PROTON DYNAMICS IN TIN(II) CHLORIDE DIHYDRATE STUDIED BY NMR

Hideko KIRIYAMA, Osamu NAKAMURA*, and Ryôiti KIRIYAMA
The Institute of Scientific and Industrial Research,
Osaka University, Suita 565

The proton T_1 and $T_{1\rho}$ in single crystal and polycrystalline $SnCl_2 \cdot 2H_2O$ were measured. The $T_{1\rho}$ exhibits a minimum around 270 K. Both T_1 and $T_{1\rho}$ are dominated by three-fold reorientations of water molecules. The activation energy is 49 kJ/mol. The deuteron NMR spectra suggest the combined motion of the 180° flip and the three-fold rotation. Near T_{tr} 218 K, the lg T_1 vs. $1/T$ curve shows a casp shaped dip as a critical phenomenon.

Tin(II) chloride dihydrate $SnCl_2 \cdot 2H_2O$ (abbreviated as SCD) undergoes a phase transition at 218 K, accompanied with a remarkable dielectric anomaly.[1] Successive studies of proton (PMR) and deuteron (DMR) magnetic resonance,[2] X-ray diffraction,[3] neutron diffraction (ND),[4] and Raman scattering[5] have elucidated that the phase transition in SCD is ascribed to the ordering of hydrogen atoms in H-bonded water layers without any significant change in the crystal structure. In order to clarify the dynamical aspect of disordered hydrogen atoms and to obtain their motional parameters, we have investigated the spin-lattice relaxation of the water protons in both laboratory (T_1) and rotating ($T_{1\rho}$) frames. Recently, Trontelj and Pirnat have reported the relaxation times in powdered SCD, with which we quite disagree.[6] While this manuscript was in preparation, another letter appeared dealing with the same subject by Menafra.[7] It appears in qualitative agreement with our work.

Single crystals about 20×15×40 mm^3 in size were grown by very slow cooling from aqueous solutions acidified with HCl.[3] Because this dihydrate is very efflorescent, polycrystalline SCD used in the present study was prepared from the same single crystal in the following ways: sample P1 was freshly crushed grains, while P2 and P3 were solidified of its melts by slow and rapid cooling, respectively. Each sample was kept in a sealed glass ampoule to protect from atmospheric moisture.

The T_1 and $T_{1\rho}$ were measured on a Bruker pulse spectrometer B-KR 322S(4-60MHz) equipped with a modified Bruker variable temperature accessary. A Nicolet signal averager 1074 following a Bruker B-C Transi-Store was used when necessary. The T_1 measurement was made with the conventional 180°- τ - 90° pulse sequence at 60, 20, and 4.5 MHz. The $T_{1\rho}$ value was determined mainly at 20 MHz by applying a 90° pulse followed immediately by a variable length pulse, phase shifted by 90° from the initial pulse; the r.f. strength H_1 of a spin-locking pulse was less than 15 G. Continuous wave DMR experiments were performed on a bridge type spectrometer JEOL

JNM-W-8 operating at 8 MHz. All measurements were made in a gas flow cryostat;
the   temperature of a sample was kept constant within 0.2 K.

