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RAMAN SCATTERING STUDY OF THE PHASE TRANSITION IN TIN(II) CHLORIDE DIHYDRATE

Hiroshi MORISAKI*, Hideko KIRIYAMA, and Ryôiti KIRIYAMA
The Institute of Scientific and Industrial Research,
Osaka University, Yamadakami, Suita, Osaka 565

The Raman spectra of $SnCl_2.2H_2O$ and its deuterated analogue were measured between 110 and 300 K. Of eight peaks observed, the band at 253 cm^{-1} showed a drastic change in its location below T_{tr}, indicating the presence of a lattice mode coupled with the hydrogen ordering in the O-H··O hydrogen bonded network.

Tin(II) chloride dihydrate, $SnCl_2.2H_2O$, undergoes a phase transition with a striking dielectric anomaly at 218 K.[1] This transition has been investigated extensively by various experimental techniques, and found to be associated with the ordering of protons of the water of crystallization, although the mechanism of the phase transition is not fully understood yet.[2,3] In some ferroelectrics such as potassium dihydrogen phosphate, the proton ordering has received wide attention in relation to its ferroelectric phase transition.[4] As for $SnCl_2.2H_2O$, on the other hand, there is so far no indication of ferroelectric or antiferroelectric characters below the transition temperature.[1] Light scattering is one of the most useful techniques to investigate the triggering mechanism of the phase transition, because the relevant lattice modes in crystals are Raman active. Recently, Davies and Tench have measured the Raman spectra of anhydrous and hydrated tin(II) chloride in the course of a study of some crystalline tin(II) chloride complexes containing $SnCl_3^-$ ions.[5] We will show, in this note, some experimental results of the Raman scattering in $SnCl_2.2H_2O$ and its deuterated analogue, and then propose a possible mechanism of the phase transition in this compound.

The crystal structure of $SnCl_2.2H_2O$ has been determined in detail by means of X-ray[6] and neutron diffractions[2] as well as by nuclear magnetic resonance[3]. No significant structural change was detected by X-rays after the phase transition and also upon deuteration. The crystal is monoclinic with space group $P2_1/c\text{-}C_{2h}^5$. The unit cell contains four molecules of the pyramidal dichloroaquatin(II) complexes, $SnCl_2(H_2O)$, and this coordinated water molecule at an apex of each pyramid, at the same time, forms a two-dimensional hydrogen bonded network with another type of non-coordinating water molecule.

Samples for the experiments were cut from large single crystals of $SnCl_2.2H_2O$ and $SnCl_2.2D_2O$ grown in their aqueous solutions. Since the crystal surfaces change into opaque dehydrated materials in vacuum, the samples were sealed in small glass capsules and then mounted in a cryostat. The temperature of the sample was always controlled within ±1 °C for the measurements. The Raman spectra were obtained by using a 45 mW He-Ne (6328 Å) laser as an excitation source. The spectrometer used was a Spex Model 1400 with a double grating monochrometer. The detector was an EMI 9558A photomultiplier tube with S-20 photocathode and a lock-in amplifier.

Representative spectra of $SnCl_2.2H_2O$ and $SnCl_2.2D_2O$ are shown in Fig.1 and their frequencies are summarized in Table 1. There was no essential difference between the ordinary and deuterated crystals. At least eight peaks were observed below 300 cm^{-1} at room temperature in both cases. No further peak could be detected above 300 to 1000 cm^{-1}. Of course, we have noted by infrared spectroscopy the presence of bending and stretching modes of the water molecules at much higher wave numbers, that is at about 1620 and 3520 cm^{-1} for $SnCl_2.2H_2O$, respectively. Labeling A to G to each peak as shown in the figure, we notice that the peak G shifts to a higher frequency side appreciably at low temperatures, while the other peaks change their frequencies with temperature only slightly.

The temperature dependence of the peak G frequency is illustrated in Fig. 2 where the shift of the peak D is also indicated as a reference. It would be noted that the energy of the peak G shows a drastic change at the transition temperature (T_{tr}), namely at 218K for $SnCl_2.2H_2O$ and at 234 K for $SnCl_2.2D_2O$, and increases remarkably below T_{tr} with decreasing temperature. Such anomalous effect continues as below as about 150 K for both crystals, although the increasing rate of the peak energy reduces gradually.

