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The effect of deuteration on the motion of ammonium ions and the structural phase transition in NH_4AuCl_4

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Abstract. The effect of deuteration on the motion of ammonium ions and/or the structural phase transition in NH_4AuCl_4 was studied by means of ^{35}Cl nuclear quadrupole resonance measurements. The transition temperature shifted by 5 K from 28.5 K for NH_4AuCl_4 to 33.5 K for ND_4AuCl_4 . Spin–lattice relaxation caused by the modulation of the electric field gradient due to the motion of nearby ammonium ions was observed. The activation energy of the motion of the ammonium ions was determined to be 0.8 and 1.8 kJ mol^{-1} for NH_4AuCl_4 and ND_4AuCl_4 , respectively. By the use of the simple harmonic oscillator model, the barrier height V_0 and the number of wells n of the potential for the reorientation of the ammonium ions were determined as $V_0 = 4.2 \text{ kJ mol}^{-1}$ and $n = 4$ from the above activation energies for the NH_4^+ and ND_4^+ reorientations.

1. Introduction

In the ammonium compounds, a structural phase transition is often observed, which seems to be caused by the locking of the rotational motion of NH_4^+ ions. We have previously reported, on the basis of nuclear quadrupole resonance (NQR) measurements, that ammonium tetrachloroaurate (III), NH_4AuCl_4 , shows such a structural phase transition at 28.5 K [1]. The NQR spin–lattice relaxation time T_1 is determined to be below $\simeq 100$ K from the modulation of the electric field gradient (EFG) due to the motion of NH_4^+ ions in the crystal. This makes it possible to obtain information about the molecular motion of NH_4^+ ions from the NQR measurements. Recently, the quantum effect on the small-angle reorientational motion of NH_4^+ ions has been attracting attention as a mechanism of suppression of the structural phase transition in $(\text{NH}_4)_2\text{MCl}_6$ ($M = \text{Te, Pt, Pd, Pb}$) [2–6]. Deuteration is expected to have a non-negligible effect on the molecular motions of NH_4^+ ions in other systems as well. In the present paper, we report, on the basis of the analysis of the ^{35}Cl NQR data, the effect of deuteration on the motion of the ammonium ions and/or the structural phase transition in NH_4AuCl_4 .

2. Experimental procedure

Au_2O_3 was dissolved in DCl acid solution. This solution was mixed with an ND_4Cl solution in D_2O . By the slow evaporation of the resulting solution in a vacuum desiccator over P_2O_5 , $\text{ND}_4\text{AuCl}_4 \cdot \frac{2}{3}\text{D}_2\text{O}$ crystals were prepared. The water of crystallization was completely removed

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by keeping the sample in a vacuum at $\simeq 100$ °C for 10 h. The polycrystalline sample of ND_4AuCl_4 was sealed in a glass tube with helium gas as the heat exchange gas.

A pulsed spectrometer based on the Matec gated amplifier 515A was used. The resonance frequency was determined by plotting the echo height as a function of the carrier frequency. The spin–lattice relaxation time T_1 was determined by observing the recovery of the echo height, employing the pulse sequence $\pi-\tau-\pi/2-\tau_e-\pi$, where τ_e was set at $\simeq 120$ – 250 μs . The spin–spin relaxation time T_2 was determined by observing the decay of the echo height using the pulse sequence $\pi/2-\tau-\pi$. The sample temperature was controlled using an electronic controller (Ohkura EC-61A and Oxford DTC 2 for above 77 K and below 77 K, respectively) and measured with an accuracy of ± 0.5 K by the use of copper versus constantan and gold + 0.07% iron versus chromel thermocouples above 77 K and below 77 K, respectively.

3. Results

The temperature dependences of the ^{35}Cl NQR frequencies of ND_4AuCl_4 indicate the onset of a structural phase transition at $T_c = 33.5$ K as shown in figure 1. Below T_c , the high- and low-frequency lines of the high-temperature phase split into four and two lines, respectively. Figure 2 shows the spin–lattice relaxation time T_1 and the spin–spin relaxation time T_2 as functions of temperature. The decay of the echo height against the spacing time τ was exponential in the T_1 -measurements while it followed a Gaussian decay function [5] in the case of T_2 -measurements.

