A ^{35}Cl NQR Study on Exchange Interactions between Paramagnetic $[IrCl_6]^{2-}$ Ions

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The ^{35}Cl and ^{37}Cl NQR frequencies and spin-lattice relaxation times T_{1Q} in paramagnetic M_2IrCl_6 (M = NH_4, Cs) were measured at 4 - 350 K. The observed temperature dependences were attributed to EFG fluctuations caused by lattice vibrations and magnetic field fluctuations caused by paramagnetic ions. The exchange parameters J in the NH_4 and Cs salts were calculated from ^{35}Cl NQR T_{1Q} to be 8.6 K and 1.8 K respectively. ^{37}Cl data yielded 9.1 K and 2.1 K respectively. The obtained lattice constant dependence of J values was explained by considering Ir-Cl. . . Cl-Ir superexchange interaction.

Key words: Cl NQR;Superexchange Interaction; Paramagnetic Salt; Spin-lattice Relaxation.

1. Introduction

Electron spin dynamics in paramagnetic solids has been intensively studied by measurements of magnetic resonance, magnetic susceptibility, *etc.* Information on the microscopic structure and dynamics of electron spins can be effectively obtained by magnetic resonance techniques such as ESR, NMR and NQR. Among these, the ^{35}Cl NQR method, although having experimental limitations, has the following advantages:

1. Resonance signals can be observed even from nuclei located close to paramagnetic atoms. This seems to originate from the small gyromagnetic ratio of ^{35}Cl compared with NMR nuclei such as ^{1}H.

2. Different resonance signals correspond to different lattice sites in crystals. This is due to the narrow resonance linewidths and the high sensitivity of the frequency measurements. Applying these benefits, we have studied spin dynamics in solid paramagnetic systems in which we measured NQR relaxation in ^{35}Cl nuclei in counter ions [1].

In the present study, we selected paramagnetic $[IrCl_6]^{2-}$ ions as a target in which the monitoring Cl atoms are directly bonded to the paramagnetic metal ion. We employed ammonium and cesium salts having different inter-spin distances but the same antifluorite structure and intended to compare the obtained results with those reported on K_2IrCl_6 [2]. From ^{35}Cl and ^{37}Cl NQR measurements we expected to obtain reliable information on electron spin dynamics such as exchange interactions.

2. Experimental

Cs_2IrCl_6 was prepared by passing chlorine gas through a mixture of equivalent amounts of Ir metal powder and CsCl, and heating up to 970 K in a quartz tube. $(NH_4)_2IrCl_6$ was prepared by adding an NH_4Cl aqueous solution to an Na_2IrCl_6 hydrochloric acid solution. $(NH_4)_2IrCl_6$ was recrystallized from 3 N hydrochloric acid containing approximately 1 percent of nitric acid to avoid reduction. This solvent was used in all preparation processes described above for the same purpose.

The ^{37}Cl and ^{35}Cl NQR frequency and spin-lattice relaxation time(T_{1Q}) measurements were made with a home-made pulsed spectrometer [3] at 4 - 350 K by use of a conventional π-τ-$\pi/2$ pulse sequence with a $\pi/2$ pulse-width of 14 - 23 µs. The sample tempera-

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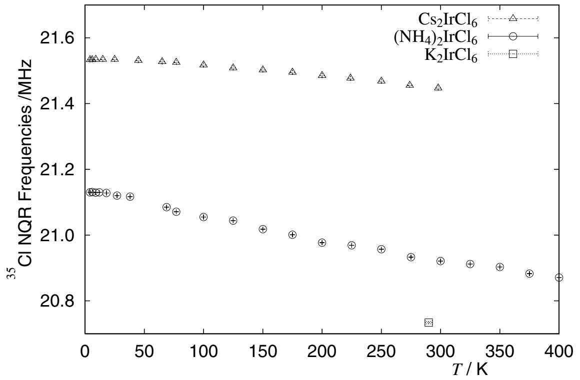

Fig. 1. Temperature dependences of ^{35}Cl NQR frequencies observed in $(NH_4)_2IrCl_6$ and Cs_2IrCl_6.