The temperature dependence of the proton T_1 is shown in Fig. 1, where the data
of a single crystal with H_o along the a^* direction are presented together with
those for the powdered samples.   The lg T_1 vs. $1/T$ plot for the single crystal and
the sample Pl follows almost the same straight line over a wide range of 200-313 K.
From this positive slope ($\omega_o \tau_c \gg 1$) the activation energy was determined as E_a=49.0
±0.5 kJ/mol in both high and low temperature phases.   At the melting point 313 K
the T_1 increases suddenly about one order in magnitude at 20 MHz and above this
temperature the slope becomes negative ($\omega_o \tau_c \ll 1$) and gentle (E_a=25 kJ/mol).   Some
indication of the T_1 minimum in solid state could be recognized over twenty degrees
below the melting point by a measurement at the lowest frequency 4.5 MHz.
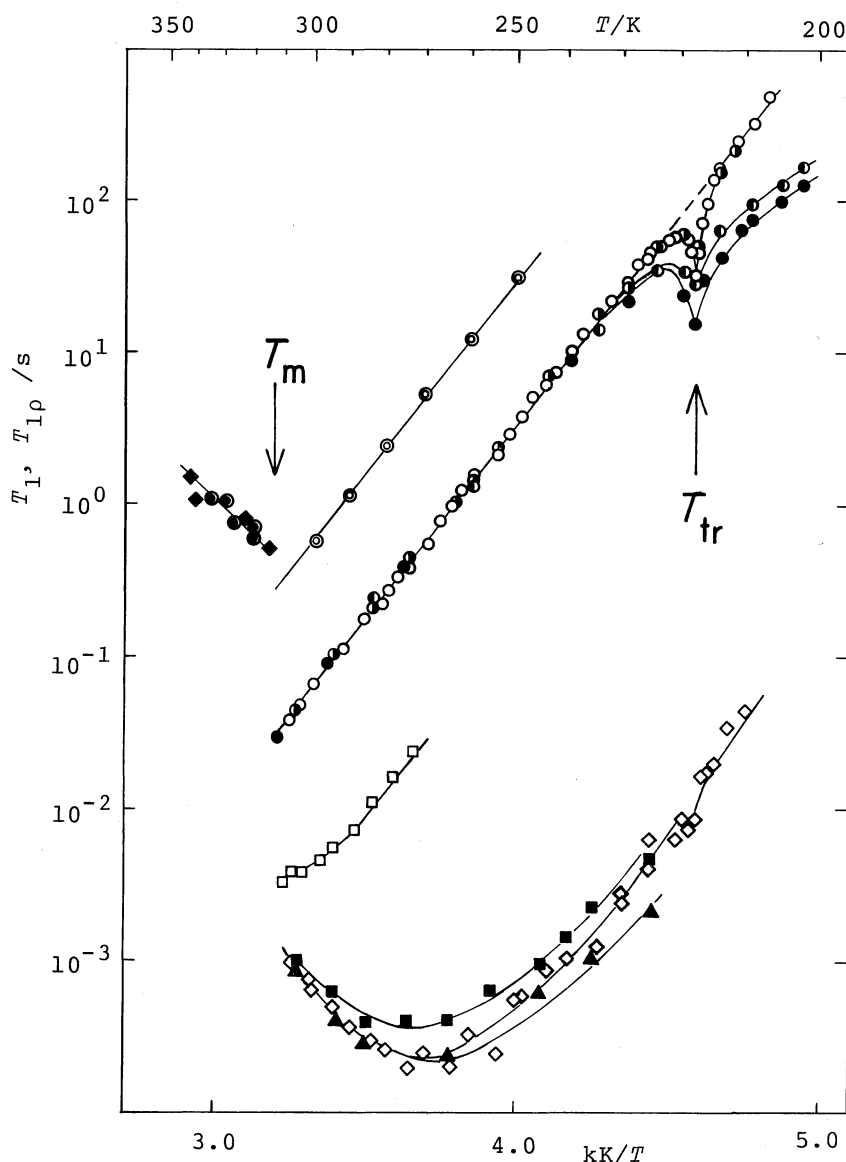

Fig.1. Proton T_1 and
$T_{1\rho}$ versus reciprocal
temperature in SCD at
various frequencies.

