^{35}Cl NQR Spin-Lattice Relaxation in Paramagnetic $CuPtCl_6 \cdot 6\,H_2O$ *

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^{35}Cl NQR spin-lattice relaxation times T_{1Q} of paramagnetic $CuPtCl_6 \cdot 6\,H_2O$ were measured as a function of temperature. Below the cooperative Jahn-Teller phase transition at $T_c = 136$ K, an almost temperature independent T_{1Q} between 0.6 and 1 ms was obtained for each line of the triplet observed. This suggests that the nuclear spin-lattice relaxation of chlorine is dominantly determined by magnetic dipolar interactions between chlorine nuclei and electron spins. No marked anomaly in the nuclear relaxation rate was detected at T_c. Above T_c, T_{1Q} for the single ^{35}Cl NQR line increased from 0.6 ms at T_c to 1.4 ms at 365 K. The rapid T_{1Q} decrease observed above ca. 390 K can be attributed to a reorientational motion of the $[PtCl_6]^{2-}$ anion with an activation energy of 1.1×10^2 kJ mol^{-1}.

Introduction

Measurements of nuclear spin-lattice relaxation which is originated from fluctuations of the magnetic coupling of resonant nuclei with the Jahn-Teller ion are, in principle, useful to obtain information about the mechanism of the structural phase transitions driven by cooperative Jahn-Teller distortion. As recently reported by Borsa and Rigamonti [1, 2], however, this type of investigation of the Jahn-Teller transition is still very rare. In the crystals so far studied, no marked anomaly in the relaxation rate has been detected [1–4], which is similar to the behaviour observed at temperatures near the structural phase transition in perovskite crystals. The main aim of this investigation is to examine the above point in detail with $CuPtCl_6 \cdot 6\,H_2O$ and to obtain information about the electron spin dynamics from the measurements of nuclear quadrupole spin-lattice relaxation in the dynamic Jahn-Teller system.

Through the temperature dependence of ESR spectra and of ^{35}Cl NQR frequencies, paramagnetic $CuPtCl_6 \cdot 6\,H_2O$ crystals are known to undergo a cooperative Jahn-Teller phase transition at $T_c = 136$ K [5–7] and to show one and three ^{35}Cl NQR lines in the high and low temperature phases, respectively. Accordingly, the temperature dependence of ^{35}Cl NQR spin-lattice relaxation times (T_{1Q}) was measured for the lines of both phases.

Experimental

A homemade pulsed NQR spectrometer [8, 9] was employed for the observation of the spin-echo signals arising from ^{35}Cl nuclei in the sample. T_{1Q} was determined by a $\pi - \tau - \pi/2 - \tau_e - \pi$ pulse sequence, where the spacing time τ was varied and τ_e was set constant (ca. 100 μs). The sample temperature was controlled within ± 0.2 K by employing a temperature controller [8], and was determined with a copper-constantan thermocouple. The observed temperatures were estimated to be accurate within ± 0.5 K.

Equimolar amounts of $CuCl_2$ and $H_2PtCl_6 \cdot 6\,H_2O$ were dissolved in a small amount of water [6, 10]. The solution was heated on a water bath until the precipitate became nearly dry and no hydrogen chloride was smelled. The precipitate was dissolved again in water and was filtered off. The crystals of $CuPtCl_6 \cdot 6\,H_2O$ were obtained by slow evaporation of water from the solution in a desiccator over P_2O_5 and NaOH.

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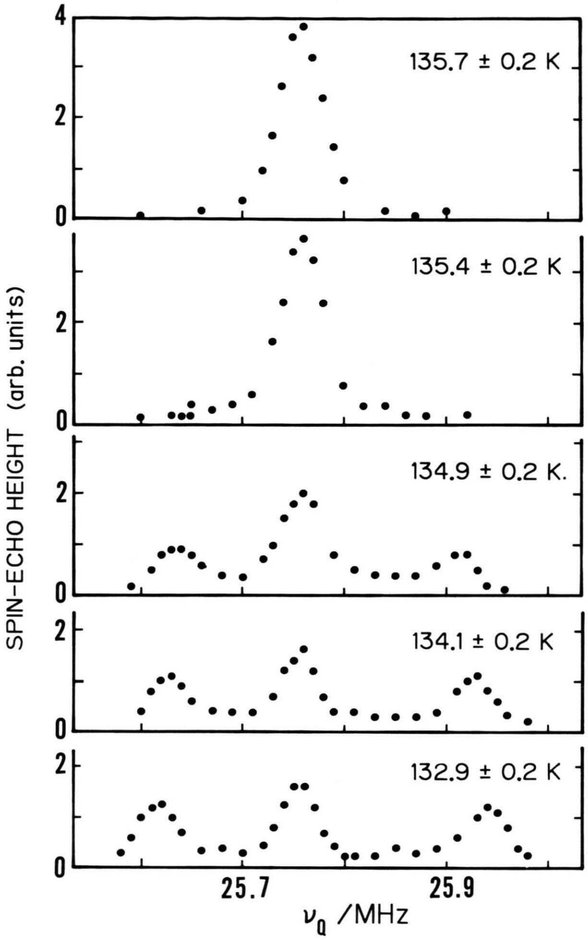