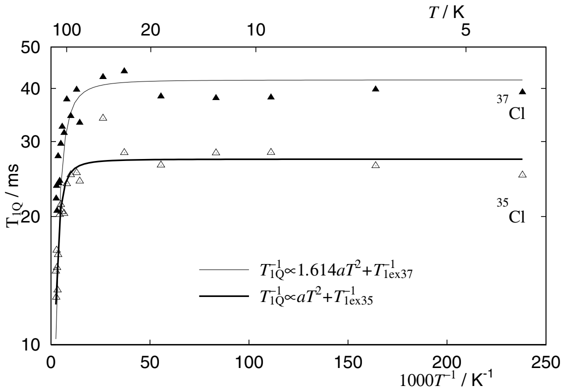

Fig. 2. Temperature dependences of ^{35}Cl and ^{37}Cl T_{1Q} observed in $(NH_4)_2IrCl_6$ and fitted theoretical curves.

ture was controlled and determined within ±0.1 K and ±3 K bellow and above 30 K, respectively.

3. Results and Discussion

The observed temperature dependences of the ^{35}Cl NQR frequencies in $(NH_4)_2IrCl_6$ and Cs_2IrCl_6 are shown in Figure 1. The ratio of the ^{35}Cl and ^{37}Cl NQR frequencies was 1.269 ± 0.001 at all temperatures studied, in agreement with the theoretical ratio within experimental errors.

From the observed NQR frequencies one can see that the electric field gradient (EFG) at the Cl nuclei in Cs_2IrCl_6 is by 3.4% larger than that in K_2IrCl_6 at room temperature.

The temperature dependences of ^{35}Cl and ^{37}Cl T_{1Q} measured in $(NH_4)_2IrCl_6$ and Cs_2IrCl_6 are shown in Figs. 2 and 3, respectively. Since T_{1Q}^{-1} in the present systems is expected to both on lattice vibrations ($\propto T^2$) and exchange interactions between electron spins (T_{1ex}^{-1}), we fitted the observed results by superimposing two contributions with an open coefficient A:

$$T_{1Q}^{-1} = \frac{T^2}{A} + T_{1ex}^{-1}. \tag{1}$$

Table 1. Relaxation times T_{1ex} due to electron spin exchange interactions derived from observed relaxation times.

	T_{1ex} (^{35}Cl) /ms	T_{1ex} (^{37}Cl) /ms
$(NH_4)_2IrCl_6$	27.3	41.9
Cs_2IrCl_6	5.72	9.55
K_2IrCl_6 [2]	35.1	–

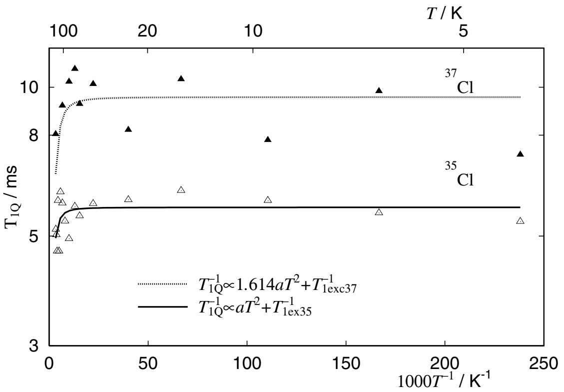

Fig. 3. Temperature dependences of ^{35}Cl and ^{37}Cl T_{1Q} observed in Cs_2IrCl_6 and fitted theoretical curves.

Since the measurement was made in the low-temperature region, the present fitting was carried out without the term of the $[\mathrm{IrCl}_6]^{2-}$ reorientation, which is expected to become important above room temperature. $A = 3.7 \times 10^6$ K^{2}s in $(NH_4)_2IrCl_6$ and $A = 3.6 \times 10^6$ K^{2}s in Cs_2IrCl_6 were obtained from the ^{35}Cl data. For ^{37}Cl, we used $1.614A$ because lattice vibrations affect T_1 by a factor of the squared quadrupole moment. The obtained values of T_{1ex} are listed in Table 1.

T_{1ex} can be expressed by use of the exchange frequency ω_e as [2]

$$T_{1ex}^{-1} = \frac{2S(S+1)}{\omega_e}\sqrt{\frac{\pi}{2}}\left(\frac{B}{\hbar}\right)^2, \tag{2}$$

$$B = -\frac{\gamma\hbar g\beta}{R^3}, \tag{3}$$

Table 2. Electron spin exchange parameters J derived from $T_{1\mathrm{ex}}$ together with values obtained from magnetic susceptibility.

