.25 \pm 0.05$. In the disordered state, HSO_4^- and DSO_4^- lines show broadening near the transition temperature. Motional narrowing theory developed in nuclear magnetic resonance is applied to analyse the broadening and the correlation time for hydrogen (deuteron) motion is obtained.

Keywords: Raman scattering, internal mode of SO_4 , $K_3H(SO_4)_2$, $K_3D(SO_4)_2$, motional narrowing theory, line broadening near T_c .

1. INTRODUCTION

It is a widely interested problem that the replacing of hydrogen with deuterium in certain ferroelectrics with hydrogen bonds causes the drastic shift of the transition temperature T_c (isotope effect). In order to make the problem simple, it is worthwhile to study the material where the hydrogen bonds are relatively isolated, that is, where the hydrogen bonds do not make a network throughout the crystal like in KDP.

In $K_3D(SO_4)_2$ (TKDS), two sulphate ions form a dimer with a deuteron and a crystal consists of dimers and potassium ions.¹ A deuteron can occupy one of the two distinct sites along an isolated hydrogen bond connecting two sulphate ions. The two sites are geometrically related by an inversion operation. One of these sites is preferentially chosen below the phase transition temperature T_c (84 K) and the inversion symmetry vanishes. If the transition mechanism is the order-disorder transition type, the structure of the high-symmetry phase can be considered as the dynamical average of the two structures.

From the spectroscopic point of view, these different deuteron environments, DSO_4^- and SO_4^{2-} , produce detectable changes in the Raman spectrum of the internal modes of the sulphate ion.² However, the rapid site change of the deuteron makes two sulphate ions on either sites equivalent in high-symmetry phase. Thus, the internal mode spectrum at a high temperature is considered to be their motional averaged feature. Slowing down of the deuteron motion near T_c has been observed as an anomalous line broadening.²

In the present work, in order to clarify the whole process of the phase transition, we now carried out Raman measurement on the ν_2 mode of crystals with various D -concentrations over a wider range of temperature down to 20 K. The two extremes of the system, TKDS and $K_3H(SO_4)_2$ (TKHS) exhibit quite different

properties. TKDS undergoes a phase transition,³ whereas on the other limit TKHS does not show any transition down to the lowest temperature.

2. EXPERIMENTAL

Single crystals were grown in mixture of D_2O and H_2O with K_2SO_4 and excess D_2SO_4 . Since the internal modes split at T_c , the concentration x of deuterium was found from the concentration dependence of T_c reported by Moritomo.⁴ The experimental setup for Raman scattering was described elsewhere.² All spectra were observed in the $a(c^*a)b$ geometry and analyzed by the same procedure as in our previous work.²

3. RESULTS AND DISCUSSION

Figure 1 shows the ν_2 spectra in the ordered phase for various x . With increasing x , the intensity of the 435 cm^{-1} line increases and that of the 440 cm^{-1} line decreases, while the 450 cm^{-1} line does not change. These facts imply that the 435 cm^{-1} line is the ν_2 internal mode of DSO_4^- and the 440 cm^{-1} line is that of HSO_4^- . Since the amount of SO_4^{2-} ions does not change in mixed crystals, the 450 cm^{-1} line is the internal ν_2 mode of SO_4^{2-} ions. We should notice that present study is the first case that Raman lines of deuterated ion is observed separately from that of hydrogen contained ion in the mixed crystal.

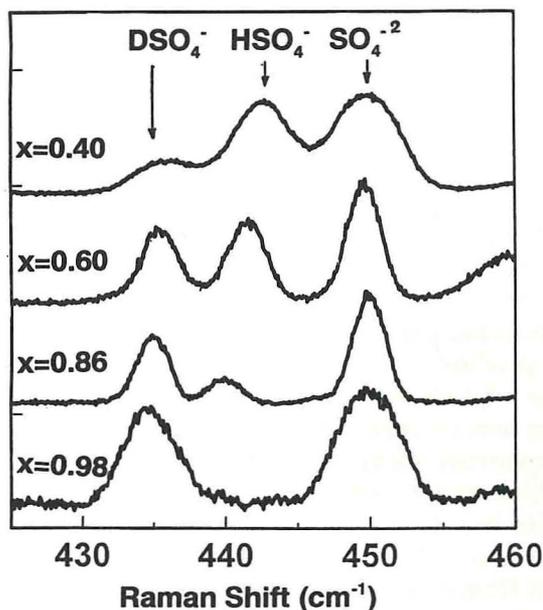


FIGURE 1 Spectra of the ν_2 modes observed in the geometry $a(c^*a)b$ in the low temperature phase, where the c^* is perpendicular to the a and b axes.

