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Isotope effect on the temperature dependence of the ^{35}Cl NQR frequency in $(NH_4)_2RuCl_6$

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HIGHLIGHTS

- ^{35}Cl NQR of $(NH_4)_2RuCl_6$, $(ND_4)_2RuCl_6$, $(NH_4)_2SnCl_6$, and $(ND_4)_2SnCl_6$ was measured.
- Isotope effect on the spatial distribution of hydrogen atoms is discussed.
- Tunneling splittings of torsional ground state of ammonium ions were estimated.
- Origin of T_{1Q} anomaly previously reported in $(NH_4)_2SnCl_6$ and $(ND_4)_2SnCl_6$ was revealed.

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ABSTRACT

The ^{35}Cl nuclear quadrupole resonance frequencies and spin–lattice relaxation times for $(NH_4)_2RuCl_6$, $(ND_4)_2RuCl_6$, $(NH_4)_2SnCl_6$, and $(ND_4)_2SnCl_6$ were measured in the temperature range 4.2–300 K. In these four compounds, it was confirmed that no phase transition occurs in the observed temperature range. At 4.2 K, discrepancies of the NQR frequency between non-deuterated and deuterated compounds, which are attributed to the difference in the spatial distributions of hydrogen (deuterium) atoms in the ground states of the rotational motion of ammonium ion, reached to 24 kHz and 23 kHz for the ruthenate compounds and the stannate compounds, respectively. The separation between the ground and the first excited states of the rotational motion of the ammonium ion was estimated to be 466 J mol^{-1} and 840 J mol^{-1} for $(ND_4)_2RuCl_6$ and $(NH_4)_2RuCl_6$, respectively, by least-square fitting calculations of temperature dependence of the NQR frequency. For $(ND_4)_2SnCl_6$ and $(NH_4)_2SnCl_6$, these quantities were estimated to be 501 J mol^{-1} and 1544 J mol^{-1}, respectively. It was clarified that the T_1 minimum, which has been observed for the stannate compounds at around 60 K as a feature of the temperature dependence, was dependent on a method of sample preparation. It is concluded that the minimum is not an essential character of the ammonium hexachlorostannate(IV) since the crystals prepared in strong acid condition to prevent a partial substitution of chlorine atoms by hydroxyl groups, did not show such T_1 minimum.

1. Introduction

Many ammonium hexachlorometallates(IV), $(NH_4)_2MCl_6$ (M denotes metal, e.g. Pt, Ir, Sn, Pb, Te), crystallize to the cubic K_2PtCl_6 type structure ($Fm\bar{3}m$) at the ambient temperature. In this structure, octahedral hexachlorometal complex ion is situated at (0,0,0) and at face centers of the unit cell. Chlorine atoms are located on the crystal axes. Meanwhile, ammonium ion is situated at (1/4,1/4,1/4), site symmetry of which is tetrahedral ($\bar{4}3m$), and N–H vector is directed toward empty corners of one eighth of the unit cell [1]. Since the rotational potential barrier of ammonium ions in the crystals is very low, ammonium ions reorient between each four directions of the triad axes at high temperatures [2,3]. At low temperatures, this classical motion turns to the quantum mechanical tunneling motion and a correlation between lattice constants and tunneling frequencies has been investigated by neutron scattering and nuclear magnetic relaxation measurements [1,3,4]. These tunneling frequencies are very low and distribute 13,500–10 MHz, corresponding to 5400–4 mJ mol^{-1}. To be more detailed, it was suggested by the neutron diffraction measurements that a hydrogen atom does not exist on the triad axis of the crystal but is located slightly apart from the triad axis and ammonium ion reorients between six orientations having N–H bond on a cone around the triad axis [5–12]. This small-angle jumps of ammonium ions near the high-temperature equilibrium orientations is often called as limited jumps [9].