4. Discussion

The phase transition temperature $T_c = 33.5$ K of ND_4AuCl_4 is higher by 5 K as compared with $T_c = 28.5$ K for NH_4AuCl_4 . As shown in figure 1, we observed for ND_4AuCl_4 the

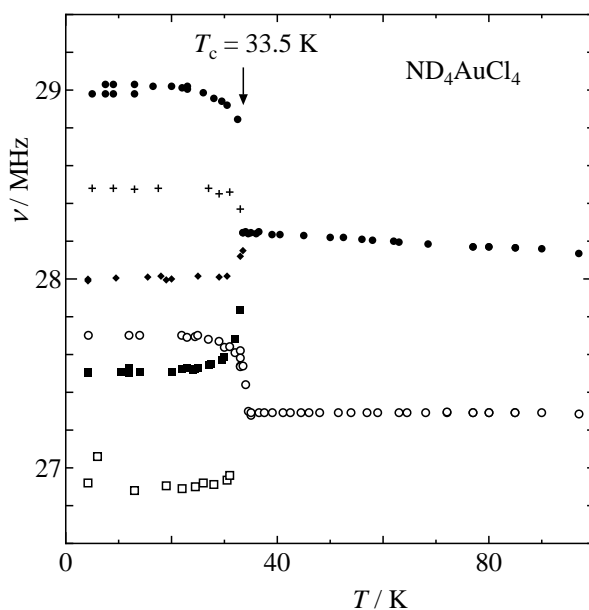


Figure 1. Temperature dependences of ^{35}Cl NQR frequencies of ND_4AuCl_4 .

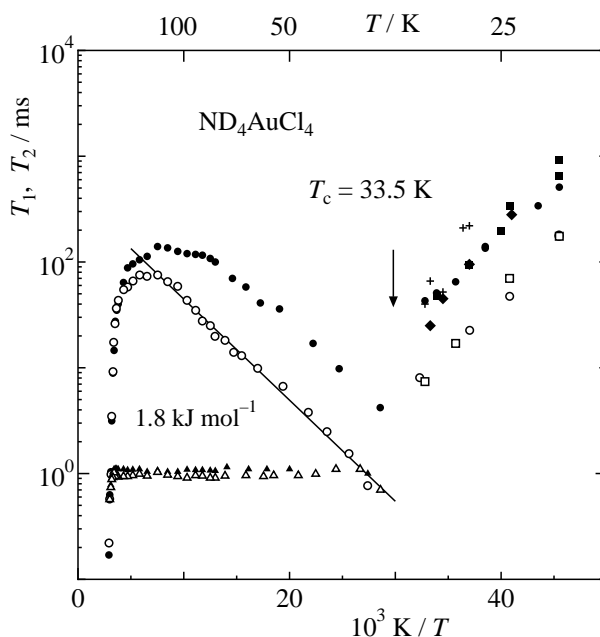


Figure 2. Temperature dependences of the ^{35}Cl NQR spin–lattice and spin–spin relaxation times T_1 and T_2 , respectively, of ND_4AuCl_4 . T_1 -data are shown using the same symbols for the respective NQR lines as in figure 1. Solid and open triangles indicate T_2 -values of the high- and low-frequency lines, respectively, in the high-temperature phase.

high- and low-frequency lines of the high-temperature phase split into four and two lines, respectively, below T_c . In the previous study of NH_4AuCl_4 , the outer doublet of the quartet was missing [1]. However, we have observed the corresponding outer doublet in NH_4AuCl_4 also in the present study. The two frequencies observed in the high-temperature phase can be assigned to the crystallographically inequivalent chlorines in the complex anion AuCl_4^- , assuming the same crystal structure as for the isomorphous compound RbAuCl_4 [7]. The temperature dependence of the NQR frequencies is almost continuous across T_c , suggesting a strong nature of the second-order phase transition. As for the temperature dependence of T_1 in the vicinity of T_c , more precise measurements will be necessary to judge whether it is continuous or not.

The spin–spin relaxation time T_2 in the high-temperature phase is almost constant at $\simeq 1$ ms except for the temperature range in which the spin–lattice relaxation time T_1 becomes shorter than 1 ms, and it determines T_2 . The steep T_1 -decrease observed above $\simeq 290$ K can be explained by sudden and infrequent 90° jumps of the square-planar AuCl_4^- ions about the pseudo- C_4 axis as described in a previous paper [1]. The T_2 -value of ND_4AuCl_4 (1.06 ms at 77 K) is longer than that of NH_4AuCl_4 (0.44 ms at 77 K), which was determined by fitting the decay of the echo height as a function of the space-time τ to a Lorentzian decay function [1, 5]. This indicates the appreciable contribution to T_2 for NH_4AuCl_4 from the dipolar coupling with protons of ammonium ions performing fast reorientational motions.

The spin–lattice relaxation time T_1 decreases with decreasing temperature over the temperature range 100–35 K as shown in figure 2. This temperature dependence can be interpreted in terms of the relaxation mechanism caused by the modulation of the EFG due to the motion of nearby ammonium ions in the crystal [1, 8, 9]. On the assumption of a relaxation

mechanism due to the modulation effect, the activation energy of the motion of the ammonium ions was determined to be 0.8 and 1.8 kJ mol⁻¹ for NH₄AuCl₄ [1] and ND₄AuCl₄, respectively.

