

## NMR and NQR spin-lattice relaxation in partially deuterated $(\text{NH}_4)_2\text{SnCl}_6$

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The chlorine-NQR and the deuteron-NMR relaxation have been investigated in  $(\text{ND}_x\text{H}_{4-x})_2\text{SnCl}_6$  ( $x=0,0.4$ ) in the temperature range 4–300 K. Besides the large cross-relaxation maximum observed in both natural and partially deuterated compounds at about 55 K the  $^{35}\text{Cl}$ -NQR relaxation rate shows two smaller maxima at 20 and 30 K in the deuterated salt only. These maxima are shifted to a higher temperature for  $^{37}\text{Cl}$  isotope. The peak at 30 K has a corresponding tunneling channel in the  $^2\text{D}$ -NMR relaxation rate. Deuteron spin-lattice relaxation rates, measured at 13.86 and 52.37 MHz, besides the level-crossing maxima, also show classical maxima related to molecular motions against a barrier about 15% of the full potential. All these effects are caused by limited jumps in a substructure at the bottom of the potential.

Ammonium hexachlorostannate has attracted much research which was predominantly concerned with the investigation of the ammonium-ion motions. The ion experiences a barrier to rotation about the threefold axis of only 600 K.<sup>1</sup> Such low barrier makes possible the tunneling rotation at low temperatures and classical reorientation at ambient temperature. The tunneling and reorientation regimes have been thoroughly investigated for  $\text{NH}_4^+$  by inelastic neutron scattering (INS) and NMR.<sup>1,2</sup> The tunneling splitting for the  $\text{ND}_4^+$  ion is strongly reduced because of the larger moment of inertia. The deuteron-NMR spectra supplied complementary information on ammonium-ion mobility in  $(\text{ND}_4)_2\text{SnCl}_6$ .<sup>3</sup> NMR spectra gave evidence for a distortion of anticipated cubic crystalline field symmetry around ammonium ions.

Some details were given for the mechanism of the deuteron-induced low-temperature phase transitions in  $(\text{ND}_4)_2\text{TeCl}_6$  (Refs. 4 and 5, and references therein). Rotations about symmetry axes of the octahedral  $\text{MCl}_6^{2+}$  ion take place and bring chlorine atoms to new equilibrium positions out of locations along the edges of the unit cell. Displacement of chlorines leads to a shift of the ammonium ion's minimum-energy orientation along the D-Cl hydrogen bond out of the [111] direction. Neutron-diffraction studies gave evidence of such an arrangement in  $(\text{ND}_4)_2\text{SnCl}_6$ .<sup>6–8</sup> It was shown that N-D bonds have a number of equilibrium positions making an angle  $\Delta=25^\circ$  with the [111] and equivalent directions. As equilibrium positions represent local potential minima at the bottom of the main potential, we may expect jumps of the ions between them.

As many details of the previous work await explanation, we aim in the following to study the limited jump motion using  $\text{NH}_3\text{D}$  as a probe. In addition, it appeared to us worthwhile to also investigate the NQR tunneling cross relaxation.

### I. DEUTERON-NMR SPIN-LATTICE RELAXATION

The spin-lattice relaxation of deuterons moving around with reorienting  $\text{ND}_4^+$  ions was analyzed by many authors.<sup>9–12</sup> Thermally activated reorientations characterized by a correlation time  $\tau_c = \tau_0 \exp[E_a/T]$  and in the case of  $\text{ND}_4^+$  are performed around the tetrahedron symmetry axes. The quadrupole interaction of the deuteron quadrupole moment  $eQ$  with the intramolecular electric-field gradient (efg)  $eq$  along the N-D bond dominates and being modulated by reorientations drives the spin-lattice relaxation at a rate given by Ref. 12, which, after the powder average, leads to

$$\frac{1}{T_1^{\text{reor}}} = \frac{3}{40} \omega_Q^2 [J(\omega_L) + 4J(2\omega_L)], \quad (1)$$

where  $\omega_Q = e^2 Qq \hbar^{-1}$  is the quadrupole coupling constant and  $J(n\omega_L) = \tau_c (1 + n^2 \omega_L^2 \tau_c^2)^{-1}$ . A maximum appears when  $\omega_L \tau_c = 0.616$ .

