

# <sup>35</sup>Cl NQR Spin-Lattice Relaxation Mechanism in Ni(H<sub>2</sub>O)<sub>6</sub>SnCl<sub>6</sub> and Mg(H<sub>2</sub>O)<sub>6</sub>SnCl<sub>6</sub> Crystals\*

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Z. Naturforsch. **49a**, 286–290 (1994); received October 16, 1993

The <sup>35</sup>Cl NQR spin-lattice relaxation mechanism in isomorphous Ni(H<sub>2</sub>O)<sub>6</sub>SnCl<sub>6</sub> and Mg(H<sub>2</sub>O)<sub>6</sub>SnCl<sub>6</sub> crystals is reported. The spin-lattice relaxation time  $T_{1Q}$  in the Ni compound is determined mainly by a paramagnetic relaxation. However, above ca. 400 K  $T_{1Q}$  decreased rapidly and a  $\log T_{1Q}$  vs.  $T^{-1}$  curve was almost linear. This steep decrease of  $T_{1Q}$  was explained by reorientational motions of the anions with an activation energy of 73 kJmol<sup>-1</sup>. In addition, a double minimum in  $T_{1Q}$ , which can be interpreted as arising from the fluctuation of the electric field gradient (EFG) at the chlorine site caused by cationic thermal motions, was observed around room temperature. The temperature dependence of the <sup>35</sup>Cl NQR  $T_{1Q}$  in the Mg salt is re-analysed in the light of the EFG-modulation effect caused by a 180° flip motion of the H<sub>2</sub>O molecules and an overall reorientational motion of the [Mg(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup> octahedral cations as a whole.

**Key words:** Complex compounds, Molecular dynamics, Nuclear relaxation, Nuclear quadrupole resonance, Electric field gradient.

## Introduction

Ni(H<sub>2</sub>O)<sub>6</sub>SnCl<sub>6</sub> crystals are trigonal (space group R $\bar{3}$ ,  $a = 7.09$  Å,  $\alpha = 96^\circ 45'$ ,  $Z = 1$ ) and have a slightly distorted CsCl-type structure composed of [Ni(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup> octahedron and [SnCl<sub>6</sub>]<sup>2-</sup> octahedron [1]. Each chlorine atom is surrounded by five H<sub>2</sub>O groups, and especially three hydrogen atoms are closer to a chlorine atom and make weak O–H...Cl hydrogen bonds [1]. The temperature dependences of the <sup>35</sup>Cl NQR frequencies in the Ni salt along with M(II) (H<sub>2</sub>O)<sub>6</sub>SnCl<sub>6</sub> (M(II) = Ca, Mg, Mn, and Co) and M(II) (D<sub>2</sub>O)<sub>6</sub>SnCl<sub>6</sub> (M(II) = Ca, Mg, Co and Ni) crystals have previously been studied [2]. These compounds are isomorphous with the Ni complex [3, 4], and they gave a single <sup>35</sup>Cl NQR signal from 77 K to the temperature at which the signals fade out [2]. Furthermore, all of them showed an unusual temperature dependence with a positive temperature coefficient, which was assigned to the hydrogen bonds [2].

The temperature dependence of the <sup>35</sup>Cl NQR spin-lattice relaxation time  $T_{1Q}$  in Mg(H<sub>2</sub>O)<sub>6</sub>SnCl<sub>6</sub> has re-

cently been measured [5]. Above ca. 350 K  $T_{1Q}$  decreased very rapidly with increasing temperature and  $\log T_{1Q}$  vs.  $T^{-1}$  plots were almost linear between ca. 370 and 420 K. Below ca. 350 K  $T_{1Q}$  increased gradually with decreasing temperature. This is a typical temperature variation of  $T_{1Q}$  observed for [M(IV)Cl<sub>6</sub>]<sup>2-</sup> octahedral ions [6–10]. In the present investigation the temperature dependence of the <sup>35</sup>Cl NQR  $T_{1Q}$  in the Ni compound was measured. Since it is a paramagnetic substance, its  $T_{1Q}$  was expected to be governed by the fluctuation of a hyperfine interaction, especially a magnetic dipole-dipole interaction between a chlorine nucleus and unpaired electrons in the paramagnetic Ni<sup>2+</sup> ions. In addition to this paramagnetic relaxation, however, a double  $T_{1Q}$  minimum was observed that is attributable to the EFG fluctuation caused by cationic thermal motions. The former  $T_{1Q}$  results for the Mg compound is re-analysed in the light of this relaxation mechanism.