For some deuterated compounds, $(ND_4)_2M'Cl_6$ (M′ = Pt, Pd, Pb, Te), so called deuteration induced phase transitions occur at low

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temperatures (27–48 K) and deuterated ammonium ions are ordered in the low temperature phases having lower symmetry [6–8], although the hydrogenous analogues, $(NH_4)_2M'Cl_6$, do not have corresponding phase transitions. The mechanism of these transitions can be qualitatively explained as follows. With decreasing temperature, the motion of the ammonium ions becomes slow. Because of the larger moment of inertia the deuterated ammonium ions localize more strongly at the potential minimum directions than the hydrogenous ammonium ions. Ammonium-ammonium interaction mediated with the complex ion causes the N–H bonds to point to one of these directions resulting in the phase transition. That is to say, the strength of interaction between hydrogen of the ammonium ion and chlorine of the metal complex ion seems to play a large role for the strong isotope effect.

$(ND_4)_2SnCl_6$ and $(ND_4)_2IrCl_6$ undergo no phase transition down to the liquid helium temperature. However, a phenomenon attributed to tunneling motion of ammonium ion was revealed on the temperature dependence of the nuclear quadrupole resonance frequency of these compounds [13,14]. Lattice constants of these compounds are intermediate length, namely, longer than those of $(NH_4)_2PdCl_6$ and $(NH_4)_2PtCl_6$ but shorter than those of $(NH_4)_2PbCl_6$ and $(NH_4)_2TeCl_6$. Though $(NH_4)_2RuCl_6$ is expected to undergo no phase transition because of the lattice constant fairly close to that of $(NH_4)_2IrCl_6$ [4,15], a heat capacity anomaly like that in $(NH_4)_2PbCl_6$ and $(NH_4)_2TeCl_6$ has been suggested at 93 K [16]. In this study nuclear quadrupole resonance measurements for $(NH_4)_2RuCl_6$ and $(ND_4)_2RuCl_6$ were carried out to clarify the phase relationship and isotope effects. Furthermore, $(NH_4)_2SnCl_6$ and $(ND_4)_2SnCl_6$ were also measured to compare the isotope effects, although nuclear quadrupole resonance of these complex have been investigated [13,17].

2. Experimental

$(NH_4)_2RuCl_6$ (98% purity) purchased from Aldrich Chem. Co was used to measure NQR signal without further purification. The deuterated analogue was prepared with a temperature gradient recrystallization method from conc. deuterated hydrochloric acid (37 wt.% = ca.12 M, 99.5% atomic D) solution of $(NH_4)_2RuCl_6$. It spent 70 days on the recrystallization. Black crystals obtained were dried over P_2O_5 in a desiccator. The isotopic purity was estimated to be more than 90% atomic D by infra-red measurement, and to be 96% atomic D by high-resolution ^1H NMR measurements. K_2RuCl_6 purchased from Johnson Matthey Co. was recrystallized with the temperature gradient method from conc. hydrochloric acid (35 wt.%).

For $(NH_4)_2SnCl_6$, two samples were used for the measurement of NQR. A sample of 99.999% purity (metal base) purchased from Johnson Matthey Co. is denoted by **A** in the following. Second sample recrystallized from ca. 25 wt.% hydrochloric acid solution after preparation from tin(IV) chloride and ammonium chloride is denoted by **B**. For $(ND_4)_2SnCl_6$, two samples were also used to measure NQR signal. Sample denoted by **C** and **D** were recrystallized from solutions of 15 wt.% and 35 wt.% deuterated hydrochloric acid, respectively. The isotopic purities were estimated to be 98% atomic D for both samples.

^{35}Cl NQR measurement was conducted using a pulsed spectrometer based on the Matec gated amplifier 515A [18] from the liquid helium temperature to room temperatures. Since the signal of K_2RuCl_6 was very weak, the signal was accumulated more than thousand times. The spin–lattice relaxation time (T_{1Q}) was determined by observing the recovery of the echo-height $M(\tau)$ using the pulse sequence $\pi-\tau-\pi/2-\tau'-\pi$. For nonexponential recovery, T_{1Q} was determined as a time interval, in which a signal function $S(\tau) = (M_0-M(\tau))/2M_0$ defined using the equilibrium value M_0 decreases to $1/e$ of the initial value $S(0)$.