Fig. 1. The ^{35}Cl NQR frequencies and line-shapes of $CuPtCl_6 \cdot 6H_2O$ at various temperatures in the vicinity of $T_c = 135.5 \pm 0.5$ K. Spin-echo heights are plotted against frequency.

Results and Discussion

The single ^{35}Cl NQR line observed at high temperature phase is split into a triplet below T_c [5, 6]. In the present investigation, we have accurately measured the temperature dependence of ^{35}Cl NQR frequencies especially in the vicinity of $T_c = 135.5 \pm 0.5$ K by plotting the echo heights against the frequency. The results are shown in Figure 1. No broadening of the center line with decreasing temperature through T_c was observed. This suggests the occurrence of a discontinuity of the resonance frequency at T_c and, therefore, it is concluded that the phase transition is of first order.

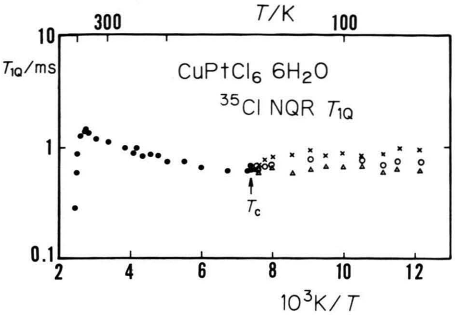

Fig. 2. Temperature dependences of spin-lattice relaxation times T_{1Q} for ^{35}Cl NQR lines of $CuPtCl_6 \cdot 6H_2O$. Below T_c, the T_{1Q} values are indicated by ×, ▵, and ○ for the high, middle, and low frequency lines of the triplet, respectively.

The temperature dependence of ^{35}Cl T_{1Q} is shown in Figure 2. Below T_c, T_{1Q} of each line of the triplet was almost temperature independent with short values between 0.6 and 1.0 ms. This suggests that T_{1Q} is dominantly determined through magnetic dipolar interactions between chlorine nuclear magnetic moments and electron spins. No marked anomaly in the nuclear relaxation rate has been detected at T_c. This resembles the results already obtained in some systems showing the cooperative Jahn-Teller structural phase transitions [1, 2]. The conclusion is that the expected critical slowing down of some electron-phonon coupled mode, if it exists, is not an appreciable relaxation mechanism when the phase transition is of first order [1]. This is supported from the present study.

For $T > T_c$, T_{1Q} increased from 0.6 ms at T_c to 1.4 ms at 365 K. This is explainable provided that electron spin correlation time is dominated by the temperature-dependent electron spin-lattice relaxation time. This mechanism is discussed in detail in the following section.

Above ca. 390 K, T_{1Q} decreased very rapidly with increasing temperature. This decrease of T_{1Q} is ascribable to an overall reorientational motion of $[PtCl_6]^{2-}$ [11]. From the linear portion of log T_{1Q} vs. T^{-1} plots, an activation energy of 1.1×10^2 kJ mol^{-1} was obtained for the motion.

Nuclear Spin-Lattice Relaxation due to Magnetic Dipolar Interactions with Electron Spins

Below ca. 370 K, ^{35}Cl T_{1Q} can be considered to be dominantly determined by the magnetic dipolar interaction between chlorine nuclei and electrons. For nuclear spin $I = 3/2$, T_{1Q} due to this mechanism can be written by use of the transition probability W_1 between nuclear spin states $|3/2\rangle$ and $|1/2\rangle$ or $|-3/2\rangle$ and $|-1/2\rangle$, as

$$T_{1Q}^{-1} = 2W_1 = \tfrac{3}{2}\gamma_N^2 \int_{-\infty}^{\infty} \exp(-i\omega_Q\tau)\langle h_+(\tau)\,h_-(0)\rangle\,d\tau, \tag{1}$$

where γ_N and ω_Q are the nuclear gyromagnetic ratio of chlorine and the angular chlorine NQR frequency, respectively. The symbol $h(\tau)$ indicates the effective local field produced at chlorine nuclei due to the paramagnetic ions, and the brackets $\langle\ \rangle$ indicate an ensemble average [4, 12, 13].

