

Raman Scattering Study of $K_3H(SO_4)_2$ and $K_3D(SO_4)_2$ Single Crystals

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Raman scattering from single crystals of $K_3H(SO_4)_2$ and its deuterated analogues has been observed at 295 and 45 K. The spectra do not depend on the scattering geometries. Scarcely any effect of deuteration on frequencies was noted for most of the Raman lines. The Raman lines of the internal modes split into two peaks in the ordered phase of DKHS. The splitting is attributed to the ordering of deuterons.

[Raman scattering, phase transition, hydrogen bond, $K_3H(SO_4)_2$, isotope effect]

Ferroelectrics with hydrogen bonds show a remarkable isotope effect of the transition temperature (T_c) when deuterons are substituted for hydrogens.¹⁾ The tunneling model proposed by Blinc²⁾ has been considered to be the physical origin of this phenomenon. As far as we know, however, no direct evidence of the tunneling model has been discovered experimentally. Recently Ichikawa³⁾ and Ichikawa *et al.*⁴⁾ found a relationship between T_c and the length of the hydrogen bond in the KH_2PO_4 family. This relationship shows that the isotope effect can be explained by taking account of elongation of the hydrogen bonds with deuteration (geometrical isotope effect). It also holds well in several other crystals which have a dimensionality lower than three dimensions, such as squaric acid⁵⁾ (two dimensions), and $PbHPO_4$ ⁶⁾ (one dimension).

In $M_3H(XO_4)_2$ crystal, where M stands for alkaline ions and X for sulfur or selenium ion, a hydrogen connects two XO_4 ions to form one dimer.⁷⁻¹⁰⁾ The hydrogen bond 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.

We choose $K_3H(SO_4)_2$ (KHS) and its

deuterated analogue (DKHS) as objective materials because a single crystal with clear single domains can be obtained easily. Hydrogen compound, KHS, does not undergo a phase transition in the temperature region from room temperature to liquid helium temperature,¹¹⁾ whereas DKHS shows a phase transition at 84 K.¹¹⁾ From the structural study with X-ray diffraction by Noda *et al.*,¹²⁾ the hydrogen bond of KHS 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 DKHS probably maintains its length so that the potential is the double minimum one 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 KHS and DKHS is reported in this paper.

Thin platelike single crystals of KHS (DKHS) were grown with slow evaporation from aqueous solutions of K_2SO_4 and excess H_2SO_4 (D_2SO_4) at room temperature.¹³⁾ Specimens with single domains were cut under a polarized microscope and polished with wet filter papers. The phase transition temperature T_c of DKHS was confirmed to be 84 K with the dielectric measurement at 100 kHz.

The light source was Ar^+ laser with the wavelength of 514.5 nm and the scattered light

was analyzed with a double monochromator, Jobin Yvon HG-2S. Raman scattering was observed in the back-scattering geometry. The accuracy of peak frequencies is $\pm 1 \text{ cm}^{-1}$ except the $936 \text{ (} 942 \text{ in DKHS) cm}^{-1}$ peak. The accuracy of the 936 cm^{-1} peak is about $\pm 3 \text{ cm}^{-1}$ due to its broad linewidth. Temperature of the specimen was controlled within $\pm 0.1 \text{ K}$ by means of a closed-cycle He-gas refrigerator.

The crystal symmetry of KHS is $A2/a^{10}$ with $Z=4$. All of the lattice vibration modes are classified into $39A_g + 39B_g + 45A_u + 45B_u$, where the A_g and B_g species are Raman active. Ions relevant to this analysis are assumed to be K^+ , $H^+(D^+)$ and SO_4^{2-} ions. In the ordered phase of DKHS, the symmetry is inferred to change to $P2_1/a^{14}$ and the factor group analysis gives the modes, $42A_g + 42B_g + 42A_u + 42B_u$, where deuterons are treated to form ions, DSO_4^- .

