Chlorine-35 NQR Study of a Structural Phase Transition in $(ND_4)_2PdCl_6$*

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Temperature dependences of ^{35}Cl NQR frequencies and spin-lattice relaxation times were measured at 4.2 to 400 K for natural and deuterated ammonium hexachloropalladate. It was confirmed that only the deuterated salt undergoes a first order phase transition at 30 K. The crystal structure of the low-temperature phase is predicted to be the same as that of the deuterated ammonium hexachloroplatinate and hexachloroplumbate. The mechanism of the deuteration-induced phase transition is discussed.

Key words: Isotope Effect; Phase Transition; Chlorine NQR; Spin-lattice Relaxation; Deuterated Ammonium Hexachloropalladate.

Introduction

It is well known that the rotational motion of ammonium ions in ammonium hexahalometallates, which have the cubic antifluorite structure ($Fm\bar{3}m$) at room temperature, is very weakly hindered in the crystals [1]. The positive correlation between the lattice constant and the rotational potential barrier has been pointed out by NMR and neutron scattering investigations. Recently it was found that in some deuterated ammonium hexachlorometallates, $(ND_4)_2MCl_6$ [M = Te, Se, Pt, Pd, Pb] there exists at low temperatures a low-symmetry phase, the counterpart of which does not exist in the corresponding natural salt [2–7]. This strong isotope effect seems to be dependent on the lightness of the ammonium ion for a motion in the potential field produced by the surrounding complex ions.

Four deuterated salts (tellurate, selenate, platinate, and plumbate) have been investigated to observe NQR signals by now. We have succeeded in observing signals in the low-temperature phase of the platinate [8] and the plumbate [9] and have predicted, on the basis of the three equal-intensity NQR signals observed, that the crystal structure of the low-temperature phase is orthorhombic. Since the lattice constant of the palladate at room temperature is almost the same as that of platinate [1], it may be expected that the low-temperature phase of both salts are also isomorphous. It has been suggested, however, by neutron powder diffraction of $(ND_4)_2PdCl_6$ that the crystal symmetry of the low-temperature phase is tetragonal [10]. Moreover, rather different transition entropies of 16.7 [5] and 10.1 JK^{-1} mol^{-1} [4] for $(ND_4)_2PdCl_6$ and $(ND_4)_2PtCl_6$, respectively, are reported. In this investigation we try to clarify the relationship between the structures of the low-temperature phases of $(ND_4)_2PtCl_6$ and $(ND_4)_2PdCl_6$. Although the temperature dependences of the NQR frequencies and spin-lattice relaxation time of $(NH_4)_2PdCl_6$ has been reported by Pelzl *et al.* [11], we performed the measurements by ourselves in order to compare the data with those of the deuterated salt.

Experimental

$(NH_4)_2PdCl_6$ (99.99%) from Aldrich Chem. Co was used without further purification. $(ND_4)_2PdCl_6$ was prepared by dissolving $(NH_4)_2PdCl_6$ in heavy water (99.8% D atomic) and introducing Cl_2 gas (99.9%) into the solution. The dark red precipitate obtained was dried on P_2O_5 in a dessicator. The isotopic purity was estimated to be 98 atomic % by use of high resolution ^{1}H NMR measurements.

^{35}Cl NQR signals were measured with a pulsed spectrometer based on the Matec gated amplifier 515 A [12].

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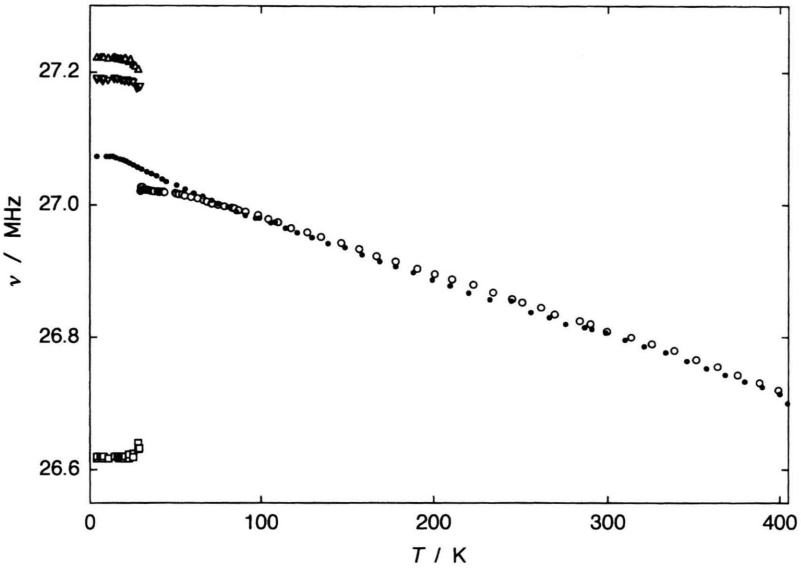

Fig. 1. Temperature dependences of ^{35}Cl NQR frequencies ν of $(NH_4)_2$-$PdCl_6$ (full circles) and $(ND_4)_2PdCl_6$ (open marks).

