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A Raman scattering study of the isotope effect in $(\text{NH}_4)_2\text{PbCl}_6$

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Abstract. Raman spectra of $(\text{NH}_4)_2\text{PbCl}_6$ and $(\text{ND}_4)_2\text{PbCl}_6$ crystals have been recorded in the temperature range 5 K–300 K. $(\text{NH}_4)_2\text{PbCl}_6$ undergoes only one structural phase transition at $T_{c1} = 78$ K from a cubic (O_h^3) to a trigonal structure (C_{3i}^2), whereas $(\text{ND}_4)_2\text{PbCl}_6$ undergoes structural phase transitions from a cubic (O_h^3) to a trigonal structure (C_{3i}^2) at $T_{c1} = 79$ K, and to a monoclinic or orthorhombic structure at $T_{c2} = 34$ K. Continuous changes of the Raman-active modes at T_{c1} in both compounds show that the structural transition from cubic to trigonal is one of second order and results from distortions with symmetry related to the T_{1g} irreducible representation at the Γ point. Discontinuous behaviours of the Raman modes at T_{c2} in $(\text{ND}_4)_2\text{PbCl}_6$ show that the second structural transition is one of first order.

1. Introduction

In the past, the ammonium hexachlorometallates, $(\text{NH}_4)_2\text{MCl}_6$, have attracted extensive research work that has been devoted to the study of the ammonium-ion dynamics. The ammonium-ion motion has been investigated in the tunnelling regime by means of inelastic scattering and nuclear magnetic resonance [1–5]. In these studies a very low potential barrier for ammonium rotation has been found to increase in the series $M^{4+} = \text{Pd}^{4+}, \text{Pt}^{4+}, \text{Sn}^{4+}, \text{Pb}^{4+}$ and Te^{4+} [6].

Recently, a so-called ‘deuterium-induced phase transition’ was observed for $(\text{ND}_4)_2\text{MCl}_6$ ($M = \text{Pd}, \text{Pt}, \text{Te}, \text{Se}$) at low temperatures [7–13]. In particular, $(\text{ND}_4)_2\text{TeCl}_6$ undergoes phase transitions at 88.0, 48.1, 46.8 and 31.9 K, whereas $(\text{NH}_4)_2\text{TeCl}_6$ shows only one transition at 86.7 K [14]. At room temperature, ammonium hexachloroplumbate, $(\text{NH}_4)_2\text{PbCl}_6$ (abbreviated as ACP), crystallizes in the same anti-fluorite-type structure as $(\text{NH}_4)_2\text{TeCl}_6$ [15]. And at 80 K, ACP undergoes the same ferrotorotative structural phase transition as $(\text{NH}_4)_2\text{TeCl}_6$ [16]. One may expect the lead compounds to show an analogous strong isotope effect, like the tellurium compounds. In this paper molecular motions in and phase transitions of natural and deuterated ACP have been investigated by measuring temperature dependences of Raman scattering spectra.

2. Experimental procedure and results

Single crystals of natural and deuterated ACP used in the measurement of the Raman scattering have been grown by the aqueous solution method. For the growth of $(\text{ND}_4)_2\text{PbCl}_6$ (abbreviated as DACP), a crystal solution containing deuterium was used. The Raman spectra were excited using radiation at 514.5 nm with power of 150 mW from a Spectra-Physics argon-ion laser and measured in back-scattering geometry using a Spex-14018 double monochromator in the temperature range 5 K–300 K. Low-temperature measurements were carried out using a cryostat cooled with liquid helium.

At room temperature, both ACP and DACP crystallize in the cubic symmetry O_h^5 ($Fm\bar{3}m$). And their Raman-active modes are internal A_{1g} , E_g and T_{2g} modes of the PbCl_6^{2-} octahedron; internal A_1 , E and $2T_2$ modes of the $\text{NH}_4^+/\text{ND}_4^+$ tetrahedron; and an external T_{2g} mode. The experimentally measured Raman shifts of these modes at three different temperatures are listed in table 1.

Table 1. The experimentally measured Raman shifts for $(\text{NH}_4)_2\text{PbCl}_6$ at 120 K and 10 K, and for $(\text{ND}_4)_2\text{PbCl}_6$ at 120 K, 50 K and 10 K. Superscripts a and b indicate the bending and stretching T_2 modes of the ammonium tetrahedron, respectively; superscript e indicates the external mode. The unit for the Raman shift is cm^{-1} .

