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Structural phase transitions in deuterated ammonium hexachloroplumbate(IV), $(ND_4)_2PbCl_6$, studied by ^{35}Cl nuclear quadrupole resonance

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Abstract. The ^{35}Cl NQR frequency and the spin–lattice and spin–spin relaxation times were measured as functions of temperature, in order to study the structural phase transitions in deuterated ammonium hexachloroplumbate(IV) $(ND_4)_2PbCl_6$. It was shown that the phase transition at 81 K is of a second-order type with an overdamped soft mode, while the deuteration-induced transition at 38 K is of first order. Three NQR frequencies (17.99, 17.86 and 16.35 MHz at about 15 K) were observed below 38 K suggesting an orthorhombic symmetry in the deuteration-induced low-temperature phase. The averaged value of these frequencies almost coincides with the frequency extrapolated from that (17.348 MHz at 39 K) above 38 K. The splitting (about 1.6 MHz) of the frequency below 38 K is quite large compared with that (0.45 MHz) of $(ND_4)_2PtCl_6$, which shows a similar phase transition induced by deuteration at 27.5 K. This indicates a large distortion of the crystal lattice in the present compound.

1. Introduction

It is known that cubic antifluorite crystals A_2MX_6 (A = monovalent cation; M = metal with oxidation number 4; X = halogen) undergo various types of phase transition depending on a delicate balance between interionic A–X and X–X overlap interactions [1]. From nuclear quadrupole resonance (NQR), neutron diffraction and group-theoretical studies of the phase transitions in the cubic antifluorite crystals, Armstrong and co-workers [2–7] concluded for the case of the ferrodistortive (zone-centre) phase transitions as follows. When the normal mode with E_g symmetry is frozen, the quasi-tetragonal low-temperature structure is not associated with static rotation of a complex anion, whereas, when the symmetry of the soft mode is T_{1g}, the complex anion rotates about its fourfold symmetry axis through a phase transition, so as to reduce the halogen–halogen (X–X) repulsive energy.

In the case of $(NH_4)_2TeCl_6$ and $(NH_4)_2PbCl_6$, the crystal transforms from cubic to trigonal symmetry, in which a rotation of the complex anion about its threefold axis instead of the fourfold axis takes place because tetragonal distortion of lattice requires so much deformation of the ammonium ion from the T_d symmetry [1, 8].

The energy balance between A–X and X–X interactions is so delicate that a dramatic change in structure is observed by merely replacing NH_4^+ by ND_4^+. In $(NH_4)_2MCl_6$ (M = Te,
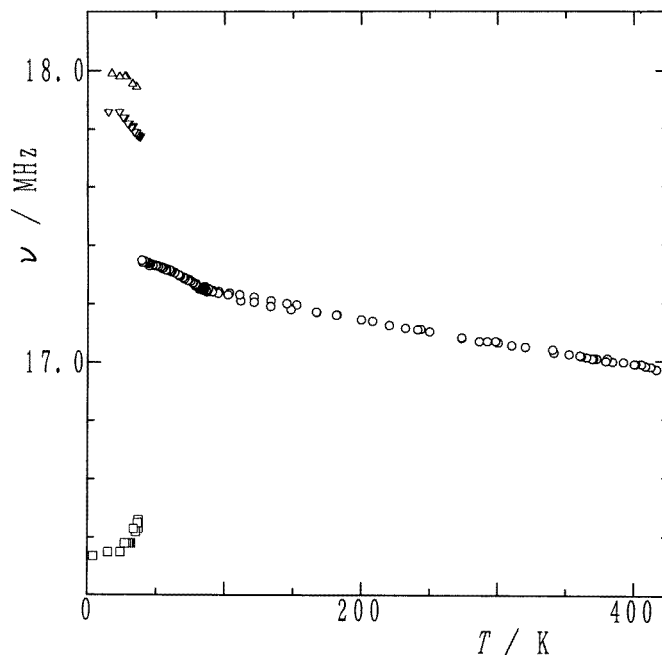
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Figure 1. Temperature dependences of the ^{35}Cl NQR frequencies of $(ND_4)_2PbCl_6$.

Pt, Pd or Pb), deuteration gives rise to a new structural phase transition which does not exist in normal ammonium salts [1, 9–11].