The spin-lattice relaxation time was determined by observing the recovery of the echo height, employing the pulse sequence $\pi - \tau - \pi/2 - \tau' - \pi$, where τ' was set at about 150 μs.

Results

Figure 1 shows the temperature dependences of ^{35}Cl nuclear quadrupole frequency, ν, for $(NH_4)_2PdCl_6$ and $(ND_4)_2PdCl_6$. Only one resonance signal was observed for $(NH_4)_2PdCl_6$, and it exhibits a smooth temperature dependence indicating that no phase transition takes place. This behaviour agrees very well with that reported [11]. The resonance line of $(ND_4)_2PdCl_6$, however, splits into three lines below 30.0±0.5 K, two of which are shifted to high frequencies and the other one to low frequences. This abrupt splitting indicates the occurrence of a first order phase transition at this temperature.

The spin-lattice relaxation times, T_{1Q}, of $(NH_4)_2PdCl_6$ and $(ND_4)_2PdCl_6$ were determined between 4.2 and 400 K and are shown in Figure 2. T_{1Q} of the natural salt smoothly increased with decreasing temperature, while the deuterated salt exhibited a broad maximum (110 ms) at ca. 170 K and became gradually shorter, down to 30 ms at 30 K. Below 30 K the spin-lattice relaxation times for the three resonance signals became abruptly longer and then elongated steeply with decreasing temperature.

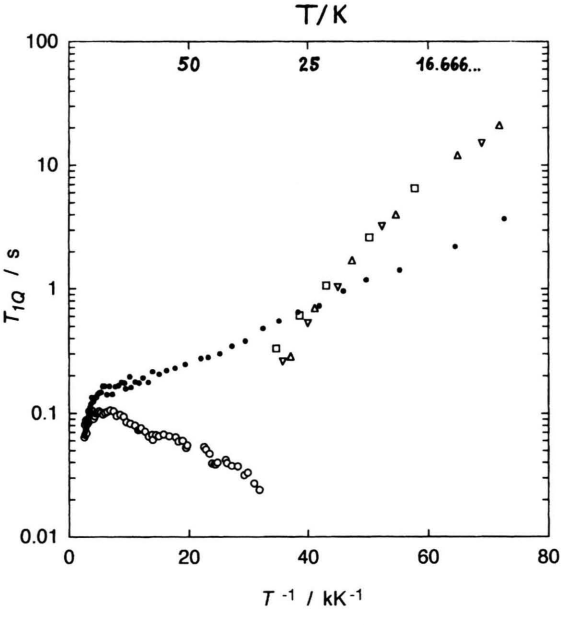

Fig. 2. Temperature dependences of ^{35}Cl NQR spin-lattice relaxation times T_{1Q} of $(NH_4)_2PdCl_6$ (full circles) and $(ND_4)_2PdCl_6$ (open marks).

Discussion

The transition temperature of 30.0 K, determined for $(ND_4)_2PdCl_6$ as the temperature at which the NQR signal splits, agrees well with the temperature of 30.2 K de-

Table 1. Some characteristic parameters for the palladate, platinate, and plumbate: reduced splitting $\Delta\nu/\nu$, transition temperature T_c, transition entropy ΔS_{trs}, lattice constant a_0 for natural salt at room temperature, activation energy E_a for the reorientational motion of ammonium ion in the natural salt.

Compound	$\Delta\nu/\nu$	T_c/K	ΔS_{trs}/ JK^{-1} mol^{-1}	a_0/Å	E_a/ $kcalmol^{-1}$
$(ND_4)_2PdCl_6$	0.0224	30.0	16.7[c]	9.826[f]	0.61[f]
$(ND_4)_2PtCl_6$	0.0181[a]	27.5[a]	10.1[d]	9.854[f]	0.68[f]
$(ND_4)_2PbCl_6$	0.0948[a]	38.0[b]	7.5[e]	10.155[f]	1.41[f]

a: [8], b: [9], c: [5], d: [4], e: [17], f: [1].

termined by heat capacity measurement [5]. The three NQR signals observed in the low-temperature phase indicate that three kinds of non-equivalent chlorine atoms exist in a unit cell of the crystal structure. The distribution of the three frequencies quite resembles those of $(ND_4)_2PtCl_6$ [8] and $(ND_4)_2PbCl_6$ [9]. The center of gravity of the frequencies at 4.2 K almost conincides with the frequency which is extrapolated from the frequencies in the high-temperature cubic phase (The discrepancy is 1.3% of the whole splitting magnitude, while its is 6.6% for platinate and 2.2% for plumbate). This strongly suggests that the low-temperature phases of these three complex salts have the same crystal structure. The reduced splitting, $\Delta\nu/\nu$ ($\Delta\nu$ and ν denote the whole splitting magnitude and the averaged frequency of the three frequencies, respectively), can be assumed to represent the degree of deformation of the crystal lattic from cubic structure. It is remarkable that there exists the correlation only between the reduced splitting and the transition temperature, as shown in Table 1.