In the present case, the magnetic dipolar coupling between the chlorine nucleus and unpaired electrons on the paramagnetic ions can be calculated in the principal axes frame of the electric field gradient (EFG) produced at the quadrupolar nucleus (^{35}Cl), because there exists no definite quantization axis for the electron spin in the zero field. For the present case, we assume that

$$\langle S_z(\tau)\,S_z(0)\rangle = \langle S_x(\tau)\,S_x(0)\rangle = \langle S_y(\tau)\,S_y(0)\rangle = \tfrac{1}{3}S(S+1)\exp(-\tau/\tau_e) \tag{2}$$

and

$$\langle S_i(\tau)\,S_j(0)\rangle = 0 \quad \text{for} \quad i \neq j \text{ and } i, j = x, y, z\,. \tag{3}$$

Here, S and S_i ($i = x, y, z$) are the resultant spin quantum number of electrons and the components of the electron spin operator, respectively, and τ_e denotes the electron spin correlation time. On assuming that the correlation between local fields produced by electron located at different sites (pair correlation) is negligible, one obtains the following expression for the nuclear spin-lattice relaxation rate originating from the coupling with paramagnetic ions having unpaired electrons with S:

$$T_{1Q}^{-1} = 3\left(\tfrac{9}{2}\right)\gamma_N^2\gamma_e^2\hbar^2\left[\tfrac{1}{3}S(S+1)\right]\Lambda\, j(\omega_Q), \tag{4}$$

$$\Lambda = \sum_i \left\{|F_i^{(1)}|^2 + \tfrac{1}{18}|F_i^{(0)}|^2 + \tfrac{1}{2}|F_i^{(2)}|^2\right\}, \tag{5}$$

$$j(\omega_Q) = \frac{2\tau_e}{1+\omega_Q^2\tau_e^2}\,. \tag{6}$$

Here, γ_e is the gyromagnetic ratio of the electron and the $F_i^{(q)}$'s, with $q = 0, 1, 2$, are the spatial parts of the dipolar Hamiltonian between the resonant nucleus and the i-th paramagnetic ion [14]. $|F_i^{(q)}|^2$ is written as

$$|F_i^{(0)}|^2 = (1 - 3\cos^2\theta_i)^2/r_i^6, \tag{7}$$

$$|F_i^{(1)}|^2 = \sin^2\theta_i\cos^2\theta_i/r_i^6, \tag{8}$$

$$|F_i^{(2)}|^2 = \sin^4\theta_i/r_i^6, \tag{9}$$

where r_i is the distance between the resonant nucleus (^{35}Cl) and the i-th paramagnetic ion (Cu^{2+}), and θ_i is the angle between the z axis of the EFG produced at a ^{35}Cl nucleus and the distance vector r_i. The electron spin correlation time τ_e is given by the temperature-dependent electron spin-lattice relaxation time T_{1e} and the temperature-independent characteristic time τ_s for the spin flip between neighboring electrons [15]. Among τ_e, T_{1e}, and τ_s one has

$$\tau_e^{-1} = T_{1e}^{-1} + \tau_s^{-1}\,. \tag{10}$$

Since $\omega_Q\tau_e \ll 1$ usually holds because of very short τ_e, (4) can be written as

$$T_{1Q}^{-1} = 3\left(\tfrac{9}{2}\right)\gamma_N^2\gamma_e^2\hbar^2\left[\tfrac{1}{3}S(S+1)\right]\Lambda\, 2\tau_e\,. \tag{11}$$

Accordingly, we obtain a temperature-independent T_{1Q} when τ_e is solely determined by τ_s. On the other hand, T_{1Q} becomes temperature-dependent when T_{1e} dominates τ_e. The fact that T_{1Q} increases from 0.6 ms at T_c to 1.4 ms at 365 K is interpreted along this line.

The geometric factor Λ, involving the positional parameters of paramagnetic ions, was estimated from the crystal structure data of the isomorphous

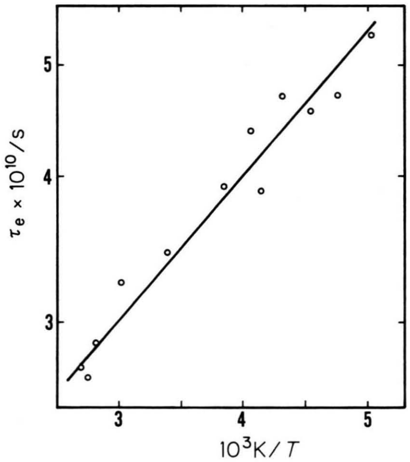

Fig. 3. The temperature dependence of the electron spin correlation time τ_e estimated from the ^{35}Cl T_{1Q} values determined at various temperatures between ca. 200 and 370 K.