## Experimental

The sample was made in the same way as described in [2]. The polycrystalline sample was sealed in a glass tube and annealed at ca. 400 K for 24 hours to strengthen the intensity of the NQR signal.

The temperature variation of  $T_{1Q}$  was measured with a pulsed NQR spectrometer and a cryostat de-

\* Presented at the XIIth International Symposium on Nuclear Quadrupole Resonance Spectroscopy, Zürich, Switzerland, July 19–23, 1993.

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scribed in [11]. The temperature of the specimen was controlled within  $\pm 0.5$  K and the sample temperature was determined within  $\pm 1$  K.  $T_{1Q}$  was determined by a  $180^\circ - \tau - 90^\circ - \tau_e - 180^\circ$  pulse sequence, where  $\tau_e$  was fixed at 100–200  $\mu\text{s}$  through a single measurement of  $T_{1Q}$  at any temperature. The error of  $T_{1Q}$  was estimated to be within  $\pm 10\%$ .

## Results and Discussion

The temperature variation of the  $^{35}\text{Cl}$  NQR  $T_{1Q}$  in the Ni compound is shown in Figure 1. Although the Ni and Mg salts are isomorphous and the temperature dependence of the  $^{35}\text{Cl}$  NQR frequencies of the two compounds is very similar [2], the temperature dependences of their  $T_{1Q}$  are very different owing to the paramagnetism of the Ni salt [5, 12]. However, at high temperatures both  $T_{1Q}$ 's decreased very rapidly on heating. A similar steep decrease of  $T_{1Q}$  has frequently been observed for  $^{35}\text{Cl}$  NQR in compounds forming  $[\text{M}(\text{IV})\text{Cl}_6]^{2-}$  octahedral ions and was interpreted in terms of an activation of reorientational motions of the anions [5–12]. Hence the present rapid  $T_{1Q}$  decrease seems to be explained by the same relaxation mechanism. The activation energy, estimated from the gradient of a linear portion of the  $\log T_{1Q}$  vs.  $T^{-1}$  curve shown in Fig. 1, was 73  $\text{kJ mol}^{-1}$ .

The most interesting feature of the present  $T_{1Q}$  results is a double minimum around room temperature. A similar minimum has been observed in some  $^{14}\text{N}$  NQR  $T_{1Q}$  measurements [13] and was interpreted in terms of fluctuations of the magnetic internuclear interactions. However, if the present  $T_{1Q}$  minimum were due to nuclear dipole relaxation, a minimum of a similar magnitude should be observed in the isomorphous Mg compound. Furthermore, there is no phase transition in this temperature region [2].

In some compounds nuclear relaxation has been observed where motions of molecules or atomic groups close to the resonant quadrupole nuclei fluctuate the EFG at the nuclei [14–19]. This relaxation mechanism can be responsible for the present double minimum in the Ni compound. However, since the  $^1\text{H}$  NMR  $T_1$  in the Ni compound is, because of the paramagnetic relaxation, too short to observe a temperature variation due to cationic motions, information about the motions is not available. Hence, unfortunately, this assumption cannot be verified by a fitting calculation using motional parameters of the cation

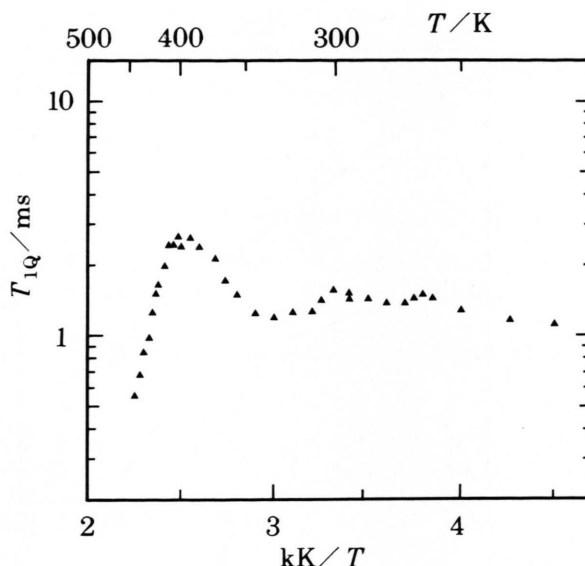


Fig. 1. Temperature dependence of the  $^{35}\text{Cl}$  NQR spin-lattice relaxation time  $T_{1Q}$  in  $\text{Ni}(\text{H}_2\text{O})_6\text{SnCl}_6$ .

motions obtained from NMR  $T_1$  measurements like other compounds [14–19]. However, this double minimum reminds us of a double minimum in the  $^1\text{H}$  NMR  $T_{1\rho}$  observed in the Mg compound [5], which is interpreted in terms of the dipolar relaxation caused by successive thermal motions of the cations as a whole, uniaxial and overall reorientations. Here we assume that the EFG relaxation induced by cation motions is responsible for the observed  $T_{1Q}$  double minimum.