3. Results

3.1. Ammonium and potassium hexachlororuthenate(IV)

The temperature dependences of the ^{35}Cl nuclear quadrupole resonance frequencies ν_Q of $(NH_4)_2RuCl_6$, $(ND_4)_2RuCl_6$, and K_2RuCl_6 (abbreviated to ACRu, DACRu, and KCRu, respectively, in the following) are shown in Fig. 1. Although the observed NQR frequencies of KCRu were ca. 5 kHz lower than those reported by Fergusson and Scaife [19] in the temperature range 80–300 K, the temperature coefficients observed in this temperature range were in good agreement with the reported value (0.04 kHz K^{-1}). The frequencies below 100 K gradually shifted to high-frequency side and the deviation from an extrapolation from a high-temperature region becomes ca. 20 kHz at 4.2 K.

ACRu and DACRu exhibited smooth temperature dependences of the frequencies between 4.2 K and 300 K suggesting no phase transition. The resonance frequencies of both complexes were separated ca. 16 kHz at 300 K and the difference became smaller with decreasing temperature. At around 40 K the two frequencies were once coincident, then those came apart again with decreasing temperature and the difference reached to 24 kHz at 4.2 K. These behavior closely resembles that of ammonium hexachloroiridate(IV) [14]. At high temperature region, absolute values of the temperature coefficients of the frequency were very small ($d\nu_Q/dT = -0.15$ kHz K^{-1}) for both complexes.

Fig. 2 shows the temperature dependences of the spin–lattice relaxation time (T_{1Q}) of ^{35}Cl for ACRu and DACRu. T_{1Q} of ACRu at the temperatures lower than 200 K was longer than those of $(NH_4)_2PtCl_6$ [20] and $(NH_4)_2PdCl_6$ [21], though ACRu is a paramagnetic substance. Ru^{4+} has $d\varepsilon^4$ electron configuration in the hexachlororuthenate(IV) ion and a magnetic ground state of ACRu is a singlet due to the spin–orbit interaction [22,23]. Hence the contribution of paramagnetic relaxation should be small. T_{1Q} of DACRu exhibited a very shallow minimum at 40 K suggesting an existence of additional relaxation processes in this complex.

3.2. Ammonium hexachlorostannate(IV)

Figs. 3 and 4 show the temperature dependencies of the ^{35}Cl NQR frequency and the spin–lattice relaxation time, respectively,

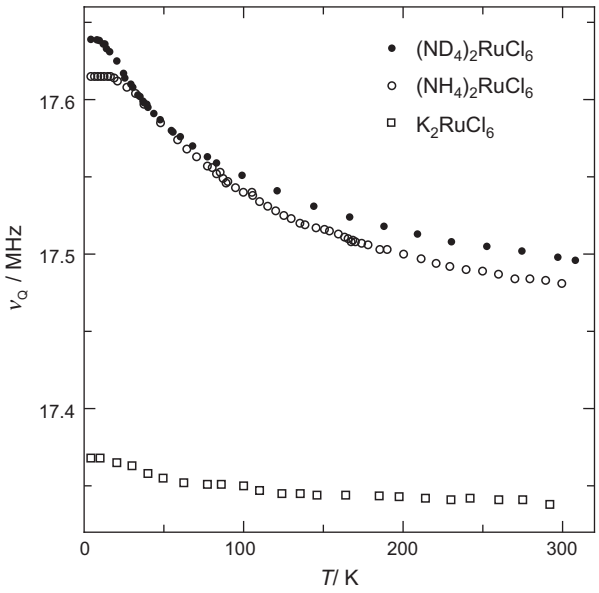

Fig. 1. The temperature dependence of ^{35}Cl NQR frequencies determined between 4.2 K and ca. 300 K for $(NH_4)_2RuCl_6$ (open circle), $(ND_4)_2RuCl_6$ (solid circle), and K_2RuCl_6 (open square).