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RAMAN SCATTERING STUDY OF $K_3D(SO_4)_2$

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Abstract Raman scattering from single crystals of $K_3D(SO_4)_2$ has been observed in both of the disordered and ordered phases. No effect of deuteration on frequencies was found for most of the Raman lines. The internal mode ν_2 splits into four peaks in the ordered phase and the temperature dependence of the splitting has an index half of that given by the mean field theory. The anomalous broadening of the ν_2 line was found above Tc and explained successfully with the application of motional narrowing theory developed in NMR.

INTRODUCTION

In $K_3H(SO_4)_2$ (TKHS) crystal and its deuterated analogue (TKDS), a hydrogen connects two SO_4 ions to form one dimer [1–4] The hydrogen is confined within a dimer and does not extend to other dimers. This system, the so-called "zero dimensional hydrogen bond system", provides an appropriate system for the study of the geometrical isotope effect, because we can restrict the problem within a dimer. This situation makes it simple to elucidate the role of hydrogen in the hydrogen bond for the phase transition.

Hydrogen compound, TKHS, does not undergo a phase transition down to liquid helium temperature, whereas TKDS shows a phase transition at 84 K.[5] From the structural study with X-ray diffraction by Noda et al.,[6] the hydrogen bond of TKHS with a double minimum potential at room temperature contracts with decreasing temperature to the length with a single minimum potential. On the other hand, the hydrogen bond of TKDS probably maintains its length so that the potential is the double minimum one still in the low-temperature region.

In order to understand the phase transition mechanism, it is necessary to reveal the dynamical character from the viewpoint of the lattice vibration. The Raman scattering study of TKDS is reported in the present paper.

EXPEIMENTAL

Crystals were grown with slow evaporation from aqueous solutions of K_2SO_4 and excess D_2SO_4 at room temperature.[7] Specimens with a single domain were cut under a polarized microscope and polished with wet filter papers. The phase transition temperature Tc was found to be 72 K with the dielectric measurement at 100 kHz. The detail of the instrument for Raman scattering were described elsewhere.[8]

RESULTS AND DISCUSSION

Figure 1 shows spectra above 300 cm^{-1} at 295 and 38 K. The spectra of the internal modes do not depend essentially on the scattering geometry. The number of lines observed in the present study is less than that expected from the factor group analysis, which shows that 18 intenal modes belong to each Ag and Bg species. These facts imply that the SO_4^{2-} ions do not have the crystal symmetry C_{2h} but the site symmetry C_1.

The frequency shift due to the deuteration is hardly observed except for the 942 cm^{-1} line at 295 K. Corresponding line in TKHS has been reported at 936 cm^{-1}. The frequency shift due to deuteration is positive, +6 cm^{-1}. The feature is different from the case of other ferroelectrics such as KDP, where most of the internal modes of PO_4^{3-} decrease in frequency with deuteration. The splitting of each line in the spectrum at 38 K indicates exactly that TKDS undergoes a phase

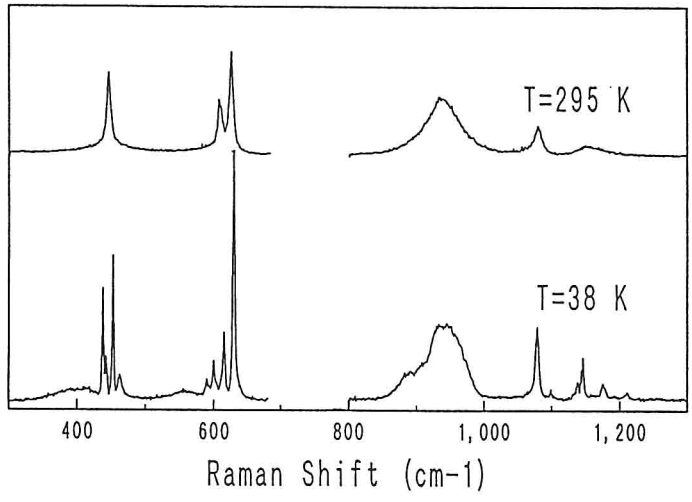

FIGURE 1 Raman scattering spectra of TKDS in the geometry a(c^*a)b.