Tunneling introduces additional splittings to the level scheme and spectral densities as respective frequencies also become active, e.g.,  $J(\omega_i \pm n\omega_L)$  with  $n=1,2$ . Very effective relaxation channels may appear under level-crossing conditions  $\omega_i = n\omega_L$  when tunneling and Zeeman energy reservoirs are in direct contact.

The limited jump model was introduced and its contribution to the deuteron spin-lattice relaxation was evaluated by Ingman *et al.*<sup>9</sup> It was assumed that the main potential, instead of having a minimum at [111] and related tetrahedral orientations, has a three-minima around each of them. The new equilibrium positions of the ion are found for N-D bonds making an angle  $\Delta$  with, e.g., the [111] direction. The  $\text{ND}_4^+$  ion performs limited jumps between the minima as an entity and all N-D bonds always make the same angle with respective tetrahedral directions. One can consider just one deuteron moving in the vicinity of the [111] direction and obtain Eq. (10) in

Ref. 9 for the relaxation rate due to limited jumps and after the powder average we receive

$$\frac{1}{T_1^{\text{jump}}} = \frac{9}{40} \omega_Q^2 \sin^2 \Delta \cos^2 \Delta [J_1(\omega_L) + 4J_1(2\omega_L)], \quad (2)$$

where  $J_1(n\omega_L) = \tau_1(1 + n^2\omega_L^2\tau_1^2)^{-1}$  with  $\tau_1$  being the correlation time of limited jumps. The ratio  $r$  of maximum relaxation rates cf. (1) and (2) due to limited jumps and reorientation allows an estimation of  $\Delta: r = 3 \sin^2 \Delta \cos^2 \Delta$ .

We may also anticipate tunneling between closely spaced pairs of minima separated by a small potential. Although the limited jumps have still features of rotational motion of the ion, the tunneling of single particles is translational. Tunneling would introduce additional terms with  $J_1(\omega_i \pm n\omega_L)$  into (2).

Results of the deuteron spin-lattice relaxation rate  $T_1^{-1}$  measurements are given in Fig. 1 for selected NMR frequencies. A strong frequency-dependent maximum was observed just above 50 K. Its high-temperature side gives the activation energy  $E_a = 650$  K, close to the barrier obtained before for the fully deuterated compound.<sup>3,9</sup> The low-temperature slope gives lower and diversified values, namely,  $E_a = 240$  K for  $\nu_L = 9.19$  and 13.86 MHz,  $E_a = 450$  K for  $\nu_L = 52.37$  MHz. The  $E_a$  values are close to energies of the first and second torsional levels. Below 40 K the relaxation rates increase indicating contributions from new motional processes: limited amplitude classical jumps (*cl*) and tunneling-Zeeman level crossing (*t*) (Fig. 1).