Very recently a neutron powder diffraction measurement for $(ND_4)_2PtCl_6$ was performed [13] and the structure of the low-temperature phase was tentatively determined to belong to the space group $P4_2/n$ with four formula units in a unit cell. If the complex ions occupy the inversion-symmetry site (4d or 4c site in Wyckoff notation) in this structure, the above NQR result is consistent with this structure.

Above ca. 320 K, the T_{1Q} values of the two salts become equal, as shown in Figure 2. This fairly steep shortening with increasing temperature can be attributed to thermal excitation of a reorientation of the $[PdCl_6]^{2-}$ ion [6, 9, 14]. Though the T_{1Q} behaviour of $(NH_4)_2PdCl_6$ below 250 K looks as for an ionic crystal, it could not be elucidated only on the basis of a Raman process. The motion of the ammonium ions should affect T_{1Q} like in the case of $(NH_4)_2PtCl_6$ [15].

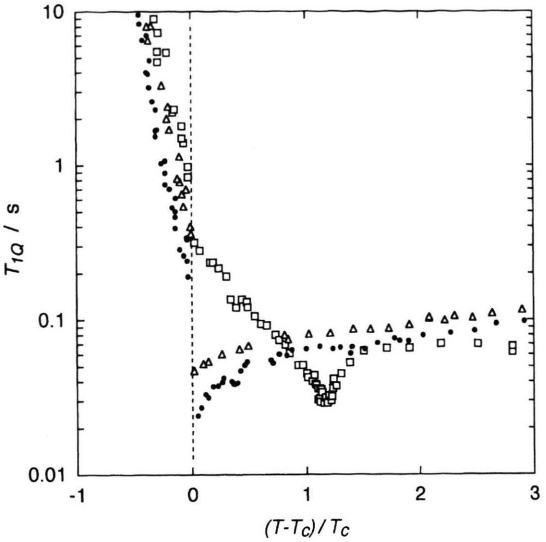

Fig. 3. Plots of ^{35}Cl NQR spin-lattice relaxation time T_{1Q} vs. reduced temperature $(T-T_c)/T_c$ for the deuterated palladate, platinate [8], and plumbate [9]. T_c denotes the deuteration-induced phase transition temperature. ●: $(ND_4)_2PdCl_6$, △: $(ND_4)_2PtCl_6$, □: $(ND_4)_2PbCl_6$.

Below ca. 170 K, T_{1Q} of the deuterated salt became shorter with coming close to the transition temperature. This suggests that a rotational lattice mode of $[PdCl_6]^{2-}$ is softed [6, 8, 16]. These characteristic features resemble those of the platinate, as shown in Figure 3. As for $(ND_4)_2PbCl_6$, which transforms from the high-temperature cubic phase to the low-temperature deuteration-induced phase via a trigonal intermediate phase, T_{1Q} at just above the deuteration-induced phase transition was not so short as those of the palladate and the platinate, but elongated with decreasing temperature to the transition [9]. A similar elongation of T_{1Q} was observed in $(ND_4)_2TeCl_6$, which exhibits a complex isotope effect [2]. No rotational soft-mode accompanies the deuteration-induced phase transition in the plumbate and the tellurate. It could be concluded that the rotational soft mode of the complexion does not play an important role in the mechanism of the deuteration-induced phase transition for the palladate, platinate, and plumbate. Namely, the phase transitions are of a strong first order and it is expected that there is no correlation of the symmetry between the high- and low-temperature phases.

The T_{1Q} value of $(ND_4)_2PdCl_6$ at temperatures far below the transition point are longer than those of $(NH_4)_2PdCl_6$. This suggests that the $[PdCl_6]^{2-}$ ion is more tightly bound in the low-temperature phase of the deuterated crystal than in the natural crystal. This feature is also the same as that of the platinate [8].

The basic mechanism of the deuteration-induced phase transition is orientational ordering of ammonium ions, as previously described [3, 6–8, 13]. The N–D bond direction of the ammonium ion in the high-temperature phase does not coincide with the crystallographic triad axis [13, 18]. We suppose that the ammonium ion is transformed from the disordered state to the ordered state by the ammonium-ammonium interaction acting on the ordering as follows. When one ammonium ion turns to one of the three directions, another ammonium ion turns preferably to a specific direction through the ammonium-ammonium interaction. The deuterated ammonium ion will be more strongly localized to the three directions than the hydrogenous ammonium ion since the moment of inertia of the deuterated ammonium is larger than that of hydrogenous ammonium ion. Therefore the interaction is effectively weaker in the natural salts than in the deuterated salts. This will be the reason why the natural salt does not undergo the phase transition. As for the ammonium-ammonium interaction, we could consider a direct interaction and a mediated interaction through coupling with motions of the complex ion. To conclude, the rotational of the complex ion does not seem to relate to the mediated interaction.

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