	$(\text{NH}_4)_2\text{PbCl}_6$		$(\text{ND}_4)_2\text{PbCl}_6$		
	120 K	10 K	120 K	50 K	10 K
A_{1g}	301.1	302.3	298.2	298.6	295.7
E_g	220.0	219.6	222.6	222.4	222.1
T_{2g}	161.2	160.1 163.9	156.2	155.9 158.7	153.0, 163.0 166.7
A_1	3146.5	3146.1	2275.4	2275.4	2264.4
E	1668.2	1670.7	1191.4	1190.8	1186.2, 1191.3
T_2^a	1404.6	1400.7 1405.9	1074.7	1072.7 1075.9	1070.7, 1075.8 1086.0
T_2^b		3224.9	2420.7	2416.4	2398.2, 2413.2
T_{2g}^e	123.3	114.1 125.5		110.7	110.6, 118.7 130.8
Lattice mode		33.6			26.0, 32.3, 36.9 42.8, 67.6

It is seen from table 1 that the three degenerate modes T_{2g} , T_2^a and T_{2g}^e split into two lines for ACP and three lines for DACP at 10 K. The temperature dependences of the Raman shift of the internal T_{2g} mode of the PbCl_6^{2-} octahedron in the range of 5 K–150 K for both ACP and DACP are shown in figure 1. Both T_{2g} modes continuously split into two lines below liquid nitrogen temperature. From room temperature to about 60 K there is only one Raman line for each mode, and at about 60 K two-Raman lines were first observed. With temperature further decreasing, the two-Raman-lines pattern becomes clearer and clearer with a monotonic increase of the magnitude of the splitting. This continuous splitting of

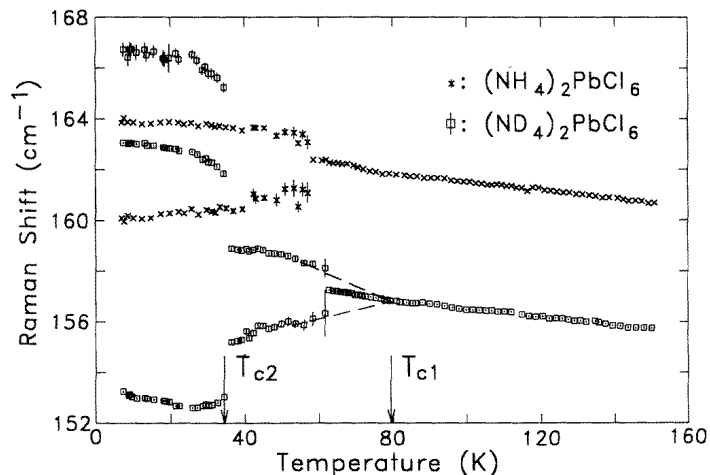


Figure 1. The temperature dependence of the Raman shift of the internal T_{2g} mode of the PbCl_6^{2-} octahedron for ACP and DACP. The Raman shift was fitted using a program; the height of the vertical line at each datum point represents double the fitting error.

the T_{2g} mode for both ACP and DACP indicates a structural phase transition occurring, and the transition temperature T_{c1} can be approximately evaluated by extrapolating the splitting in the opposite direction; see the dashed lines in figure 1. For ACP the two-lines pattern remains invariant as the temperature decreases to 5 K. For DACP the two lines split further into three lines, abruptly, at a temperature of about 34 K, which indicates another structural phase transition.

The internal A_{1g} mode of the PbCl_6^{2-} octahedron also shows features of phase transitions at low temperature. Figure 2 shows the temperature dependences of the Raman shift of this mode in the range 5 K–280 K for ACP and DACP. For both compounds the single-line pattern of the A_{1g} mode is conserved from ambient temperature to 5 K. For ACP the Raman shift has only one maximum at 78 K, which is 2 K lower than the result obtained by NQR and NMR methods [16]. For DACP the Raman shift has an abrupt change at 34 K besides a maximum at 79 K. The phase transition temperatures T_{c1} and T_{c2} correspond to the maximum and the abrupt change of the Raman shift, respectively.