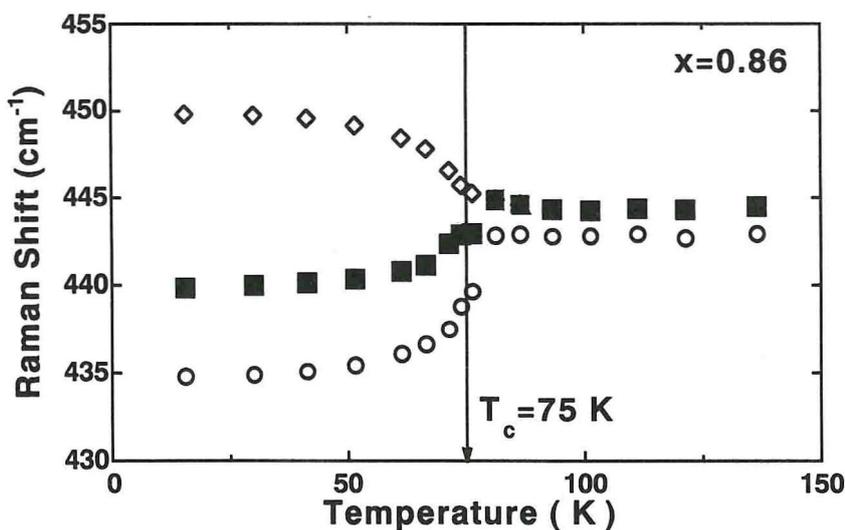


FIGURE 2 Temperature dependence of the ν_2 modes of HSO_4^- (■), DSO_4^- (○) and SO_4^{2-} (◇) for $x = 0.86$.

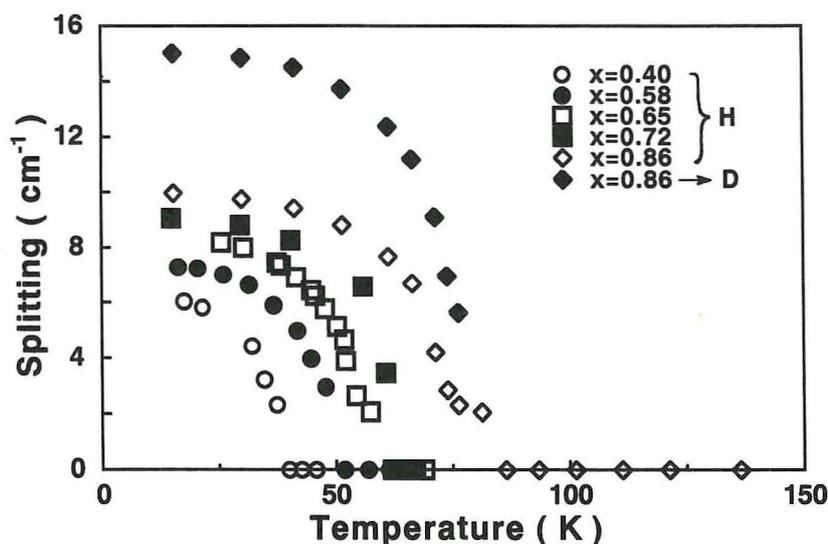


FIGURE 3 Temperature dependence of the splitting between $\omega(HSO_4^-)$ and $\omega(SO_4^{2-})$. The splitting for DSO_4^- is also plotted for $x = 0.86$.