In order to facilitate discussions of the effect of deuteration on the motion of the ammonium ions in NH₄AuCl₄, the following n -fold-symmetry potential with the barrier height V_0 and the rotation angle ϕ is assumed for the reorientation of the ammonium ions about an axis that passes through the N atom:

$$V(\phi) = \frac{V_0}{2}[1 - \cos(n\phi)]. \quad (1)$$

At the bottom of the well, the above potential is approximated as follows:

$$V(\phi) \approx \frac{V_0}{2} \left[1 - \left(1 - \frac{n^2\phi^2}{2} \right) \right] = \frac{V_0}{4} n^2 \phi^2. \quad (2)$$

Therefore, the angular frequency ω_l of the librational motion at the bottom of the well can be written as equation (3) within the harmonic oscillator approximation:

$$\omega_l = n \left(\frac{V_0}{2I} \right)^{1/2}. \quad (3)$$

Here, I denotes the moment of inertia of the ammonium ion. Since the degree of freedom is three for the libration in the three-dimensional space, the zero-point energy of the libration is

$$\frac{3}{2} \hbar n \left(\frac{V_0}{2I} \right)^{1/2}.$$

The activation energy E_a , which is obtainable from the T_1 -measurements of the magnetic resonance, can be thought to be the energy difference between the zero-point energy level and the potential barrier height V_0 . That is,

$$V_0 = E_a + \frac{3}{2} \hbar n \left(\frac{V_0}{2I} \right)^{1/2}. \quad (4)$$

The moment of inertia I_D of the ND₄⁺ ion can be assumed to be twice that (I_H) of the NH₄⁺ ion. Hence, with the activation energies $E_a(H)$ and $E_a(D)$ of the respective ammonium ions NH₄⁺ and ND₄⁺ known and assuming the same potential curve for the two ions, the simultaneous equations (5) and (6) can be solved for V_0 and I_H :

$$V_0 = E_a(H) + \frac{3}{2} \hbar n \left(\frac{V_0}{2I_H} \right)^{1/2} \quad (5)$$

$$V_0 = E_a(D) + \frac{3}{2} \hbar n \left(\frac{V_0}{2I_D} \right)^{1/2} = E_a(D) + \frac{3\sqrt{2}}{4} \hbar n \left(\frac{V_0}{2I_H} \right)^{1/2}. \quad (6)$$

Putting $E_a(H) = 0.8$ kJ mol⁻¹, $E_a(D) = 1.8$ kJ mol⁻¹ in equations (5) and (6), the barrier height $V_0 = 4.2$ kJ mol⁻¹ was obtained. The moment of inertia I_H was calculated to be 4.3×10^{-47} kg m² with the assumption that $n = 4$, i.e., in the case of fourfold potential wells. This value of the moment of inertia agrees very well with the expected value of 4.5×10^{-47} kg m² for the NH₄⁺ ion with the N–H distance of 1.0×10^{-10} m and the T_d symmetry. For the present system, it is concluded that the deuteration does not affect the potential curve for the reorientation of the ammonium ions and only lowers the zero-point vibrational energy level of the ammonium ion. To understand the possible orientations of the ammonium ion in the present crystals, we have examined the inter-atomic distances of the isomorphous crystal structure of RbAuCl₄ [7] because the detailed crystal structure of NH₄AuCl₄ is not known. The ammonium cation existing on the crystal twofold symmetry

axis is expected to have four different orientations in which the formation of hydrogen bonds with the chlorine atoms is possible. The reorientation among these orientations accompanies the change of the hydrogen-atom positions and hence causes the modulation of the EFG at the positions of the chlorine atoms. When the reorientational motion is frozen, it is quite possible that the four crystallographically inequivalent AuCl_4^- complex anions are generated.

Provided that the effective inter-ionic interaction, which is responsible for the phase transition, depends on the rotational state of the ammonium ions, the increase of T_c caused by the deuteration can be explained as follows. The transient time τ_t and the residence time τ_r can be defined as a time for which the ammonium ion exists in a free-rotator state and a time which it spends in a single orientation in a potential well, respectively. The ratio τ_t/τ_r will be given by a Boltzmann factor $\exp(-E_a/RT)$ according to a two-state approximation [10–14]. Since the activation energy E_a increases upon deuteration, the deuteration has the effect of lowering the ratio τ_t/τ_r . If the effective inter-ionic interaction is negligible in a free-rotator state, the inter-ionic interaction will be enhanced by the deuteration, leading to an increase of T_c .

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