Furthermore, additional peaks in both solids appeared near 220-240 cm^{-1} below 190 K and grew up with decreasing temperature as shown in Fig. 3. The peak at 164 cm^{-1} was obvious especially in the low temperature phase of the deuterated sample.

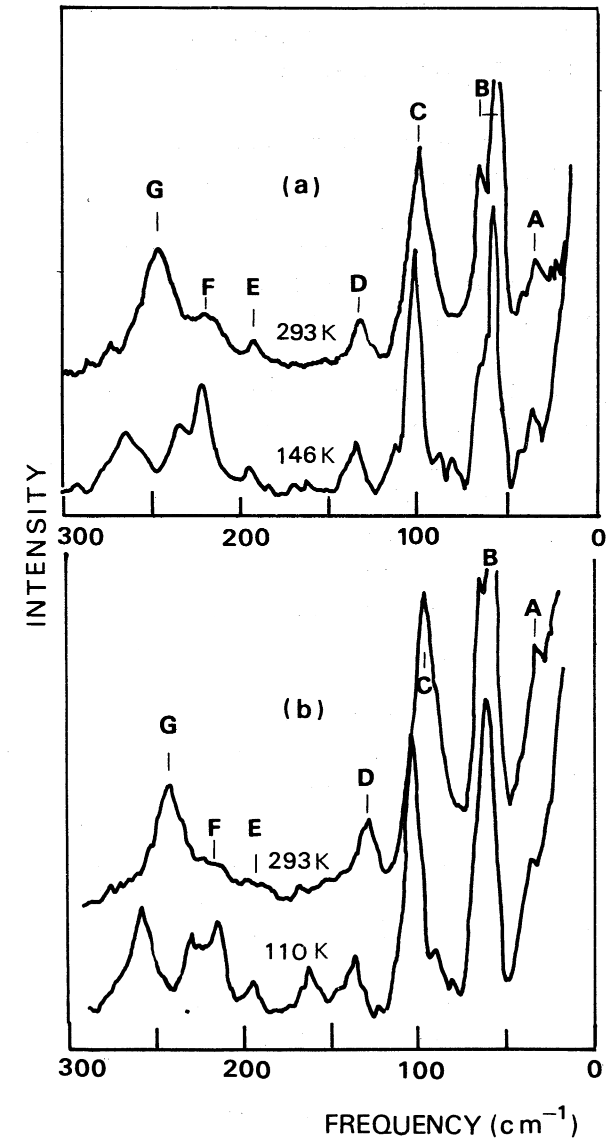

Fig. 1 Representative Raman spectra in the high and low temperature phases of (a) $SnCl_2.2H_2O$, (b) $SnCl_2.2D_2O$

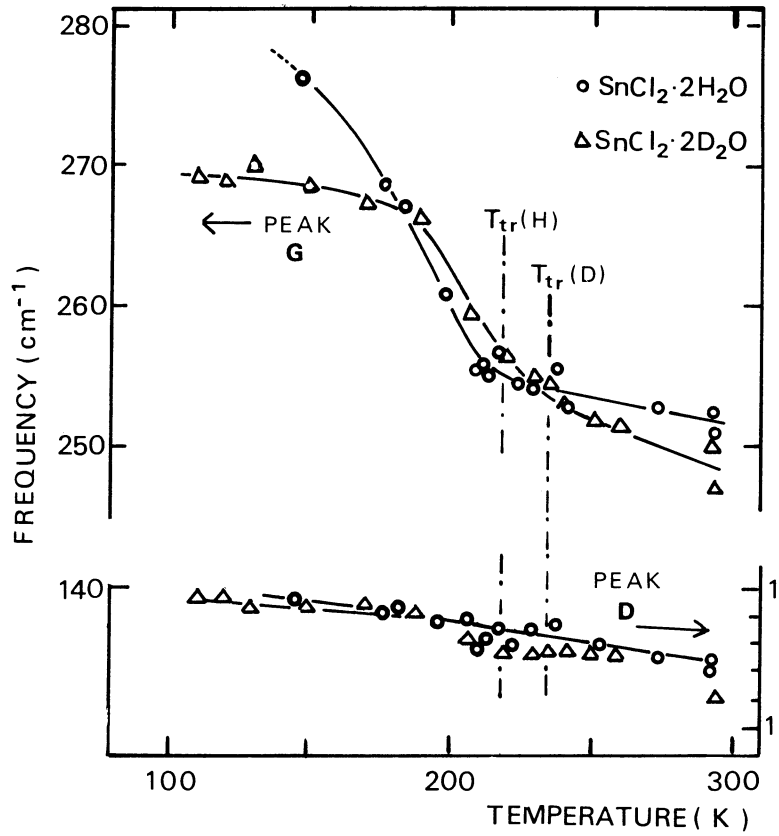

Fig. 2 The temperature dependence of the peak G and D frequencies in $SnCl_2.2H_2O$ and $SnCl_2.2D_2O$