On the other hand, no clear effect of the EFG modulation due to cationic motions on  $T_{1Q}$  in  $\text{Mg}(\text{H}_2\text{O})_6\text{SnCl}_6$  was found [5]. However, one can recognize a shallow and broad dip in  $T_{1Q}$  around 200 K. In order to make this clearer,  $\log T_{1Q}$  is plotted against  $\log T$  in the range from 100 to 364 K in Figure 2. Around 200 K one finds a small deviation from the linear dependency.

On the basis of this one can explain this part of the temperature dependence of  $T_{1Q}$  in terms of EFG fluctuations due to lattice vibrations [20]. The straight line in Fig. 2 was obtained by fitting the equation

$$T_{1Q,1} = \alpha T^{-n} \quad (1)$$

to the data from 100.6 to 154.7 K and from 222.1 and 286.0 K. The result was

$$T_{1Q,1}/\text{s} = 1.2 \times 10^5 (T/\text{K})^{-2.4} \quad (2)$$

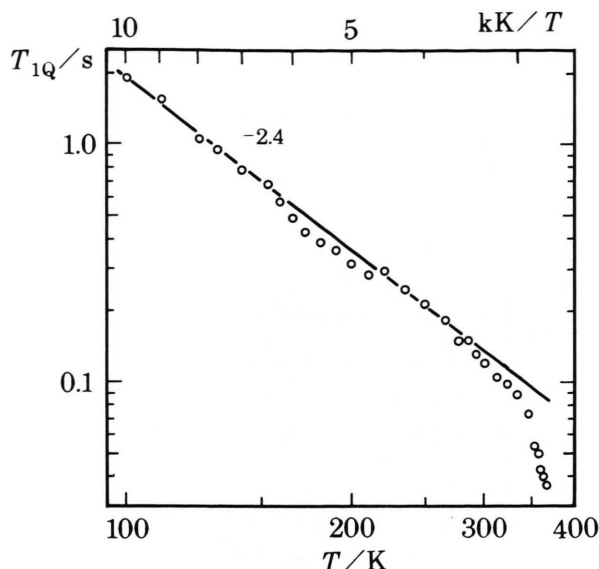


Fig. 2. Log-log plot of  $^{35}\text{Cl}$  NQR  $T_{1Q}$  in  $\text{Mg}(\text{H}_2\text{O})_6\text{SnCl}_6$  versus temperature. The gradient of the straight line is  $-2.4$ .

Next let us consider the dip in  $T_{1Q}$  around 200 K. Since no phase transition exists in this temperature region [2], an additional relaxation mechanism is responsible for it. The temperature variation of the  $^1\text{H}$  NMR  $T_1$  observed in the Mg compound using a Larmor frequency of 18 MHz showed a minimum around the same temperature, which minimum arises from the dipolar relaxation due to a  $180^\circ$  flip motion of the water molecules [21]. Thus this motion may cause the observed  $T_{1Q}$  dip, too. Furthermore, we confirmed by the  $T_{1Q}$  measurement on  $\text{Mg}(\text{D}_2\text{O})_6\text{SnCl}_6$  that there is no effect of deuteration on  $T_{1Q}$ . Hence it does not seem unreasonable to ascribe this dip to the same relaxation mechanism as assigned to the double minimum in the Ni compound.

In the preceding investigation on the Mg compound [5], we interpreted the rapid  $T_{1Q}$  variation above room temperature as being due to a reorientational motion of  $[\text{SnCl}_6]^{2-}$  ions, whose activation energy is  $115 \text{ kJ mol}^{-1}$ . This value resembles that for an overall reorientational motion of the  $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$  cations as a whole ( $116 \text{ kJ mol}^{-1}$ ). Therefore, this rapid temperature variation can be explained in terms of the cationic motion as well as the anionic motion [14, 16, 18]. As a matter of fact, the similarity of the activation energies evaluated from NQR  $T_{1Q}$  and

NMR  $T_1$  justifies the attribution of the rapid  $T_{1Q}$  decrease to the EFG relaxation due to motions of molecules or atomic groups close to the resonant nuclei [14–18]. Moreover, in an isomorphous  $\text{Ca}(\text{H}_2\text{O})_6\text{SnCl}_6$  crystal activation energies of the overall reorientation and the anion reorientation differ by  $18.5 \text{ kJ mol}^{-1}$  [22].

