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Anomaly of the Raman Linewidth of the Internal ν_2 Mode near the Phase Transition Point of $K_3D(SO_4)_2$

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The linewidth of the internal mode ν_2 of SO_4^{2-} ion of the antiferroelectric $K_3D(SO_4)_2$ shows the anomalous broadening with lowering temperature near the phase transition point. The broadening is well explained by a mechanism resembling the motional narrowing phenomenon in the nuclear magnetic resonance theory. The characteristic time of the motion of deuteron in a hydrogen bond is estimated to be on the order of 10^{-13} s.

[$K_3D(SO_4)_2$, Raman scattering, internal mode, motional narrowing]

Tripotassium hydrogen disulfate $K_3H(SO_4)_2$ (TKHS) does not show any phase transition from room temperature to liquid helium temperature, whereas its deuterated analogue (TKDS) undergoes the antiferroelectric phase transition at 84 K.[1] This difference suggests an important role of hydrogen in the phase transition mechanism. The structure of the hydrogen bond in TKHS has been studied by Noda *et al.*[2] In addition to this, it is important for understanding the phase transition mechanism to reveal the dynamical properties such as the characteristic time of hydrogen or deuteron motion in the hydrogen bond.

The crystal of TKDS consists of K^+ ions and $D(SO_4)_2^{3-}$ dimers.[3] A single dimer is formed by two SO_4^{2-} ions connected by a hydrogen bond. The hydrogen bonds are isolated from each other and do not constitute a network through a crystal. Thus, as a result of the motion of a deuteron between two double-well potential minima in the hydrogen bond, a SO_4^{2-} ion is transformed to a DSO_4^- ion and *vice versa* with a characteristic time. This transformation, in turn, causes the fluctuation of the local field of SO_4^{2-} ions. One can observe this fluctuation through the Raman spectrum of the internal modes of SO_4^{2-} ions.[4]

Deuterated crystals were grown in D_2O with K_2SO_4 and excess H_2SO_4.[5] The phase transition temperature T_c was found to be 72 K from the measurement of dielectric constant. The rate of deuteration is about 85%.* The experimental setup for Raman scattering was described elsewhere.[6] Temperature stability of the specimen was maintained within 0.1 K with a closed-cycle He-gas refrigerator and a temperature controller.

Based on the preliminary observation, we focused our attention to the ν_2 line because we obtained the spectra with a high signal-to-noise (S/N) ratio. Furthermore, the ν_2 spectrum seems to consist of only a single line so that the change of the spectrum with temperature can be detected accurately. However, the situation is slightly complicated near T_c as mentioned later. Other internal modes were not available for the present purpose: the ν_1 line at 942 cm^{-1} is broad as described previously[6] and the temperature dependence of its linewidth was not so steep because the broadening is presumably due to an inhomogeneous origin. This broadening interrupts the precise detection of the change in spectral shape due to the phase transition. The poor S/N ratios of the ν_3 lines are not enough to obtain reliable data. One of the two ν_4 lines shows a broadening near T_c while the other does not. The S/N ratio of the former line is

* Y. Moritomo and Y. Tokura: presented at the annual meeting of Phys. Soc. Jpn. (1992).

less than that of the ν_2 line.

Spectra of the ν_2 lines were analyzed on the assumption that the shape of each line is Lorentzian. Gaussian fitting was also attempted. However, over the entire temperature range considered here, the Lorentzian fitting gave better results than Gaussian fitting. Broadening due to the instrument itself was compensated.

Figure 1 shows the typical spectra of the internal ν_2 mode of the sulfate ion observed at several temperatures above T_c. As shown in the figure, the line shape near T_c is distorted. The distortion of the line seems to be caused by the superposition of a few lines, which is expected in the order disorder phase transition. The Raman selection rule for internal modes is broken in the paraelectric phase when the phase transition is of order-disorder type.[7] In other words, a part of the spectrum in the ordered phase is observed even in the disordered phase. In the case of TKDS, four ν_2 modes, two strong lines and two weak ones, are observed in the ordered phase.[6] Hence, we infer that the ν_2 spectrum near T_c consists, in principle, of four lines. However, it is presumably approximated with the superposition of two lines which correspond to the two strong lines in the ordered phase.