Figure 1 shows spectra of KHS above 400 cm^{-1} at 295 and 42 K. Most of the internal mode spectra do not depend on the scattering geometry. The factor group analysis shows that 18 internal modes belong to each A_g and B_g species. However, the number of lines observed in the present study is less than that expected from the crystal symmetry. These facts imply that the SO_4^{2-} ions do not obey the crystal symmetry C_{2h} but do obey the site symmetry C_1 . Spectra at 42 K show no evidence which indicates a phase transition.

Spectra of DKHS are shown in Fig. 2. Spectra do not depend on the scattering geometry as in KHS, showing that SO_4^{2-} ions obey site symmetry C_1 in both the high- and low-temperature phases. The frequency shift due to the deuteration is hardly observed except for the 936 cm^{-1} line of KHS, which shifts to 942 cm^{-1} in DKHS. This 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 observed at 45 K indicates that DKHS undergoes a phase transition. The slight distortion of the 942 cm^{-1} line is inferred to be caused by the splitting, which is smaller than the linewidth. A similar phenomenon was observed in $Na_3H(SO_4)_2^{15}$ where hydrogens are at the off-centered position in hydrogen bonds.

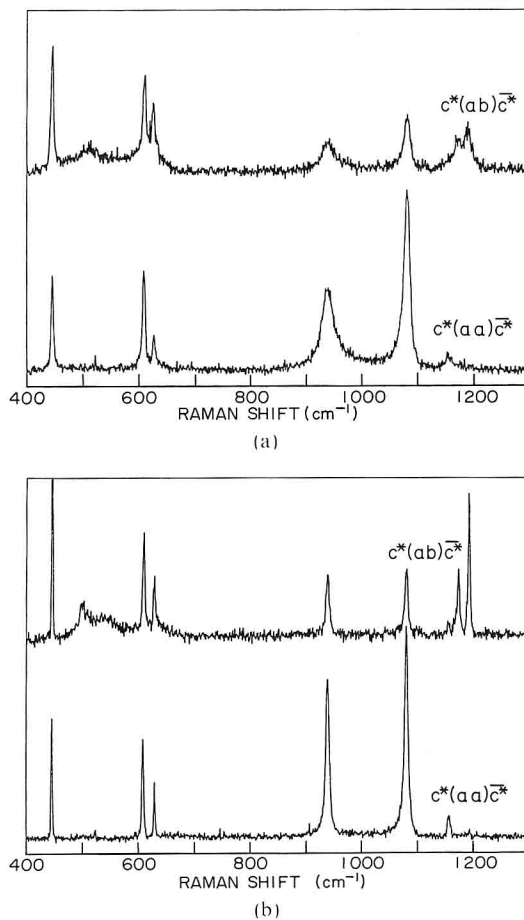


Fig. 1. Spectra of internal modes in KHS observed at (a) 295 K and (b) 42 K.

Referring to the fundamental frequency of a free SO_4^{2-} ,¹⁶⁾ we assigned lines as given in Table I except for the 936 and 1079 cm^{-1} lines. Damak *et al.*¹⁷⁾ have assigned the 936 and 1079 cm^{-1} lines as the ν_1 modes of HSO_4^- and SO_4^{2-} ions, respectively. On the other hand, the X-ray study¹²⁾ of KHS revealed that the hydrogen locates in the single minimum potential below 100 K . This means that two SO_4^{2-} ions in one dimer are equivalent to each other and only one ν_1 mode should be observed in KHS at 42 K ; that is, if the assignment of Damak is correct, the 936 and 1079 cm^{-1} lines must coincide below 100 K . Our results, however, show that these two lines are still observed separately at 42 K .

On the other hand, Moritomo* has assigned

* Y. Moritomo: unpublished.