$NiSnCl_6 \cdot 6H_2O$ crystal [16]. The contributions from the paramagnetic ions within 11^3 primitive cells around the resonant nucleus were calculated. In the calculation, the z axis of the EFG at the chlorine nucleus was assumed to be parallel to the metal-halogen bond axis. Using the calculated value of Λ, τ_e was estimated from the ^{35}Cl T_{1Q} values determined at various temperatures. The results obtained for the range 200–370 K are shown in Figure 3.

τ_e of the order 10^{-10} s was obtained. This order of magnitude is reasonable when compared with that reported for $CuSiF_6 \cdot 6H_2O$ (1.1×10^{-10} s at 300 K) [15], and copper-doped zinc Tutton's salt $K_2Zn(SO_4)_2 \cdot 6H_2O$ (1.5×10^{-10} s at 80 K) [17]. Here, τ_e is dominated by τ_s for spin flips for the former and by the transition rate of intervalley jumping between the lowest two valleys corresponding to the different direction of distortion of $[Cu(H_2O)_6]^{2+}$ for the latter.

When we assume $\tau_e \sim T_{1e}$ for the present complex in the range 200–370 K, T_{1e} can be explained by the Orbach process [18], which has an exponential dependence on temperature as

$$T_{1e} \propto \exp(\Delta/kT), \tag{12}$$

where Δ is the energy difference between the ground and the first excited states. From the ln τ_e vs. T^{-1} plot shown in Fig. 3, (Δ/k) of ca. 290 K (equivalent to 200 cm^{-1}) was obtained. The height of the saddles (potential barriers) separating two different directions of the distortion of Jahn-Teller active $[Cu(H_2O)_6]^{2+}$ ions can be expected to be ca. 100–500 cm^{-1} [19]. Therefore, the present value of (Δ/k) is very reasonable, suggesting that the electron spin-lattice relaxation is closely related to the reorientation of the distorted $[Cu(H_2O)_6]^{2+}$ ions between three potential wells.

[1] F. Borsa and A. Rigamonti, NMR and NQR in Fluids, Paramagnets, and Crystals, in: Magnetic Resonance of Phase Transitions (F. J. Owens, C. P. Poole, Jr., and H. A. Farach, eds), Academic Press, New York 1979.

[2] A. Rigamonti, Adv. Phys. **33,** 115 (1984).

[3] F. Borsa, M. Corti, and A. Rigamonti, J. Appl. Phys. **49,** 1383 (1978).

[4] M. Corti, A. Rigamonti, and A. Magistris, Phys. Stat. Sol. (b) **108,** 29 (1981).

[5] A. Sasane, T. Tanaka, A. Toba, Y. Kume, D. Nakamura, and M. Kubo, Chem. Lett. **1973,** 783.

[6] A. Sasane, H. Shinohara, Y. Mori, Y. Kume, T. Asaji, and D. Nakamura, Z. Naturforsch. **42a,** 611 (1987).

[7] S. Hirayama, M. Mizuno, T. Asaji, and D. Nakamura, to be published.

[8] K. Horiuchi, R. Ikeda, and D. Nakamura, Ber. Bunsenges. Phys. Chem. **91,** 1351 (1987).

[9] A. Ishikawa, K. Horiuchi, R. Ikeda, and D. Nakamura, J. Mol. Struct. **192,** 237 (1989).

[10] Gmelins Handbuch der Anorganischen Chemie, Pt (68), Teil C, Verlag Chemie, Berlin 1940.

[11] K. R. Jeffrey and R. L. Armstrong, Phys. Rev. **174,** 359 (1968).

[12] S. M. Myers and A. Narath, Phys. Rev. **B9** 227 (1974).

[13] See, for example, C. P. Slichter, Principles of Magnetic Resonance, Harper and Row, New York 1963, Chapter 5. – A. Abragam, The Principles of Nuclear Magnetism, Clarendon Press, Oxford 1961, p. 472.

[14] A. Abragam, The Principles of Nuclear Magnetism, Clarendon Press, Oxford 1961, p. 289.

[15] A. Birkeland and I. Svare, Phys. Scrip. **18,** 154 (1978).

[16] L. Pauling, Z. Kristallogr. **72,** 482 (1930).

[17] B. L. Silver and D. Getz, J. Chem. Phys. **61,** 638 (1974).

[18] G. E. Pake and T. L. Estle, The Physical Principles of Electron Paramagnetic Resonance, W. A. Benjamin, Inc., Reading 1973.

[19] D. P. Breen, D. C. Krupka, and F. I. B. Williams, Phys. Rev. **179,** 241 (1969).