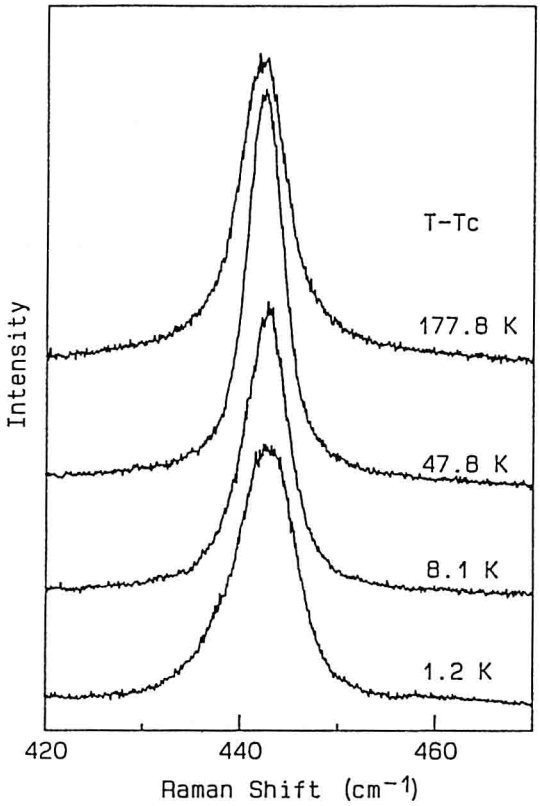

Fig. 1. Spectra of the ν_2 mode in the geometry $a(c^*a)b$ at 249.8, 119.8, 80.1 and 73.2 K from top to bottom. The temperature differences $T-T_c$ are shown in the figure.

Therefore, in addition to the one-line fitting, we attempted the fitting with two lines. In order to see which fitting is better, we compared a modified root-mean-square (rms)[8] of the difference between the observed and calculated spectra,

$$[\sum_i [F_c(\omega_i)-F_o(\omega_i)]^2/F_c(\omega_i)]^{1/2},$$

where $F_c(\omega_i)$ is the calculated Raman line and $F_o(\omega_i)$ is the observed one with a step of the frequency scan ω_i. Modified rms values are 43.7 for the two-line fitting and 65.7 for the one-line fitting at 73.2 K. These values decrease monotonically to 35.9 and 41.9 at 79.1 K, respectively. The linewidth obtained with the two-line fitting is not so different from that obtained with the one-line fitting. The two-line fitting gave a narrower linewidth by 0.1 cm^{-1} or less than the one-line fitting. An example of the two-line fitting is shown in Fig. 2. The temperature dependence of the higher frequency line is shown in the inset of Fig. 3. One should not consider that this line appears abruptly at

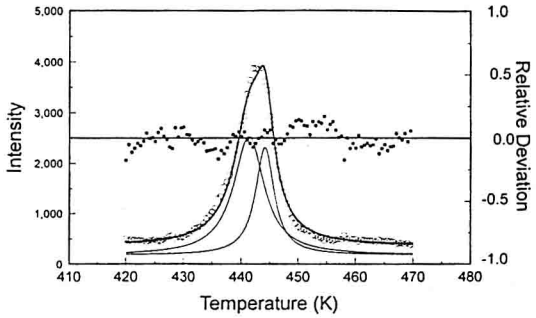

Fig. 2. An example of the two-line fitting of the spectrum at 73.2 K. The thick solid line is the calculated spectrum which is the sum of two thin solid lines. The observed spectrum for every five data points is plotted (○). Marks (■) indicate the relative deviation, $[F_c(\omega_i)-F_o(\omega_i)]/F_c(\omega_i)$ of the calculated spectrum $F_c(\omega_i)$ from the observed one $F_o(\omega_i)$.

79.1 K. For the spectra in the higher temperature region, the frequencies of two lines were so close that we could not separate them successfully. The modified rms with the one-line fitting decreases from 38.0 at 80.1 K to 29.1 at 249.8 K. In the following, we disregard the line which is only observable near T_c.

Figure 3 shows the temperature dependence of the linewidth of the ν_2 mode which is observed on the lower frequency side near T_c. The linewidth decreases down to the minimum value around 120 K with decreasing temperature, then increases divergently as the temperature approaches T_c. The increase in the linewidth near T_c is caused by the phase transition. Hence, the temperature dependence of the linewidth Δ related to the phase transition is defined here to be the difference between observed temperature dependence and the hypothetical one without the phase transition. The hypothetical temperature dependence is assumed to be linear for simplicity as indicated by a dashed line in Fig. 3. Figure 4 shows the temperature dependence of the linewidth Δ caused by the phase transition.