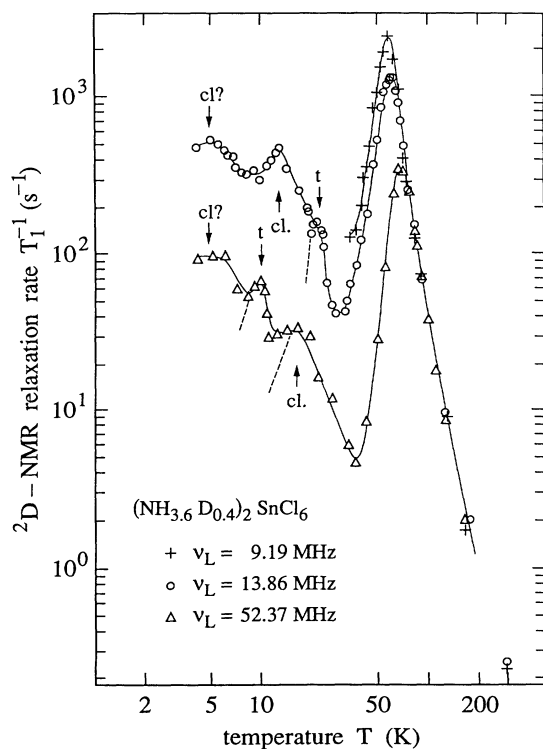


FIG. 1. Temperature variation of the  $^2\text{D}$ -NMR relaxation rate in partially deuterated  $(\text{NH}_4)_2\text{SnCl}_6$  (10% D) at three resonance frequencies.

Positions of the classical maxima at about 16 K for 52.37 MHz and 13 K for 13.86 MHz are related by a shift expected for classical motions. We attribute them to relaxation by limited jumps of  $\text{NH}_3\text{D}$  against a barrier of about 45 K. In order to evaluate an amplitude of such jumps we have taken the formula for  $r$ . We have obtained  $\Delta = 11.7^\circ$  for 52.37 MHz and  $\Delta = 22.8^\circ$  for 13.86 MHz.

At 10 K and  $\nu_L = 52.37$  MHz we see signs of a sharp maximum as well as at 23 K and  $\nu_L = 13.86$  MHz. The strong shift to higher temperature for lower frequency indicates level crossing with tunneling states. We attribute the following conditions of level crossing  $\nu_i = \nu_L = 52.37$  MHz and  $\nu_i = 2\nu_L = 27.72$  MHz or  $\nu_i = \nu_L = 13.86$  MHz, respectively. There exists probably a classical relaxation rate maximum at about 5 K due to limited jumps characterized by  $E_a = 17$  K, which may be seen more clearly if measurements below 4.2 K are made.

## II. CHLORINE-NQR SPIN-LATTICE CROSS RELAXATION

The observed chlorine-NQR relaxation rate may be composed of contributions from various mechanisms, namely, molecular reorientations, lattice vibrations, and cross-relaxation processes:<sup>13</sup>

$$\frac{1}{T_1} = \left[ \frac{1}{T_1} \right]_{\text{reor}} + \left[ \frac{1}{T_1} \right]_{\text{vibr}} + \left[ \frac{1}{T_1} \right]_{\text{cr}}. \quad (3)$$

The relaxation rate caused by reorientation of  $\text{SnCl}_6^{2-}$

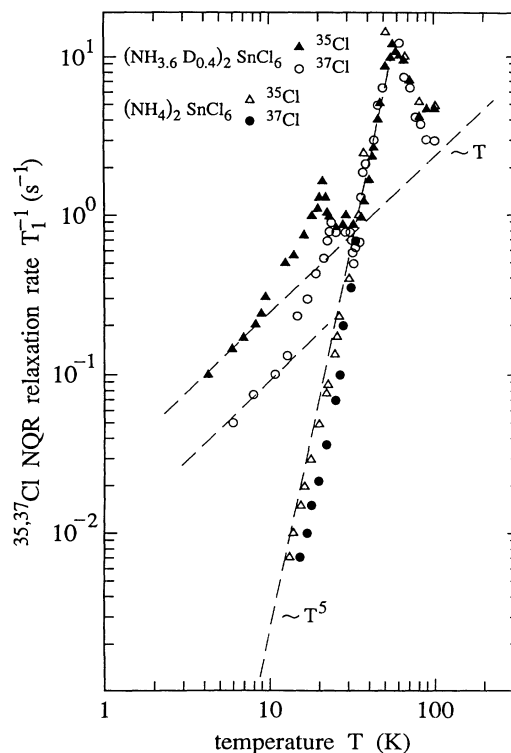


FIG. 2. Chlorine-NQR relaxation rate vs temperature for both isotopes in natural and deuterated (10% D)  $(\text{NH}_4)_2\text{SnCl}_6$ .

ions against a potential  $V$  shows an exponential dependence on temperature and was observed above 370 K. The relaxation rate due to lattice vibrations or torsional oscillations may have different efficiency, but in general we expect a power law  $\sim aT^m$ .