T_1:

  ◎ 60   MHz, H_o // [a^*]

  ○ 20   "

  □ 4.5   "

  ◐ 20   MHz, Pl

  ◑ "   P2

  ● "   P3

  ◉ 60   MHz, melt

  ◆ 20   "

$T_{1\rho}$:

  ■ H_1=15 G, powder

  ◇ H_1=10 H_o //[a^*]

  ▲ H_1= 8   powder

In the temperature range of 313 to about 240 K, the T_1 behavior for samples P2 and P3 agrees well with that for the single crystal, whereas below this range it depends largely on the methods for preparation. That is, the lg T_1 $vs.$ $1/T$ curves for P2 and P3 deflect downward and the degree of this deflection is related to the cooling rate on solidification. As evidenced from the extremely long T_1 at the lowest temperature, the original single crystal must be free from any paramagnetic impurity. These facts suggest that some significant change in the H-bonded network may be caused by the melting procedure. If a small amount of oxonium and hydroxide ions are produced by hydrolysis of the melt and consequently enclosed into the crystal lattice on solidification, then the apparent T_1 would be reduced to some extent because the oxonium ions are capable of reorienting more easily than water molecules. The activation energies in the low temperature phase for P2 and P3 were estimated to be about 30 kJ/mol, which is comparable to that given by Trontelj and Pirnat. Their sample is possibly contaminated with a lower hydrate and/or some hydroxychloride complexes.

On the other hand, as shown in Fig. 1, the lg $T_{1\rho}$ $vs.$ $1/T$ curves for a single crystal and a powdered sample show broad minima, the positions of which depend on the effective field strength H_1 in the rotating frame. The positive slope on the low temperature side apart from each $T_{1\rho}$ minimum is nearly equal to that of the T_1 curve, indicating that both relaxation rates may be dominated by the same proton motion. The T_1 depends linearly on ω_o^2, whereas the $T_{1\rho}$ does not on ω_1^2. The $T_{1\rho}$ values for the powdered sample are approximately 3—5 times larger than those expected from the T_1 data on the assumption of the weak collision case. As described previously, Menafra's data on T_1 and $T_{1\rho}$ in a single crystal appear to be in qualitative agreement with our results except for around T_{tr}. He explained the broad minimum in $T_{1\rho}$ by assuming a distribution of correlation times[7]. This assumption seems reasonable as described later.
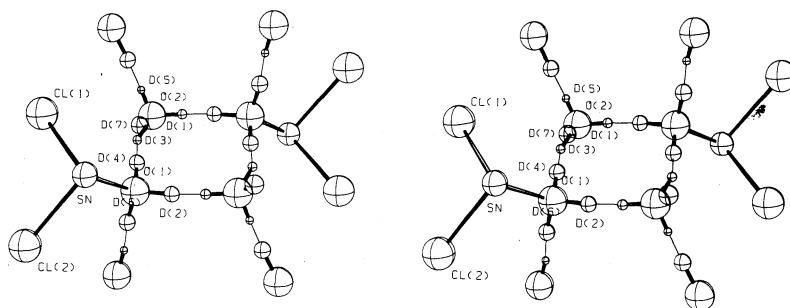

Fig. 2.   Stereoscopic view of the deuteron-disordered arrangement in the high temperature phase of SCD, as determined by ND methods. The deuteron occupancy factor is represented by the size of a circle.

An SCD crystal has two different types of water molecules; $H_2O(1)$ is coordinated to a tin(II) atom and $H_2O(2)$ does not. These two are linked each other by three $O(1)\cdots O(2)$ hydrogen bonds to form a two-dimensional network parallel to the (100) plane.[3]   The ND results, which are reproduced in Fig. 2 , suggest that in the disordered, high temperature phase both water molecules reorient about Sn-O(1) and O(2)-H(7) bonds, respectively, with a pseudo three-fold symmetry.

In fact, the proton second moment for a powdered sample gradually decreases from 32 to 9 G^2 over eighty degrees above T_{tr}.[1]   On the other hand, the DMR spectra split into 8, 4, and 8 pairs of lines below T_{tr}, when a deuterated crystal is rotated about the $a*$, b, and c axes, respectively. This finding is consistent with the crystal symmetry $P2_1/c$ determined by X-ray diffraction and ND methods, in spite of the suggested antiferroelectricity.[2,8]   Just above T_{tr} (234 K for $SnCl_2\cdot 2D_2O$ crystals) all these lines disappear and above about 270 K new signals become observable only in an angular range of about 20° around the $a*$ axis, as shown in Fig. 3 . Moreover, the number of splitting is reduced to 2 or 4 pairs of lines when the crystal is rotated around b or c and its separation $2\Delta v$ is only 80 kHz at most. The average coupling tensors for reorienting water molecules could not be deduced from such insufficient data, and then we tried to compute the splitting on the basis of the following models:

(1) the 180° flipping motion of a water molecule about its two-fold axis,

(2) the three-fold reorientation described above,

(3) the combination of the 180° flipping and the three-fold reorientation.
The calculation was simplified by assuming a coupling constant eQq=220 kHz and an asymmetry parameter η=0 for all deuteron sites determined by ND. Two models (1) and (2) were easily ruled out in view of the magnitude and the number of splitting, whereas the remaining (3) showed the angular dependence of the quadrupole splitting similar to the observed one. Thus the examination of the DMR spectra provided a valuable information on the hydrogen motion. In particular, it is noteworthy that the site exchange of hydrogen atoms occurs even between H(7) with an occupancy factor of 1 and either one of three sites H(1), H(3), and H(5) with that approximated to be 1/3.
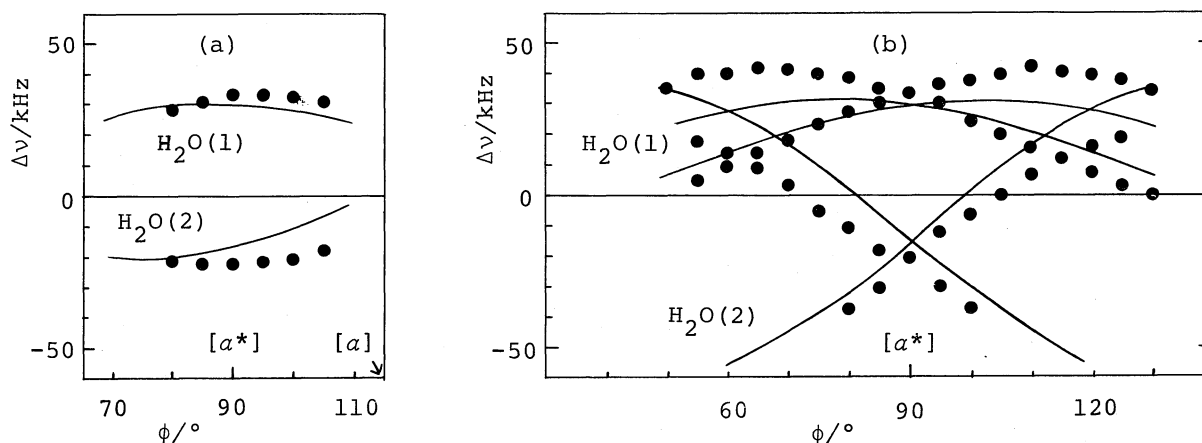

Fig. 3.   Rotation patterns of deuteron quadrupole splitting around the b axis (a) and c axis (b). Solid cruves are calculated based on model (3).

On this basis and in the first approximation, the proton relaxation process was denoted by four correlation times, namely τ_2 and τ_3 for the flipping motion and the three-fold reorientation of $H_2O(1)$, and the analogues τ_2' and τ_3' for H_2O (2). In the present case, however, the relaxation rate is clearly dominated by the intramoleular dipole-dipole interaction modulated by the three-fold reorientation. Assuming that both kinds of water molecules have the same correlation time $\tau_c (=\tau_3 =\tau_3')$, the $T_{1\rho}$ for the powdered sample can be expressed by the following equation in the weak collision limit:[9]

$$\frac{1}{T_{1\rho}} = K \left[\frac{5}{2} \frac{\tau_c}{1+\omega_o^2\tau_c^2} + \frac{\tau_c}{1+4\omega_o^2\tau_c^2} + \frac{3}{2} \frac{\tau_c}{1+4\omega_1^2\tau_c^2} \right]$$