	^{35}Cl NQR /K	^{37}Cl NQR /K	magnetic susceptibility [4] / K
$(\mathrm{NH_4})_2\mathrm{IrCl_6}$	8.6 ±2	9.1 ±3	6.7
$\mathrm{Cs_2IrCl_6}$	1.8 ±0.3	2.1 ±0.8	–
$\mathrm{K_2IrCl_6}$	11.0 (fixed)	–	11.0±1.5

$$\omega_\mathrm{e}^2 = \frac{8S(S+1)J^2}{\hbar^2}, \tag{4}$$

$$H_\mathrm{ex} = \sum_{i<j} J_{ij} S_i \cdot S_j. \tag{5}$$

Here J, γ, β, g, S_i, H_ex, and R are the exchange parameter, the gyromagnetic ratio of resonant nuclei, Bohr magneton, g-factor, ith spin, the Hamiltonian that describes the electron system and the distance between resonant nuclei and an electron spin, respectively. In the present study we assumed R, which is the Ir-Cl distance, to be constant and independent of the counter cations. Under this assumption we can express $T_{1\mathrm{ex}}$ with a constant C as

$$T_{1\mathrm{ex}} = CJ, \tag{6}$$

The values J, derived from the obtained values of $T_{1\mathrm{ex}}$, are showed in Table 2.

The relation between the evaluated J values and the cubic lattice constant a obtained at room temperature is shown in Figure 4. The relation between J and a is nearly linear. No marked change in the $\mathrm{NH_4}$ salt, in which the superexchange path by way of Cl. . . H-N hydrogen bonding is expected, is found. On the other hand, since J showed a strong dependency on a and can not be expressed by $\exp(-R)$, this result can not be explained by any ordinary direct spatial interactions between Ir atoms. This suggests that paths of exchange interactions in these compounds are indirect through some chemical interaction, rather than direct. Hence we can assume an Ir-Cl. . . Cl-Ir path by taking into account the relatively large size of the anions.

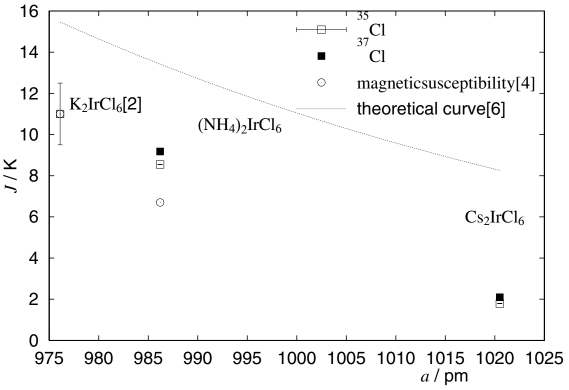

Fig. 4. Calculated and reported [2] J values. vs. lattice contant a [5]. The line represents a theoretical curve by Griffiths et al. [6].

A superexchange interaction between $[\mathrm{IrCl_6}]^{2-}$ ions by way of Ir-Cl bonds has been proposed by Griffiths, Owen, Park, and Partridge in their ESR study [6]. They expressed J through such a path as

$$J \approx 2p^2 D[1 - [1 - \exp\{-\beta(r - r_\mathrm{e})\}]^2], \tag{7}$$

where D ($\approx$ 20000 cm^{-1}), β (= 2.04), r_e (= 199 pm), p(= 0.05) and r is the Cl-Cl separation in a free $\mathrm{Cl_2}$ molecule, a reduction factor corresponding to the probability of finding the spins on Cl atoms, and the Cl. . . Cl distance between nearest neighbors, respectively. This dependence of J is shown in Figure 4. Although this assumption was intended primarily as a simple illustration of the superexchange mechanism, the obtained result showed the order-of-magnitude agreement with the present data.

4. Conclusions

1) It was shown that ^{35}Cl and ^{37}Cl NQR relaxation data can give reliable information on electron spin dynamics, especially exchange interactions.

2) The J values showed a strong dependence on the lattice constant a. This J dependence on a can roughly be understood by introducing an Ir-Cl. . . Cl-Ir superexchange path proposed by Griffiths et al. No marked influence from Cl. . . H-N hydrogen bonds in the $\mathrm{NH_4}$ salt was observed.

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