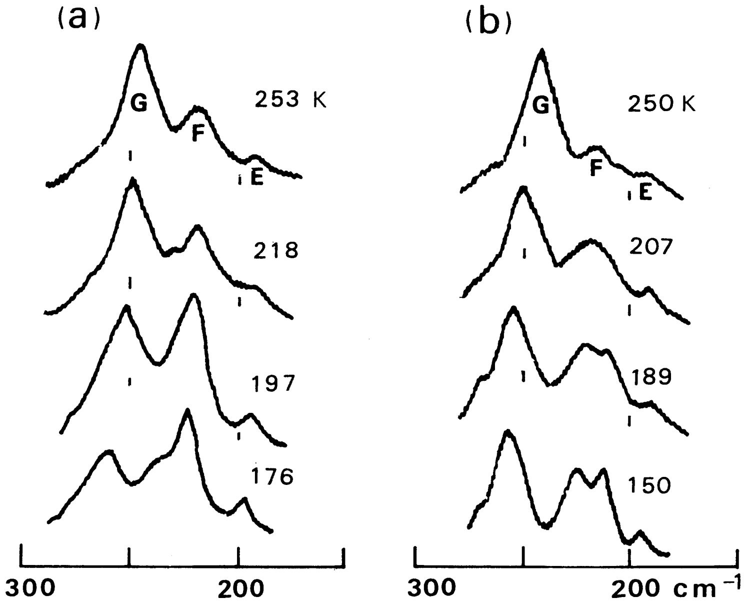

Fig. 3 The temperature dependence of the peaks E to G above and below T_{tr}; (a) $SnCl_2.2H_2O$, (b) $SnCl_2.2D_2O$

Table 1. Observed Raman frequencies in tin(II) chloride dihydrate and its deuterated analogue (in cm^{-1})

peak	$SnCl_2.2H_2O$		$SnCl_2.2D_2O$		$SnCl_2.2H_2O$[5]	a possible assignment
	293K	146K	293K	110K	room temp.	(as a MXY_2 pyramid)
A	31w	36w	31w	33w		
B	56vs	59vs	54vs	59vs	52vs	$\nu_4(A')$, $\delta_s(ClSnCl)$
	63s	65sh	62s	64sh	60vs	
				90w	85vs	
C	97vs	104vs	94vs	102vs	95vs	$\nu_6(A'')$, $\delta_{as}(ClSnO)$
D	133m	137m	132m	137m	131s	$\nu_3(A')$, $\delta_s(ClSnO)$
		168w,b		164m	165w,b	
E	195w	197w	195w,b	196w	194w	$\nu_5(A'')$, $\nu_{as}(SnCl)$
F	221m,b	225s	220w,b	218m	222w	$\nu_2(A')$, $\nu_s(SnCl)$
		240m		234m		
G	253s	276s	247s	269s	247s	
					274sh	
					323vw,b	$\nu_1(A')$, ν (SnO)?

v-very, s-strong, m-medium, w-weak, b-broad, sh-shoulder

Prior to investigate the nature of the peak G which is the main purpose of the present work, we will try to assign other peaks from the view point of molecular vibrations in the crystal. The pyramidal complex, $SnCl_2(H_2O)$, in which the tin(II) atom has a valency octet containing one unshared electron pair, is analogous to the $SnCl_3^-$ ion that gives a Raman spectrum attributed to the species of type MX_3 with a pyramidal shape of point group C_{3v}.[7,8] Assuming a lower symmetry of pyramidal MXY_2 molecule(point group C_s) to the $SnCl_2(H_2O)$ complex, six fundamental vibrations should be observed, the degenerate modes in the MX_3 species splitting into two independent ones.[9]