NQR measurements have been undertaken in order to elucidate the structure of the deuteration-induced low-temperature phase. However, the attempt failed to detect the NQR signal in the deuteration-induced phase of $(ND_4)_2TeCl_6$ [1]. Previously, we have succeeded in detecting ^{35}Cl NQR signals in the deuteration-induced phase of $(ND_4)_2PtCl_6$ and suggested that the symmetry of the complex anion is lowered to orthorhombic [12].

In the present study, we have investigated phase transitions in $(ND_4)_2PbCl_6$ by measuring the ^{35}Cl NQR frequencies ν and the spin–lattice relaxation time T_{1Q} and spin-spin relaxation time T_{2Q} as functions of temperature.

2. Experimental details

The sample of $(ND_4)_2PbCl_6$, which was used in the heat capacity measurements [11], was employed in the present NQR measurements. The isotopic purity was estimated to be 98 at.%. A pulsed spectrometer based on the Matec gated amplifier 515 A 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_{1Q} was determined by observing the recovery of the echo height, employing the pulse sequence π–τ–$\pi/2$–τ_e–π, where τ_e was set at about 250 μs. The spin–spin relaxation time T_{2Q} was determined by observing the decay of the echo height using the pulse sequence $\pi/2$–τ–π. 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 use of copper versus constantan and gold +0.07% iron versus chromel thermocouples above 77 K and below 77 K, respectively.
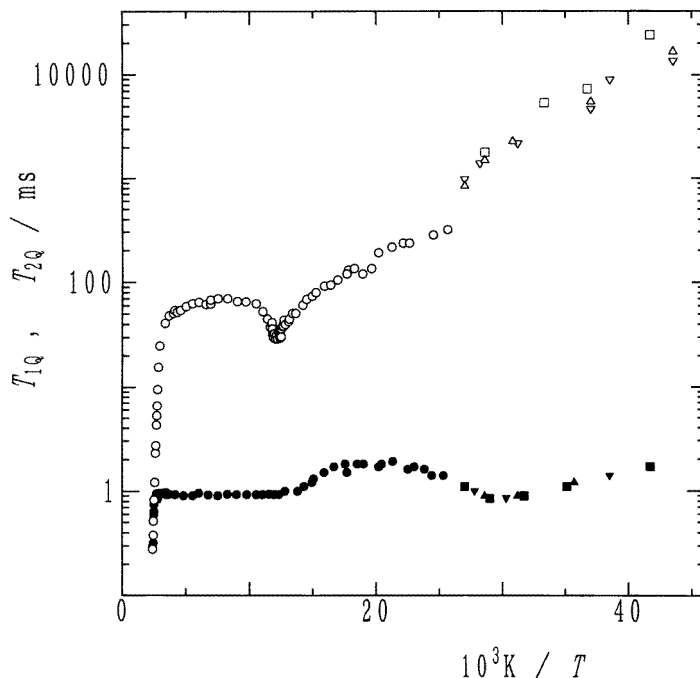
Figure 2. Temperature dependence of ^{35}Cl NQR spin–lattice relaxation times, T_{1Q} (open symbols) and spin–spin relaxation times T_{2Q} (full symbols) in (ND₄)₂PbCl₆. The T_{1Q}- and T_{2Q}-values are shown using the respective shape of symbols for the different NQR lines as used in figure 1.

3. Results

Figure 1 shows the temperature dependence of the ^{35}Cl NQR frequency in (ND₄)₂PbCl₆. A discontinuous change in the slope of the frequency shift as a function of temperature was observed at 81 K. At 38 K, the frequency split discontinuously into three components, two of which shifted to high frequencies and the other to low frequencies. The temperature dependences of T_{1Q} and T_{2Q} in (ND₄)₂PbCl₆ are shown in figure 2.

The decay of the echo height $M(\tau)$ as a function of spacing time τ between $\pi/2$ and π pulses could be fitted to the following Gaussian decay function below about 400 K (figure 3):

$$M(\tau) = M_0 \exp[-(2\tau/T_{2Q})^2]. \tag{1}$$

However, above 412 K, fitting by use of the following Lorentzian decay function gave a better result (figure 4).

$$M(\tau) = M_0 \exp(-2\tau/T_{2Q}). \tag{2}$$

T_{2Q} was determined assuming a Gaussian and a Lorentzian decay for $T \leqslant 405$ K and $T > 405$ K, respectively.