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With decreasing temperature, the ν_2 spectra show a drastic broadening of its spectral width as shown in Figure 2. In order to explain this effect, we apply the motional narrowing theory developed in the magnetic resonance[10] to the Raman spectroscopy of the order-disorder system. If a deuteron moves stochastically with the average

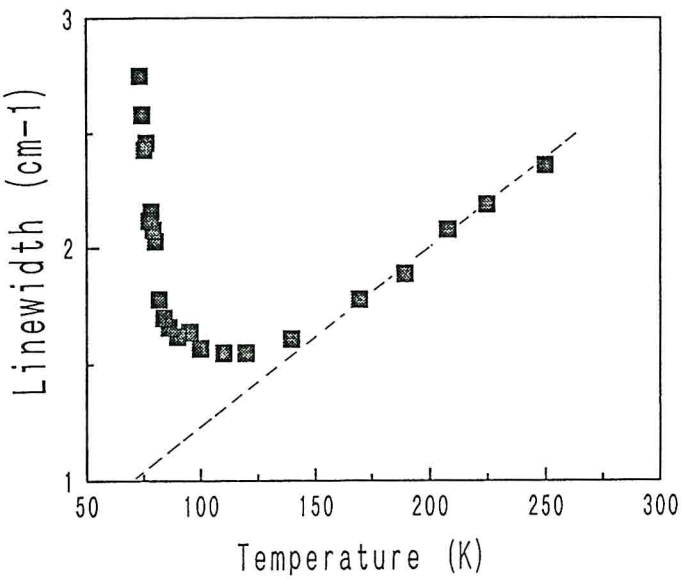

FIGURE 2 Temperature dependence of the linewidth. Dashed line indicates the part independent of the phase transition.

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

The anomalous part of the linewidth is given as $\Delta=(\delta^2/2)\Omega^{-1}$. The exact value of δ in the high temperatue phase is unknown because the slow limiting case was not realized in this study. However, it is reasonable to assume that the splitting in the low temperature phase is

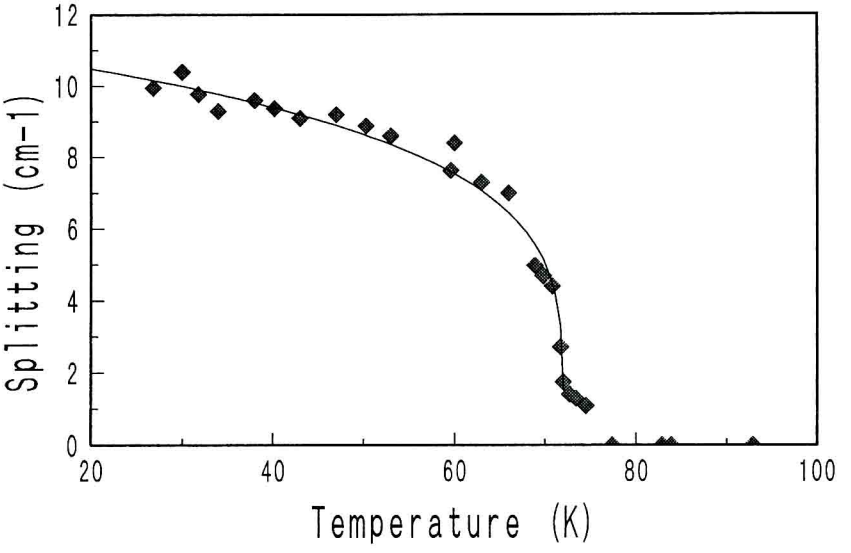

FIGURE 3 Temperature dependence of the splitting of the ν_2 mode. Solid line indicates the $(Tc-T)^{0.25}$

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One of the splittings of the ν_2 mode depends on temperature as shown in Fig. 3. The modified motional narrowing theory has proved that the frequency shift or the splitting with temperature in the ordered phase is proportional to the order parameter.[11] In Figure 3, the solid line represents $(Tc-T)^n$, where n=0.25. The value of 0.25 is just a half of the exponent given by the mean field theory. However, the physical reason of the coincidence is not clear at the present stage. We can expect that the temperature dependence of the order parameter in TKDS might be smaller than that given by the mean field theory.