Figure 2 shows the temperature dependence of the ν_2 mode frequency for $x = 0.86$. The temperature dependences of the splitting of HSO_4^- are plotted in Figure 3 for all mixed crystals. For DSO_4^- , only the splitting for $x = 0.86$ is plotted in Figure 3 because, for the low x , the frequency of DSO_4^- does not seem to depend on temperature. The reason is not clear at present. The splittings shown in Figure 3 depend on temperature as $(T_c - T)^\beta$ with $\beta = 0.25 \pm 0.05$. One (M.K.) of us showed⁵ by applying the motional narrowing theory⁶ developed in nuclear magnetic resonance that the splitting of the frequency of the nuclear magnetic resonance in

the ordered phase for the order-disorder phase transition is proportional to the long range order parameter. The same consideration can be applied to the Raman scattering, that is, the Raman frequency of HSO_4^- is the result of the weighted average of those of HSO_4^- and SO_4^{2-} ions with the favorite state of HSO_4^- . Experimentally, for example, Scott showed that the order parameter of $\text{C}_3\text{N}_3\text{H}_3$ obtained with x-ray study is proportional to the splitting obtained with Raman scattering.⁷ Thus, the results in Figure 3 indicate that the exponent of the antiferroelectric order parameter is smaller than that derived from mean field theory for ferroelectrics. The zero point vibration presumably suppresses the growth of the order parameter in the low temperature and the exponent results in a small value.

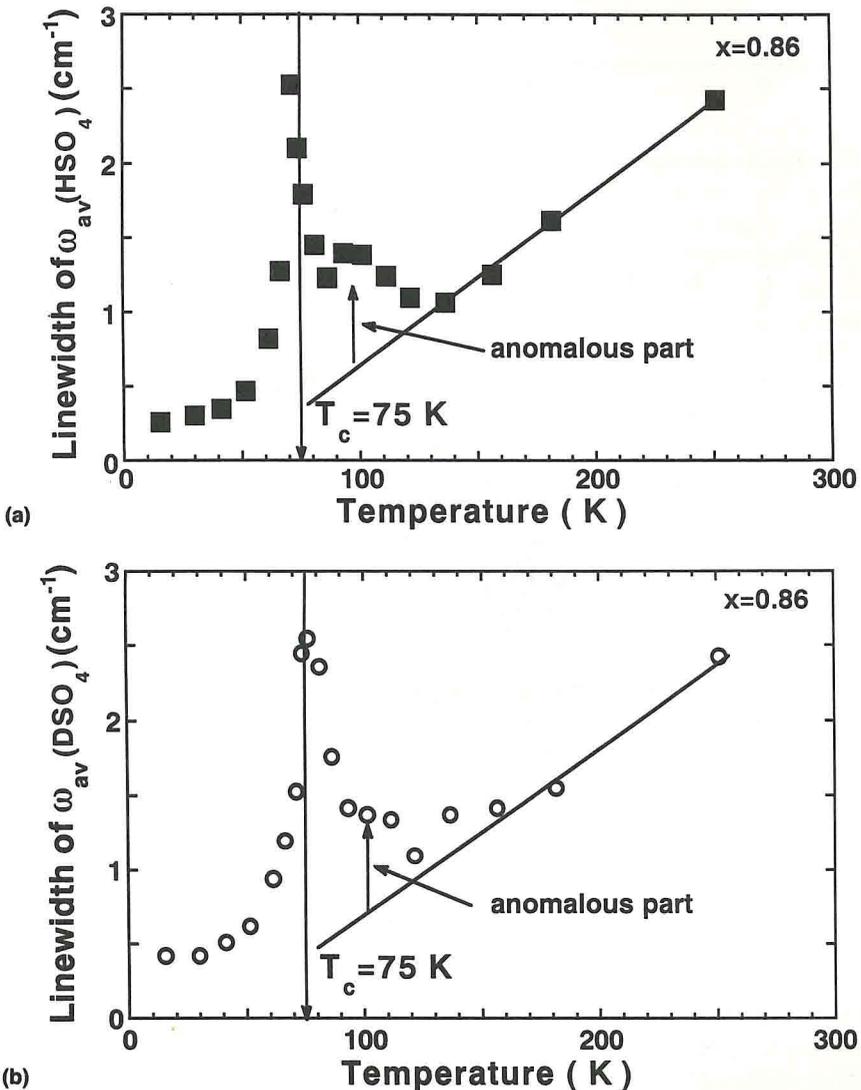


FIGURE 4 Temperature dependence of the linewidth of (a) HSO_4^- and (b) DSO_4^- .