Above about 300 K, T_{1Q} decreased exponentially with increasing temperature. From the slope of $\ln T_{1Q}$ versus $1/T$ plots, the activation energy of 72 kJ mol^{-1} was obtained for a reorientational motion of the PbCl$_6^{2-}$ complex anions. Above about 400 K, $T_{1Q} = T_{2Q}$ was found. T_{1Q} showed a sharp minimum at 81 K and discontinuously increased with decreasing temperature through 38 K.
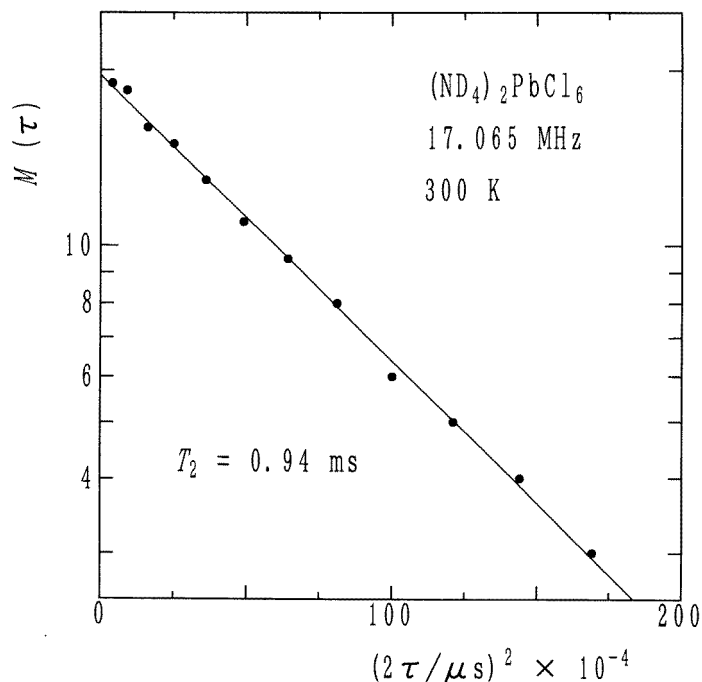
Figure 3. A Gaussian decay of the echo height $M(\tau)$ as a function of spacing time τ observed at 300 K.

On cooling through 81 K, T_{2Q} became gradually longer from a constant value of about 0.9 ms to another constant value of about 1.8 ms. On further cooling, T_{2Q} started to decrease again and a minimum was observed at about 10^3 K$/T = 30$ in T_{2Q} versus $1/T$ plots. T_{2Q} showed no appreciable anomaly at 38 K where discontinuity was observed in the temperature dependences of frequency and spin–lattice relaxation time.

The three resonance lines which were obtained below 38 K, showed almost the same values of T_{1Q} and T_{2Q} within experimental error, although T_{1Q} of the low-frequency line was observed to be slightly longer compared with those of the other two lines. This is the same tendency as observed for $(ND_4)_2PtCl_6$ [12].

4. Discussion

From heat capacity measurements, it is known that $(ND_4)_2PbCl_6$ undergoes a lambda phase transition at 80.7 K and another first-order phase transition at 38.4 K [11]. Anomalies observed in the temperature dependences of the ^{35}Cl NQR frequency and spin–lattice relaxation time can be attributed to these phase transitions. The NQR results do show that the 38 and 81 K phase transitions are at first and second order, respectively.

The 81 K transition corresponds to the phase transition of $(NH_4)_2PbCl_6$ at 78 K [11], which is associated with rotation of the complex anion about its threefold axis resulting in trigonal symmetry of crystal lattice [8]. As shown in figure 5, approaching $T_c = 81$ K from above and from below, the relaxation rate T_{1Q}^{-1} diverges according to a power law