AKNOWLEDGEMENT

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REFERENCES

1. S. Suzuki and Y. Makita,Acta Crystallogr., B34, 732 (1978).
2. I.P. Makarova, I.A. Verin and N.M. Shchagina,Sov. Phys. Crystallogr., 31, 105 (1986).
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7. G.S. Parry and L. Glasser,Z. Kristallogr., 113, 57(1960).
8. M.Kasahara, P. Kaung and T. Yagi, J. Phys. Soc. Jpn., 61, 3432 (1992).
9. V. Videnova-Adrabinska,J. Mol. Struct., 237, 367 (1990).
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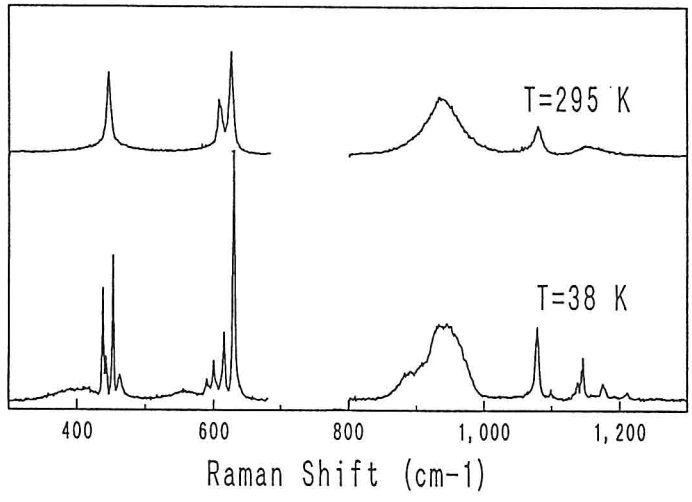

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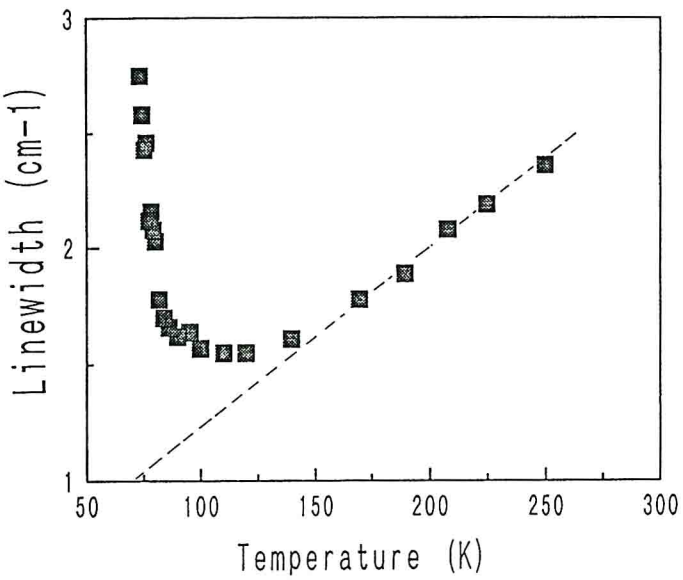

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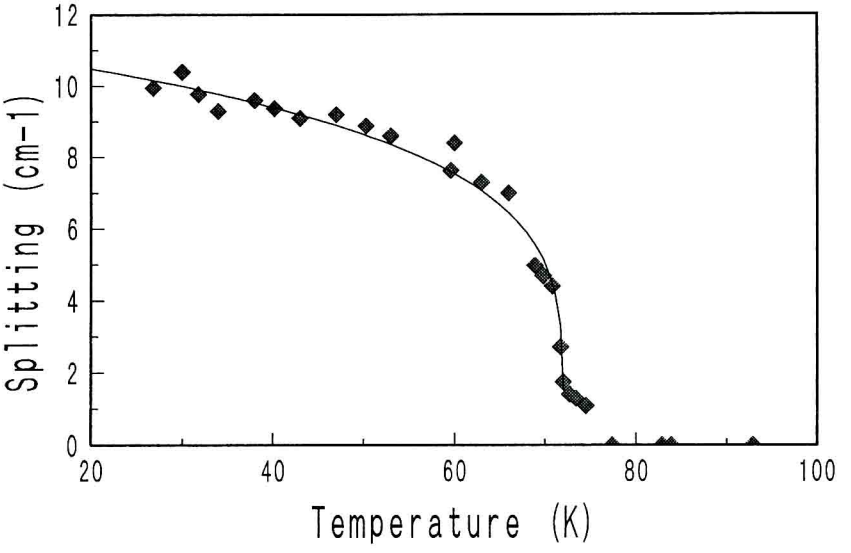

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