We assigned tentatively the peaks B to F in the spectra to the deformation and stretching modes as given in Table 1, referring to the data of $SnCl_2$ in the gaseous, molten and crystalline states and $SnCl_3^-$ in ether solution, molten and solid states.[5,7,8,10] The temperature dependence of these peak frequencies was consistent with the small change in the dimension of the pyramid with temperature determined from our X-ray and neutron diffraction studies.[11] It would be reasonable to speculate that the O-Sn stretching mode has the highest vibrational frequency of the internal modes. The peak G, though it has the highest frequency in the spectra, would not be the O-Sn stretching mode because of its anomalous temperature effect described above. In fact, the O-Sn distance in the complex was found to be almost constant, independent of temperature, which was hard to explain the increase in the peak G frequency below the transition temperature. Thus, it would be more likely that the peak responsible for the O-Sn stretching mode is far away above 300 cm^{-1}. On the other hand, the peak at 323 cm^{-1} listed in Table 1 has been also detected in crystals of $KSnCl_3.H_2O$ and $K_2SnCl_4.H_2O$[5], so that it may be impossible to assign this band to the O-Sn vibrational mode in question.

It is therefore supposed that the vibrational mode of the peak G is closely related to the ordering of protons in the hydrogen bonded network. In order to explain the large temperature dependence of the peak G frequency and incidentally its low frequency shift on deuteration, we will consider a new vibrational mode in $SnCl_2.2H_2O$, that is the OH··O stretching in the hydrogen bonded network. The theoretical force constant of the OH··O stretching estimated for the hydrogen bond is 0.33 mdyne/Å after Miyazawa and Pitzer.[12] In our case, 0.34 mdyne/Å was obtained from the peak frequency at room temperature on the assumption that each oxygen atom has the same mass as the water molecule. The hydrogen bonded network in the crystal lattice is shown in Fig. 4, where chlorine atoms are neglected for simplicity. As can be seen in the figure, the two kinds of water molecules, namely the ones coordinating(OI) and noncoordinating(OII) to a tin atom, form the oxygen tetrahedra in the two-dimensional hydrogen bonded network. The vertex oxygen OII bound only weakly to the surroundings will then have a tendency to oscillate with frequencies corresponding to the normal modes of the tetrahedron. In the whole of the crystal, they are no more than the lattice vibrations in the hydrogen bonded layer. Accordingly, the peak G of the spectra may be assigned as one of these lattice vibrational modes.

The large change in the peak G frequency below the phase transition would now be understandable, because the hydrogen bond may be strengthened by ordering of the protons. It is also noted in Fig. 2 that the proton disorder is likely to remain

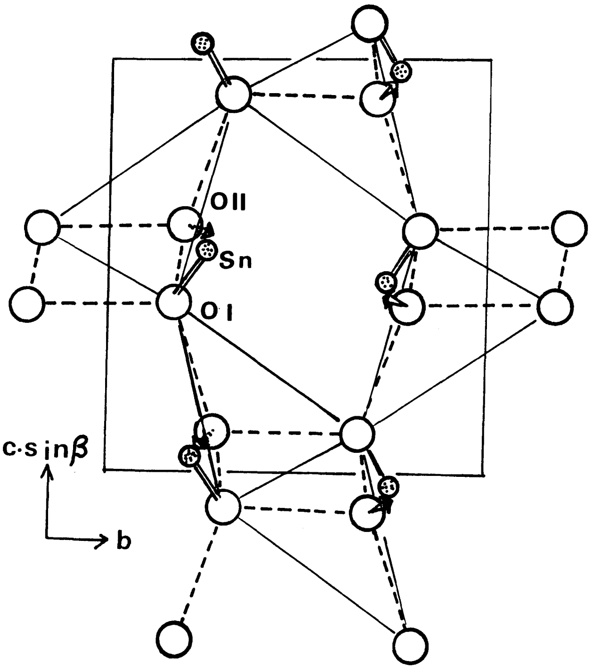

Fig. 4 The hydrogen bonded network in $SnCl_2.2H_2O$. Dotted lines indicate OH··O hydrogen bonds. Both kinds of water molecules, OI and OII, are thus linked with each other into a two-dimensional network parallel to the (100) plane.

to about 150 K which is well below the transition temperature. This finding is quite consistent with the presence of the glassy crystalline state proposed by Matsuo et al. recently.[13)]

Finally, we suggest from the above consideration that the phase transition in tin(II) chloride dihydrate at 218 K results in softening of the lattice vibration coupled with the proton tunneling mode in the hydrogen bonded network.

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* Present adress: The University of Electro-Communications, Chōfugaoka , Chōfushi,
Tokyo 182

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