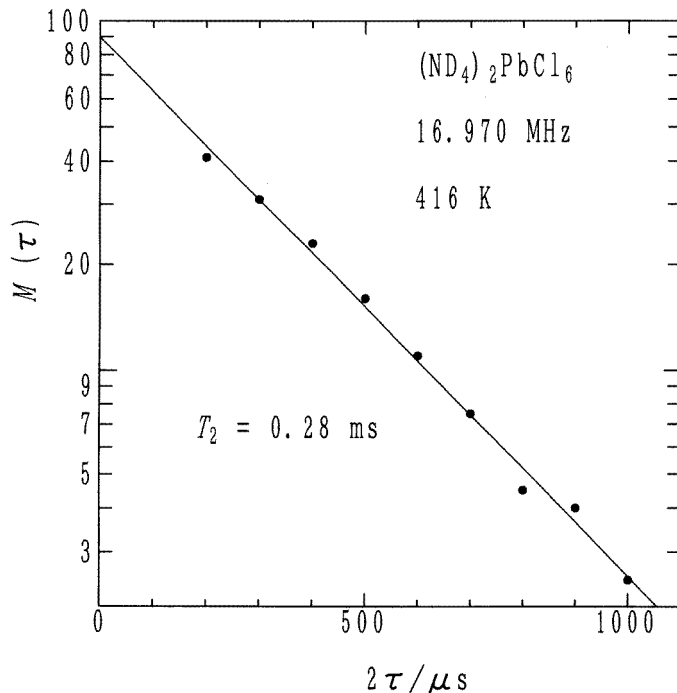$$T_{1Q}^{-1} = AT/|T - T_c|^{1/2} \tag{3}$$

Figure 4. A Lorentzian decay of the echo height $M(\tau)$ as a function of spacing time τ observed at 416 K.

which is expected for a direct spin-phonon process in the presence of an overdamped soft mode [14]. The coupling constant A was deduced as $A = 0.66$ s^{-1} K$^{-1/2}$ and $A = 0.75$ s^{-1} K$^{-1/2}$ for the temperature region above T_c and below T_c, respectively.

The 38 K transition is characteristic of (ND$_4$)$_2$PbCl$_6$, which can be thought of as induced by deuteration. The deuteration-induced phase transition in the system (ND$_4$)$_{2(1-x)}$(NH$_4$)$_{2x}$MCl$_6$ is expected to be strongly connected with the tunnelling rotation of the ammonium ion among the three orientations around the crystallographic threefold axis [1] and may be treated by use of the Ising model with a transverse field [15]. Three NQR frequencies (17.99, 17.86 and 16.35 MHz at about 15 K) were observed below 38 K, suggesting orthorhombic symmetry in the deuteration-induced low-temperature phase. Recently, a Raman scattering study also predicted a monoclinic or orthorhombic structure for the low-temperature phase [16]. The averaged value of these NQR frequencies almost coincides with the frequency extrapolated from that (17.348 MHz at 39 K) above 38 K. This result is very similar to that obtained for (ND$_4$)$_2$PtCl$_6$, which shows a similar phase transition induced by deuteration at 27.5 K [12]. According to the discussions of Armstrong and co-workers [2–7] on the relationship between the temperature dependence of the halogen NQR frequency and the structure of A$_2$MX$_6$ complex salts, when the centre of mass of the NQR frequencies is conserved, the order parameter should be of E$_g$ symmetry and it is expected that the quasi-tetragonal distortion of the lattice is not associated with static rotation of the complex anions in ferrodistortive phase transitions. The magnitude of the frequency splitting can be assumed to be proportional to the quasi-tetragonal distortion of the crystal lattice [6,7]. The splitting (about 1.6 MHz) of the present complex is quite large compared
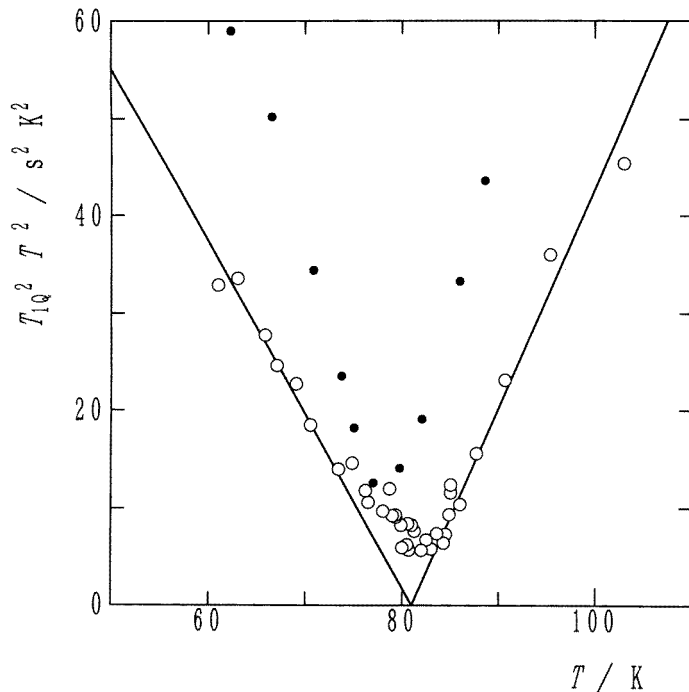
Figure 5. Temperature dependence of $T_{1Q}^2 T^2$ for ^{35}Cl NQR in $(ND_4)_2PbCl_6$ ($\bigcirc$) and $(NH_4)_2PbCl_6$ ($\bullet$). The straight lines correspond to the fit to the critical behaviour $T_{1Q}^{-1} = AT/|T - T_c|^{1/2}$. The data for $(NH_4)_2PbCl_6$ were taken from the work of Seo *et al* (1986).