For a Raman process of phonon scattering and temperatures  $T < 0.1\Theta$ , where  $\Theta$  is the Debye temperature,  $m = 5, 7, 9$  was derived. At lower temperatures, the one-phonon direct process can be effective and  $m = 1$  may be obtained.<sup>14</sup>

The cross-relaxation term may contain contributions from transitions induced by the dipolar interaction with neighboring nuclei or efg modulated by molecular motions, moreover, eventually terms due to quadrupole and tunneling level crossing which will result in additional relaxation-rate maxima.

At low temperatures where motions of the  $\text{SnCl}_6^{2-}$  octahedra are at zero-point oscillation level, we have to consider mainly intermolecular mechanisms of relaxation. The main cross-relaxation peak at 55 K is observed in the partially deuterated sample as well as in the natural salt (Fig. 2). The appearance at the same temperature for respective isotopes as well as the identical isotope dependence indicate the same origin in both compounds. The chlorine-NQR frequency equals 15.7 and 12.37 MHz for  $^{35}\text{Cl}$  and  $^{37}\text{Cl}$  in the partially deuterated compound below 50 K. These are slightly greater than observed for the natural compound due to a static contribution to efg from deuterons.

Deuterons and protons moving according to the ion reorientation modulate spin interactions with chlorines, which leads to a maximum when  $\omega_Q \tau_c \sim 1$ . As expected, this maximum coincides with the deuteron relaxation rate maximum for  $\nu_L = 13.86$  MHz (Fig. 1).

A Raman  $T^5$  dependence was observed in the natural salt for  $T_1^{-1}$  below the main peak (Fig. 2). On the other hand, for the partially deuterated sample additional peaks emerge below 35 K on a background with probably  $\sim T$  slope. The peak observed for  $^{35}\text{Cl}$  at 30 K may be due to a level crossing with tunneling states at  $\nu_t = \nu_Q = 15.7$  MHz. It is quite weak but significant for this isotope and not detectable for  $^{37}\text{Cl}$  as it would be expected at a higher temperature where reorientation al-

ready prevails. Its position is correlated with the  $\nu_t = \nu_L = 13.86$  MHz condition for the deuteron relaxation rate maximum at about 30 K.

Much strong peaks are observed for both isotopes just above 20 K. They have sharp tips at 20 and 23 K for  $^{35}\text{Cl}$  and  $^{37}\text{Cl}$ , respectively. The lower-frequency peak being present at higher temperature indicates once again level-crossing conditions to be fulfilled, namely,  $\nu_t = 2\nu_Q$ , with  $\nu_t = 31.4$  MHz and  $\nu_t = 24.7$  MHz for  $^{35}\text{Cl}$  and  $^{37}\text{Cl}$ , respectively. The decay of the maximum on the low-temperature side for the  $^{37}\text{Cl}$  isotope first indicates that the level-crossing effect supplies the prevailing relaxation channel. There is no indication of a cross relaxation due to limited jumps of deuterons and we may consider the shape of the relaxation maxima as a representation of a tunneling frequency distribution only.

Activation energy of limited jumps equals about 45 K for both NMR frequencies. We attribute these to jumps between three potential minima around the [111] direction. Still more limited amplitude jumps may lead to increased relaxation rate at 5 K. This may be due to jumps between closely spaced pairs of potential minima derived on the basis of neutron-diffraction results.<sup>6,7,9</sup> If so, those appear to be separated by about 17 K, very close to predicted the 18 K.<sup>9</sup>

It is also more likely that the tunneling frequencies measured reflect coupled states of a deuteron in the closely spaced double potential. Such positions are close to chlorines and it may explain the dominating role of tunneling in the cross-relaxation contribution to chlorine-NQR relaxation.

Features of limited jumps and tunneling reported here and left unexplained will be the subject of further studies.

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