Hence, the  $T_{1Q}$  results can be written as

$$T_{1Q}^{-1} = T_{1Q,1}^{-1} + T_{1Q,m}^{-1} (\text{H}_2\text{O flip}) + T_{1Q,m}^{-1} (\text{overall}), \quad (3)$$

where  $T_{1Q,m}^{-1}$  is the spin-lattice relaxation rate due to the EFG modulation caused by cationic motion.

For the quadrupole nucleus with the nuclear spin  $I=3/2$  and the asymmetry parameter  $\eta=0$ , the EFG relaxation rate due to a motion of molecules or atomic groups adjacent to the resonant nucleus is given by

$$T_{1Q,m}^{-1} = \frac{1}{3} \left( \frac{q'}{q} \right)^2 \frac{\omega_Q^2 \tau_c}{1 + \omega_Q^2 \tau_c^2}, \quad (4)$$

where  $q'/q$  is a fluctuation fraction of the EFG at the resonant nucleus caused by the motion,  $\tau_c$  is the correlation time of the motion, and  $\omega_Q$  is the NQR frequency in angular units [14].  $\tau_c$  can be expressed as

$$\tau_c = \tau_0 \exp(E_a/RT). \quad (5)$$

When  $\tau_c$  is much slower than  $\omega_Q$ , i.e.,  $\omega_Q^2 \tau_c^2 \gg 1$ ,  $T_{1Q,m}$  is proportional to  $\tau_c$ ,

$$T_{1Q,m}^{-1} = \frac{1}{3} \left( \frac{q'}{q} \right)^2 \tau_c^{-1}. \quad (6)$$

By using (2), (4), and (6), the  $T_{1Q}$  results were analysed. The motional parameters for the  $\text{H}_2\text{O}$ - $180^\circ$ -flip motion and the overall motion of the cation as a whole are  $\tau_0 = 7.0 \times 10^{-15} \text{ s}$ ,  $E_a = 22 \text{ kJ mol}^{-1}$  and  $\tau_0 = 1.6 \times 10^{-21} \text{ s}$ ,  $E_a = 116 \text{ kJ mol}^{-1}$ , respectively [5, 21]. The best fitted curve is drawn in Figure 3. The obtained fluctuation fractions are  $1.7 \times 10^{-4}$  and  $6.2 \times 10^{-2}$  for the  $180^\circ$  flip motion and the overall reorientation, respectively. The value of 0.062 is comparable to 0.065 for  $(\text{CH}_3)_2\text{CCl}_2$  [14], 0.06 for  $\alpha\text{-NH}_4\text{HgCl}_3$  [16], and 0.075 for  $\text{C}_5\text{H}_6\text{NAuCl}_4$  [18]. These results verify that the dip around 200 K and the rapid alteration above ca. 350 K in  $T_{1Q}$  are explainable by the EFG fluctuations caused by the  $180^\circ$  flip motion of the water molecules and the overall reorientation of the cations as a whole, respectively. However, these results do not mean that the rapid alteration cannot be assigned to the anionic reorientations.

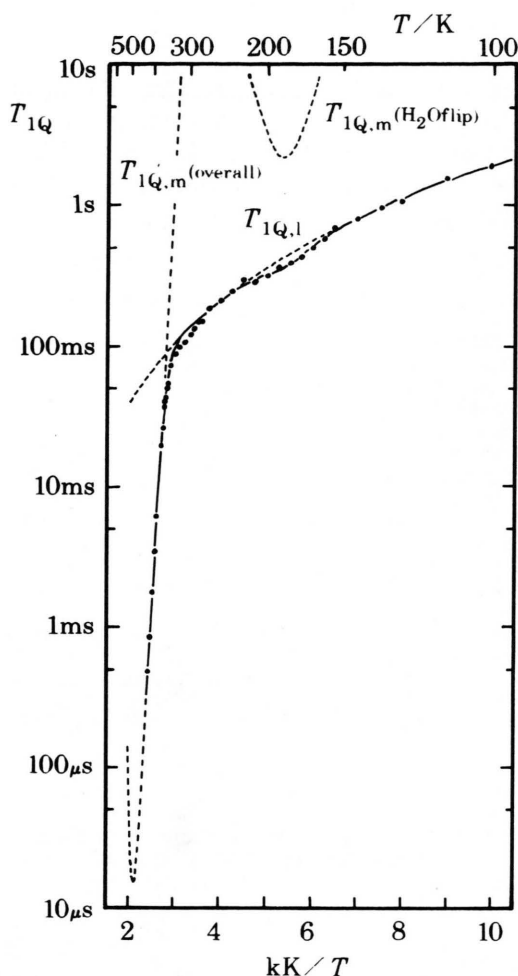


Fig. 3. The best fitted curve of  $T_{1Q}$  versus temperature observed in  $\text{Mg}(\text{H}_2\text{O})_6\text{SnCl}_6$ . The solid line was obtained by fitting (2), (4), and (6) to the  $T_{1Q}$  data. The broken lines indicate the contributions to  $T_{1Q}$  from  $T_{1Q,l}$ ,  $T_{1Q,m}$  ( $\text{H}_2\text{O}$  flip), and  $T_{1Q,m}$  (overall).