with that (about 0.45 MHz) of $(ND_4)_2PtCl_6$. This indicates a large distortion of the crystal lattice in the low-temperature phase of $(ND_4)_2PbCl_6$.

Even when the symmetry of order parameter is E_g and the phase transition is of first order, in the vicinity of the transition point the enhancement of the relaxation rate T_{1Q}^{-1} was observed for $(NH_4)_2PtBr_6$ and Rb_2PtI_6 [6,7]. However, T_{1Q}^{-1} for $(ND_4)_2PbCl_6$ shows no appreciable enhancement at 38 K, probably reflecting a strong first-order nature.

^{35}Cl T_{2Q} for $(ND_4)_2PbCl_6$ could be determined by assuming a Gaussian decay of the echo height, except for the high-temperature region. On the other hand, we have previously observed a Lorentzian decay for ^{35}Cl in a normal ammonium salt NH_4AuCl_4 in the whole temperature range studied (14–332 K) [17].

This difference may be explained as follows. In the normal ammonium salt, the fluctuating H–Cl dipole couplings dominate the phase memory time T_{2Q} of ^{35}Cl, while Cl–Cl and Pb–Cl dipole interactions within and/or between complex anions are expected to be dominant in the deuterated ammonium salt. Since ammonium ions are performing a fast reorientational motion in the crystal, the local magnetic field produced at the chlorine atom by the surrounding ammonium ions is motionally averaged out. Therefore, when the H–Cl dipole interactions are important, we may have a Lorentzian decay of echo height. Motion of a complex anion is usually very slow except in the high-temperature region. Therefore, Cl–Cl and Pb–Cl dipole interactions are not motionally averaged out, leading to a Gaussian decay. At high temperatures, complex anions reorient so rapidly that the $T_{2Q} = T_{1Q}$ relation holds. Owing to the motionally averaged Cl–Cl and Pb–Cl dipole interactions, a Lorentzian decay is expected, as indeed is observed above 412 K.

The long T_{2Q}-values obtained in the intermediate-temperature phase means a decrease in the dipole couplings with the surrounding nuclei and suggest that, with decreasing temperature, a structural change from cubic to trigonal [8] occurs so as to decrease the inter-ionic Cl–Cl overlap interactions.

T_{2Q} decreases again with decreasing temperature for 10^3 K$/T$ > 23, showing a minimum at about 10^3 K$/T$ = 30. This may be connected with the slowing down of the ND$_4^+$ ions. When the correlation time of the motion is prolonged, the spectral density at the zero angular frequency increases. Therefore, the contribution from the fluctuating electric field gradient produced by the motion dominates the spin–spin relaxation. The reason why T_{2Q} shows a minimum is not clear.

5. Conclusion

(i) The phase transitions of (ND$_4$)$_2$PbCl$_6$ at 38 K and 81 K previously reported using heat capacity measurements are confirmed to be of first and second order, respectively, using ^{35}Cl NQR measurements.

(ii) At 81 K, the spin–lattice relaxation rate T_{1Q}^{-1} diverges according to the power law

$$T_{1Q}^{-1} = AT/|T - T_c|^{1/2}$$

which is expected for a direct spin-phonon process in the presence of an overdamped soft mode.

(iii) Transforming from the high-temperature cubic phase to the intermediate phase, inter-ionic Cl–Cl distances are suggested to be increased.

(iv) In the deuteration-induced low-temperature phase, the NQR frequency splits into three components, conserving the centre of mass of the frequency.

(v) The large frequency splitting of 1.6 MHz indicates a large distortion of the crystal lattice compared with (ND$_4$)$_2$PtCl$_6$, which shows a similar phase transition induced by deuteration at 27.5 K.

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