Table I. Frequencies of Raman lines of KHS and DKHS (Unit is in cm^{-1}). The mode without A_g or B_g can be observed in both scattering geometries: $c^*(aa)\bar{c}^*$ and $c^*(ab)\bar{c}^*$.

| KHS | | | DKHS | |
|----------------|----------------|---------|----------------|------------|
| 295 K | 42 K | | 295 K | 45 K |
| 1187 (B_g) | 1191 (B_g) | ν_3 | | |
| 1172 (B_g) | 1172 (B_g) | " | 1171 (B_g) | 1174 |
| 1151 (A_g) | 1155 (A_g) | " | 1151 (A_g) | 1145, 1137 |
| | | | | 1097 |
| 1079 | 1079 | | 1079 | 1078 |
| 936 | 936 | | 942 | 945 |
| 625 | 628 | ν_4 | 625 | 628, 614 |
| 608 | 608 | | 607 | 599 |
| | | | | 554 |
| 444 | 445 | ν_2 | 444 | 460, 451 |
| | | | | 441, 436 |

the 936 and 1079 cm^{-1} lines to the ν_1 and ν_3 modes, respectively. However, in the present study three lines are observed around 1170 cm^{-1} in KHS. These three lines should be the ν_3 modes, the degeneracy of which is lifted in the C_1 symmetry. Thus, the 1079 cm^{-1} line is not the ν_3 mode. Since the ν_2 and ν_4 modes of DKHS split in the low-temperature phase, it is reasonable to expect splitting of the ν_1 mode due to the phase transition. The splitting of the 942 cm^{-1} line of DKHS seems to show that this line is assigned to the ν_1 mode. However, the clear assignment of the 936 and 1079 cm^{-1} lines is postponed until more information is obtained.

From the present results for DKHS, it is concluded that there are two types of sulfate ions in the low-temperature phase and only one type of ion in the high-temperature phase. This is explained in a similar manner to the motional narrowing theory in the magnetic resonance¹⁸⁾ as follows. If deuteron locates at one of two off-centered positions in the low-temperature phase, two ions in a dimer are inequivalent to each other: DSO_4^- and SO_4^{2-} . A doublet is expected to be observed for each ν_1 mode. If the deuteron moves between two off-centered positions in the high temperature phase and the average time of the motion is shorter than the inverse of the splitting of the doublet, this rapid motion effectively makes two ions equivalent. Therefore, the phase transition is concerned with the ordering of

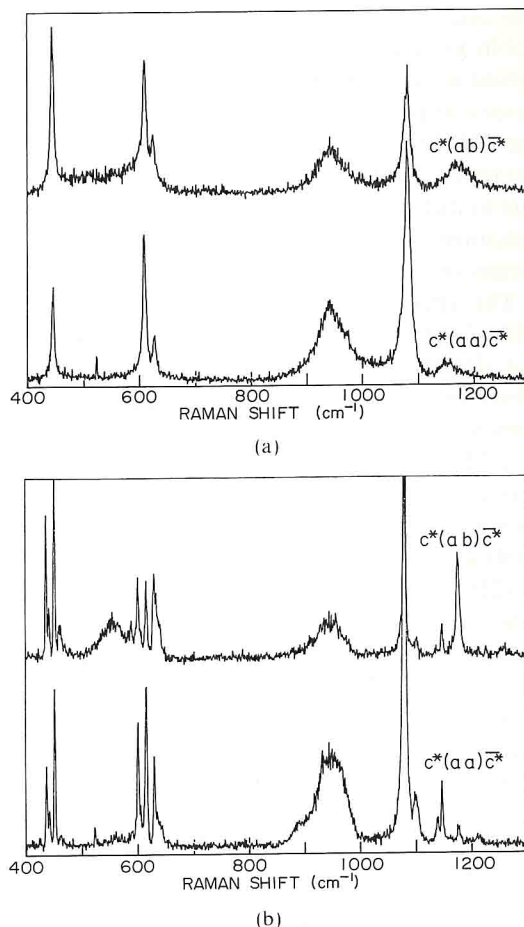


Fig. 2. Spectra of internal modes in DKHS observed at (a) 295 K and (b) 45 K.

deuterons in the hydrogen bonds. On the basis of the motional narrowing theory,¹⁸⁾ the average time of the motions in the high temperature phase (about 200 K above T_c) is estimated to be on the order of 10^{-12} s or less.

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