For the proposed three-fold reorientation the "lattice" factor K is given by $(9/40)(\gamma^4\hbar^2/r^6)$, where r is the H-H distance in a water molecule and all other symbols have their usual meanings. From the data on the $T_{1\rho}$ minimum (occuring at $\omega_1\tau_c = 0.5$ when $\omega_o = \gamma H_o \gg \omega_1 = \gamma H_1$), for example $T_{1\rho, min.} = 370$ µs with $H_1 = 15$ G and at 275 K, the value of τ_c was derived as 1.3 µs, from which $\tau_c = 6\times10^{-16} \exp(49 \text{ kJ mol}^{-1}/RT)$ s. The activation energy of 49 kJ/mol is nearly equal to twice the H-bonding energy and is consistent to the model of the combined motion of both types of water molecules.

In order to justify the proton dynamics the angular dependences of the T_1 and $T_{1\rho}$ were measured at various temperatures above T_{tr}. As they were quite.similar, only data at 303 K are given in Fig. 4. The T_1 behavior is almost isotropic, whereas the $T_{1\rho}$ is considerably anisotropic. The angular dependence of $T_{1\rho}^{-1}$ is found to be parallel to that of the proton second moment. The relaxation mechanism of both T_1 and $T_{1\rho}$ would be revealed on the basis of these results.

Finally, a sharp reduction of T_1 was observed around the phase transition temperature and its position was independent of Larmor frequency (Fig. 1). These facts indicate that the dip is due to a critical phenomenon associated with the phase transition, as is often found in some ferroelectric and antiferroelectric
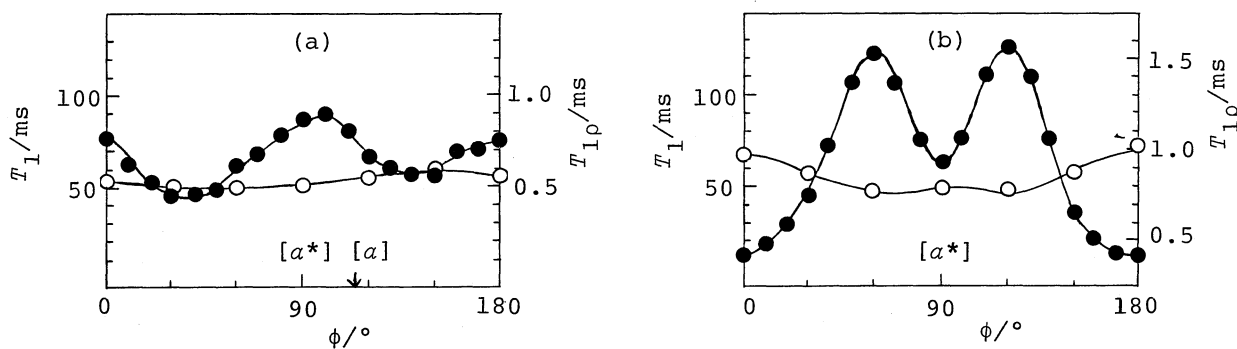

Fig. 4. The angular dependence of T_1 (O , ν_o=20 MHz) and $T_{1\rho}$ (● , H_1=10 G) at 303 K; (a) about the b axis, (b) about the c axis.

substances.   The anomalous contribution, denoted as T_1(fluc), was evaluated by substracting the normal contribution from the observed total relaxation rate. The experimental results thus obtained well satisfied a logarithmic low [10]

$$T_1 \text{ (fluc)}^{-1} \propto \lg | T - T_{tr} |$$

proposed by Tatsuzaki et $al.$ On the other hand, specific heat measurements by Matsuo et $al.$[11]   and also a statistical theory given by Salinas and Nagle[12] have provided valuable information on the phase transition.   A detailed analysis of the proton dynamics in SCD is in progress by reference to these studies.

*Present address: Government Industrial Research Institute , Osaka, Midorigaoka 1, Ikeda 563.

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