The internal modes of the $\text{NH}_4^+/\text{ND}_4^+$ tetrahedra in ACP/DACP exhibit almost the same temperature dependences as the internal modes of the PbCl_6^{2-} octahedron, except two particular behaviours of the ND_4^+ tetrahedron. One is that there are two lines corresponding to the internal E mode of the ND_4^+ ion at 10 K, and the other is that there is a small range of about 2 K around T_{c2} in which the original and shifted line for the internal A_1 mode of the ND_4^+ ion coexist.

Besides the abnormal phenomena of the internal modes of the PbCl_6^{2-} octahedra and ammonium tetrahedra around the phase transition temperatures, soft modes were observed in ACP and DACP at low temperature. Figure 3 exhibits the temperature dependence of the squared Raman shift of the soft mode in ACP. As the line width of the Rayleigh scattering peak becomes larger and larger with increase of temperature, in the range 63 K to T_{c1} , the soft mode has already shifted into the Rayleigh peak and becomes impossible to observe. The dashed line in figure 3 represents the possible variational trend of the squared shift and indicates that the squared shift goes linearly to zero at about T_{c1} as the temperature

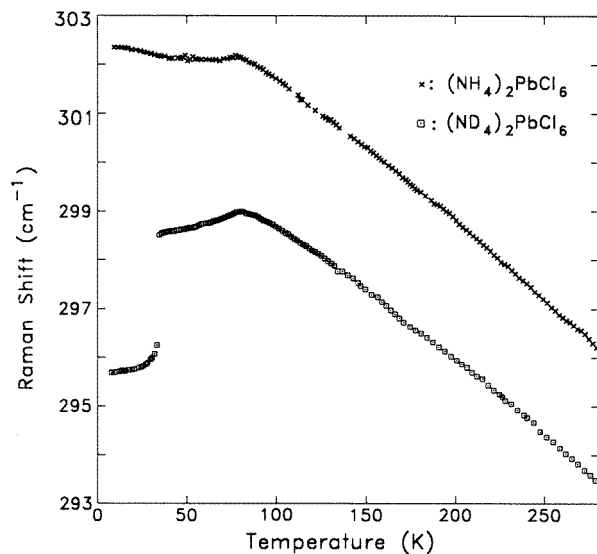


Figure 2. The temperature dependence of the Raman shift of the internal A_{1g} mode of the $PbCl_6^{2-}$ octahedron for ACP and DACP. The Raman shift was fitted using a program; the fitting error is about 0.01 cm^{-1} over the total temperature range.

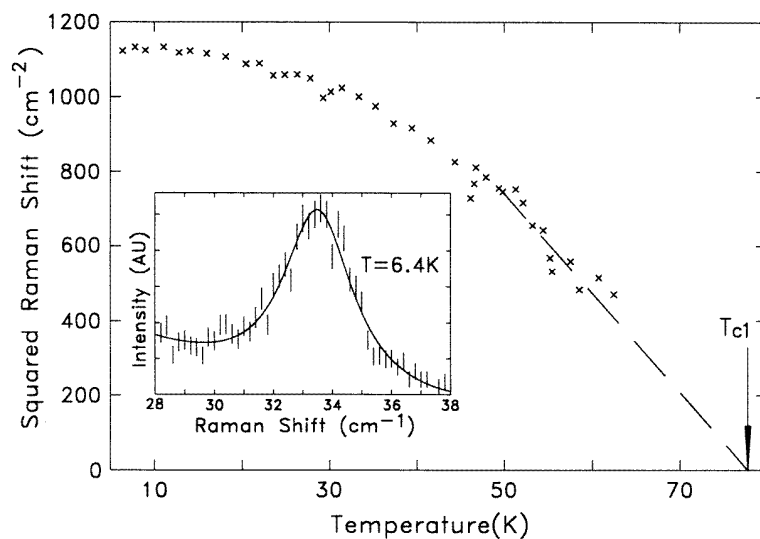


Figure 3. The temperature dependence of the squared Raman shift of the soft mode in ACP. The inset shows the Raman spectrum of this mode at $T = 6.4 \text{ K}$.

approaches T_{c1} from below. For DACP five lattice modes were observed at 10 K (table 1). Two modes with low energy undergo partial softening as the temperature increases from 5 K to T_{c2} , and disappear above T_{c2} .