They can well explain it as well as the cationic reorientations.

In isomorphous compounds such as  $\text{Ca}(\text{H}_2\text{O})_6\text{SnCl}_6$ ,  $\text{Co}(\text{H}_2\text{O})_6\text{PtCl}_6$  and  $\text{Cu}(\text{H}_2\text{O})_6\text{PtCl}_6$ , the EFG-modulation effect has not been observed [12, 22]. This seems strange, because in dipolar relaxation the same motions in isomorphous or similar crystals have effects of similar magnitude. The following examples along with the present investigation may clarify the characteristic features of this relaxation mechanism. Sagisawa et al. reported that motions of  $\text{NH}_4^+$  ions in

$\alpha\text{-NH}_4\text{HgCl}_3$  have the EFG-modulation effect but those in  $(\text{NH}_4)_2\text{HgCl}_4 \cdot \text{H}_2\text{O}$  do not have it [16]. Furthermore, the motions of  $\text{NH}_4^+$  ions in  $(\text{NH}_4)_2\text{SnBr}_6$  have the effect [15], those in  $(\text{NH}_4)_2\text{SnCl}_6$  do not have it [8].

To summarize: The motions of the same molecules in different crystals do not necessarily have similar  $q'/q$  values and may have very different ones even if the crystals are isomorphous or similar. The modulation effect with a small  $q'/q$  value is easily masked by a more effective relaxation mechanism, and hence it cannot be observed experimentally.

While three motional modes of the cations have been found in the Mg compound [5, 21], the modulation effect of a uniaxial motion of  $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$  ions does not appear in the present  $T_{1Q}$  results. This is probably because the motion does not have this effect, or even if it has the effect, the fluctuation fraction is small, like the  $\text{H}_2\text{O}$  flip, and its effect is masked by  $T_{1Q,l}$ .

In the preceding study we had observed that with increasing temperature  $T_{2Q}$  increased slightly around 200 K [5]. This can not be explained by the fluctuation of the local magnetic fields at a chlorine site caused by motions of the water molecules or the cations as a whole, judging from the correlation times of the motions. In the present investigation, by carefully looking at Figs. 2 and 3, we can notice that there are small deviations from the linear relation and the fitting curve around 300 K. These deviations are very small and could be ignored. Nevertheless, they do not seem to be negligible, when the  $T_{2Q}$  variation around 200 K is considered. The deviations could be explained by the EFG fluctuation caused by a cationic motion that is responsible for the  $T_{2Q}$  alteration around 200 K, too. Although such a motion has not been detected by the  $^1\text{H}$  NMR measurements [5, 21], all motional modes are not necessarily found out by NMR.

## Conclusions

1. The double minimum in  $T_{1Q}$  observed for  $\text{Ni}(\text{H}_2\text{O})_6\text{SnCl}_6$  results from the fluctuation of EFG at the chlorine nuclei caused by cationic motions.
2. The steep decrease of  $T_{1Q}$  above ca. 400 K observed for the Ni compound is attributed to reorientational motions of the anions with an activation energy of  $73 \text{ kJ mol}^{-1}$ .

3. The dip in  $T_{1Q}$  around 200 K observed for  $\text{Mg}(\text{H}_2\text{O})_6\text{SnCl}_6$  originates in the EFG fluctuation due to the  $180^\circ$  flip motion of the water molecules.

4. The rapid temperature variation of  $T_{1Q}$  above ca. 350 K observed for the Mg compound is explainable in terms of the overall reorientation of  $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$  ions as well as the reorientation of  $[\text{SnCl}_6]^{2-}$  ions.

#### Acknowledgements

The author would like to acknowledge Dr. T. Asaji for help in the  $^{35}\text{Cl}$  NQR  $T_{1Q}$  measurements, and the Foundation for the Supporting University of the Ryukyus (Ryukyu-Daigaku-Kohen-Zaidan) for a travel grant for the XIIth ISNQRS.

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