As a result of fast movements of hydrogen (deuteron) in the disordered phase, the ν_2 modes from HSO_4^- (DSO_4^-) and SO_4^{2-} are reduced to a single line. According to the motional narrowing theory, the linewidth depends on the characteristic time τ_c which is a measure of the hydrogen (deuteron) motion between the two minima of the potential in the hydrogen bond. For the fast case ($\tau_c^{-1} (= \Omega) > \delta$, where $2\delta = \omega(SO_4^{2-}) - \omega(HSO_4^-)$ or $= \omega(SO_4^{2-}) - \omega(DSO_4^-)$ at lower temperature), the spectrum is approximated by⁶

$$I(\omega) = \frac{\delta^2/\Omega}{(\omega - \omega_0)^2 + (\delta^2/2\Omega)^2} \quad (1)$$

where Ω is the average frequency of hydrogen (deuteron), ω_0 the motional averaged frequency, that is, the peak frequency in the disordered phase. The linewidth Δ is proportional to τ_c as

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

Thus, the observation of the linewidth gives τ_c of the hydrogen (deuteron) motion. The temperature dependences of the linewidth of HSO_4^- and DSO_4^- are shown in Figure 4(a) and (b), respectively. In addition to the usual temperature dependence of the linewidth, the anomalous line broadening Δ associated with the phase transition is found near T_c for both HSO_4^- and DSO_4^- .

In the motional narrowing analysis, one can expect the broadening of the line when there exists a motion between two separate sites, DSO_4^- (HSO_4^-) and SO_4^{2-} , and the inverse of τ_c is under the way of the transit from the fast movement to the slow one. Thus, the observation of the line broadening of HSO_4^- implies that the potential well for H is double minimum one in the mixed crystals, whereas for pure TKHS, a single minimum potential has been reported by the neutron scattering below 100 K.⁸

The characteristic time τ_c calculated by equation (2) depends on temperature

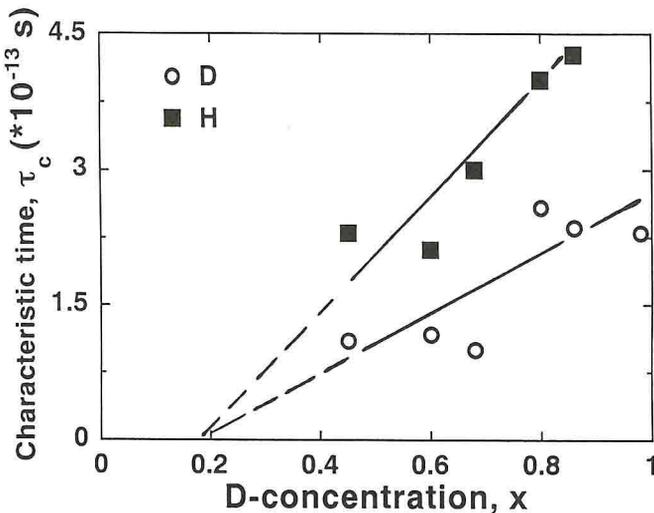


FIGURE 5 The concentration dependence of τ_c at 10 K above T_c . The solid and dashed lines are the guide for eye.

linearly near T_c . In Figure 5, τ_c 's estimated at 10 K above T_c for H and D are plotted against the concentration. Both τ_c 's decrease with decreasing x and seem to be zero around $x = 0.20$. The shorter τ_c implies the lower barrier in the double minimum potential and, in turn, corresponds to a lower transition temperature. The zero value of τ_c means that hydrogen (deuteron) move 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.⁴

On the other hand, we obtained rather unusual results that τ_c for H is slightly longer than that for D over the whole concentration range. This result indicates that the hydrogen bond for H is longer than that for D . However, this is unlikely because the length of the hydrogen bond in pure TKHS is shorter than that in pure TKDS by about 0.025 Å.^{1,8} Presumably we should simulate spectra using the exact expression instead of Equation (1). Also some interaction between the dimers should be taken into consideration.

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