3. Discussion

3.1. $(NH_4)_2PbCl_6$

The T_{2g} mode of the $PbCl_6^{2-}$ octahedron, the T_2 bending mode of the NH_4^+ tetrahedron, and the external T_{2g} mode continuously split into two lines below T_{c1} (figure 1 and table 1). The A_{1g} mode of the octahedron exhibits a continuous maximum in the value of Raman shift at $T_{c1} = 78$ K (figure 2). These behaviours of the Raman vibrational modes show that a structural phase transition takes place at $T_{c1} = 78$ K and the transition is of second order. The phase transition temperature $T_{c1} = 78$ K is 2 K lower than the result obtained by NQR and NMR methods, which may be due to the high laser power impinging on the sample. The single-line pattern of the A_{1g} mode and the A_1 mode over the total experimental temperature range indicates that there is no multifold effect of the unit cell at T_{c1} , and the transition is due to structural distortion at the Γ point. Two-line patterns of the internal T_{2g} mode, the internal T_2 bending mode, and the external T_{2g} mode at low temperature indicate that the crystal symmetry in the low-temperature phase is lower than that in the high-temperature phase. From 60 K to 5 K, the line pattern of the Raman spectra remains invariant, so ACP has the same structure over the temperature range 5 K– T_{c1} .

The observation of the soft mode in the low-temperature phase (figure 3) provides further evidence for the second-order structural phase transition at T_{c1} . Lattice soft modes have been observed via the phase transition from O_h^5 to C_{3i}^2 structure in $(NH_4)_2TeCl_6$ and $(ND_4)_2TeCl_6$ compounds [7]. According to the results of a neutron diffraction study, the space group of ACP in the low-temperature phase is C_{3i}^2 ($R\bar{3}$). Considering possible subgroups of O_h^5 that result from distortions with symmetries related to one of the irreducible representations at the Γ point [17], it is clear that for the subgroup C_{3i}^2 the soft mode corresponds to the T_{1g} rotative mode of the $PbCl_6^{2-}$ octahedron.

3.2. $(ND_4)_2PbCl_6$

From ambient temperature to 40 K, the internal modes of the octahedron and the ND_4^+ tetrahedron in DACP have almost the same temperature dependences as those in ACP. The only difference is that the structural transition temperature in DACP is shifted to 79 K. This points towards a second-order structural phase transition from space group O_h^5 ($Fm\bar{3}m$) to C_{3i}^2 ($R\bar{3}$) taking place for DACP at $T_{c1} = 79$ K. Microscopically, the transition from O_h^5 to C_{3i}^2 would involve an in-phase rotation of the $PbCl_6^{2-}$ octahedra about their threefold axis. The phase transitions for the other A_2MX_6 compounds are generally induced by a rotation about one of the fourfold axes. The different behaviour observed for ACP/DACP may arise from the steric links between the octahedra which are provided by NH_4^+/ND_4^+ tetrahedra.

At $T_{c2} = 34$ K, the A_{1g} mode of the octahedron and the A_1 mode of the ND_4^+ tetrahedron suddenly change by several wavenumbers in the Raman shift (figure 2), and the T_{2g} mode of the octahedron discontinuously splits from two lines into three lines (figure 1). The discontinuous points of the Raman shifts of the A_{1g} and T_{2g} modes are observed at the same temperature, within the accuracy of the present measurement. These discontinuous behaviours of the Raman-active modes show a first-order structural phase transition at $T_{c2} = 34$ K. For the A_1 mode of the ND_4^+ tetrahedron, two lines coexist in a small temperature range of about 2 K around T_{c2} . This may be due to there being a temperature gradient in the sample because of a high laser power.

The single-line patterns of the A_{1g} mode and the A_1 mode below T_{c2} indicate that the transition at T_{c2} is also due to a structural change at the Γ point. The three-line pattern

of the T_{2g} , T_2^a and T_{2g}^e modes and the two-line pattern of the E mode at 10 K indicate an orthorhombic or monoclinic symmetry in the phase below T_{c2} . The transition at T_{c2} would involve a sudden rotation of the PbCl_6^{2-} octahedra about one of the twofold axes. The structure of DACP in the low-temperature phase needs further study.

4. Conclusions

(1) DACP and ACP undergo the same type of second-order structural phase transition respectively at 79 K and 78 K from O_h^5 ($Fm\bar{3}m$) to C_{3i}^2 ($R\bar{3}$). The transition results from structural distortions with symmetry related to the T_{1g} irreducible representation at the Γ point.

(2) DACP undergoes further a first-order structural phase transition at 34 K from C_{3i}^2 to a monoclinic or orthorhombic symmetry.

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