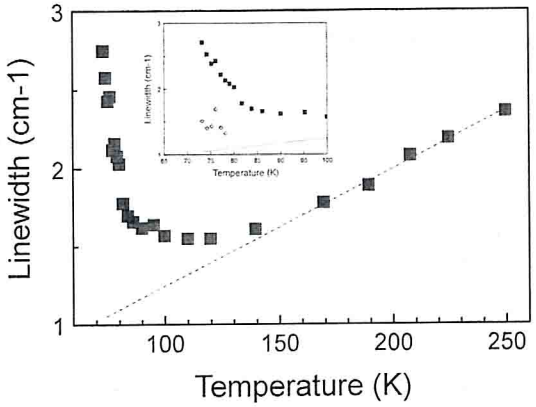

Fig. 3. The temperature dependence of the linewidth. Dashed line shows the hypothetical change of the linewidth without phase transition. Inset shows the linewidth of the higher frequency line which is observable only near T_c.

In order to discuss the anomalous broadening of the linewidth Δ, a deuteron in a hydrogen bond is assumed to move stochastically between two minima in the potential well with average frequency Ω, where Ω is the inverse of the average time of the stochastic motion. Raman frequency of a SO_4^{2-} ion changes from the frequency $\omega(DSO_4^-)$ to $\omega(SO_4^{2-})$ or *vice versa* due to the change of the deuteron position in the hydrogen bond. In the following, ω_0 stands for the average of the two frequencies, $\omega_0=(\omega(DSO_4^-)+\omega(SO_4^{2-}))/2$, and δ difference of each frequency from ω_0. According to the phenomenon of narrowing by motion of spins in the nuclear magnetic resonance theory,[9] two Raman lines are observed at $\omega_0+\delta$ and $\omega_0-\delta$ for the slow fluctuation, $\Omega<\delta$, and a single line at ω_0 for the fast one, $\Omega>\delta$. Because the two lines in the slow fluctuation case were not observed in the present study, only the fast case is considered.

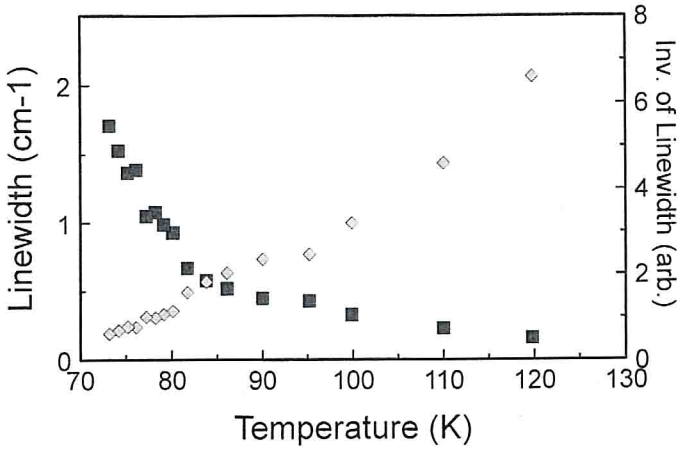

Fig. 4. The temperature dependence of the anomalous part of the linewidth (■) and its inverse (◆).

According to the discussion by Abragam, the spectrum for the fast fluctuation case is expressed[9] by

$$I(\omega) \sim \frac{\delta^2/\Omega}{(\omega-\omega_0)^2+(\delta^2/2\Omega)^2}.$$

Here, linewidth Δ is given with $\delta^2/2\Omega$.

The characteristic time Ω^{-1} is proportional to Δ. Hence, the anomalous broadening of the linewidth indicates that the deuteron motion slows down near T_c. The inverse of the characteristic time depends linearly on temperature near T_c as shown in Fig. 4. The absolute value of the characteristic time can be evaluated if one knows the value of δ, which can be obtained when an extremely slow fluctuation is realized. As mentioned above, we did not obtain δ in the present study but infer it to be on the order of 10 cm^{-1} from the splitting of the lines at low temperature in the ordered phase.[6] Thus, Ω^{-1} is estimated to be on the order of 10^{-13} s for the Δ of 2 cm^{-1} near T_c. This value is shorter than that of KD_2PO_4 by three orders.[8]

It is concluded from the present results that the phase transition of TKDS can be described with the order-disorder model although the motion of deuterons is fast compared with KD_2PO_4.

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