

NQR-NMR and Raman Study of a Structural Phase Transition in $(\text{NH}_4)_2\text{PbCl}_6$

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The temperature dependence of the chlorine NQR frequency and spin-lattice relaxation rate indicate a structural phase transformation in $(\text{NH}_4)_2\text{PbCl}_6$ at 80 K similar to that observed in $(\text{NH}_4)_2\text{TeCl}_6$ at 85 K. Both transitions are characterized by a discontinuity of the temperature derivative of the NQR frequency shift and by a cusp in the NQR spin-lattice relaxation rate, but no splitting of the NQR line is observed below T_c . These observations point towards a transition that leaves the chlorine sites equivalent, such as a small angle rotation of the MX_6^{2-} -octahedra about their threefold axis. Supplementary ^1H -NMR measurements have been performed to investigate the direct influence of NH_4^+ motion on the Cl-NQR. The phase transitions in mixed $(\text{NH}_4:\text{K})_2\text{PbCl}_6$ crystals have also been studied.

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Introduction

In the past, the ammonium-hexachlorometallates, $(\text{NH}_4)_2\text{MX}_6$, have attracted extensive research work that has been devoted to the study of the ammonium ion dynamics. The barriers to rotation of the ammonium ions in these compounds amount to a few hundred K, giving rise to tunneling splitting at low temperatures and classical hindered rotation behaviour near room temperature. The ammonium ion motion has been thoroughly investigated particularly in the tunneling regime using inelastic neutron scattering [1, 2] and proton magnetic resonance [3, 5]. The barrier height to rotation of NH_4^+ in $(\text{NH}_4)_2\text{MCl}_6$ has been found to increase in the series $\text{M}^{4+} = \text{Pd}^{4+}$, Pt^{4+} , Sn^{4+} , Pb^{4+} and Te^{4+} [6].

So far it has been assumed that the $(\text{NH}_4)_2\text{MCl}_6$ crystals remain face centered cubic (space group O_h^5) down to temperatures as low as 4.2 K. However, we find evidence for structural transformations in at least three ammonium-hexachlorometallate compounds, $(\text{NH}_4)_2\text{TeCl}_6$, $(\text{ND}_4)_2\text{TeCl}_6$ and $(\text{NH}_4)_2\text{PbCl}_6$, where the transitions drive the systems most probably to a trigonal phase. Preliminary results on $(\text{NH}_4)_2\text{TeCl}_6$ and $(\text{ND}_4)_2\text{TeCl}_6$ have been published recently [7, 8].

The present study is concerned with a structural phase transition in $(\text{NH}_4)_2\text{PbCl}_6$ and further investigations of $(\text{NH}_4)_2\text{TeCl}_6$.

The structural transformations already observed in other A_2MX_6 compounds involve a small angle rotation of the MX_6^{2-} -octahedral complexes about their fourfold axis [9]. The transitions are classified as rotational displacive type with the rotation angle as primary order parameter. There are a few exceptions, e.g. $(\text{NH}_4)_2\text{PtBr}_6$, which have an order parameter of E_g symmetry [10, 11]. The rotational displacive transitions are driven by longitudinal librational soft modes which condensate at the zone center or at the X-point of the zone boundary [12–15]. Considering only the two relevant soft modes $T_{1g}(I)$ and $A_{2g}(X)$, the structures which can be reached in the context of a Landau theory analysis are collected in Table 1. Transitions in the first column involve ferro-distortive rotations of MX_6^{2-} -octahedra in adjacent planes, those in the second column are of antiferro-distortive type giving rise to a doubling of the unit cell. A_1 , A_2 and A_3 are the components of the local order parameter and represent the amplitudes of the rotations about the fourfold axis of the MX_6^{2-} -octahedra [16, 17]. Some of the examples specified in Table 1 undergo several successive transitions. The space group refers to the phase reached from the high temperature cubic structure by the first transition. A transition which involves a ferro-distortive rotation about the threefold axis leading to the trigonal space group C_{3i}^2 has been observed for

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Table 1. Space groups induced in fcc- A_2MX_6 (space group $\text{O}_h^5/\text{Fm } 3\text{m}$) by a ferrodistorstive or antiferrodistorstive rotation of the MX_6^{2-} octahedra. The A_i describe the amplitudes of the local order parameter. Examples refer to the structure of the phase below the first transition. The transitions to the space groups listed in the two lowest lines are of second order (after [16] and [17]). The table does not include the possible space groups induced by the E_g -mode at the X-point.

Order parameter: $Q = A_1 Q_x + A_2 Q_y + A_3 Q_z$.

Coefficients	Ferro-distorstive (T_{1g} , I -Point)	Antiferro-distorstive (A_{2g} , X-point)
$A_1 \neq A_2 \neq A_3 \neq 0$	$\text{C}_i^1 (\text{P } 1)$	$\text{D}_{2h}^2 (\text{Pnnn})$:
$A_1 \neq A_2 \neq 0 = A_3$		K_2SnCl_6 [13]
$A_1 = A_2 \neq 0 = A_3$	$\text{C}_{2h}^3 (\text{B } 2/\text{m})$	$\text{D}_{4h}^{12} (\text{P } 4_2/\text{nnm})$
$A_1 = A_2 = 0 \neq A_3$	$\text{C}_{4h}^5 (\text{I } 4/\text{m})$:	$\text{D}_{4h}^6 (\text{P } 4/\text{mnc})$:
	K_2ReCl_6 [12] K_2OsCl_6 [14]	$(\text{NH}_4)_2\text{SnBr}_6$ [15]
$A_1 = A_2 = A_3 \neq 0$	$\text{C}_{3i}^2 (\text{R } 3)$:	$\text{T}_h^2 (\text{Pn } 3)$
	$(\text{NH}_4)_2\text{TeCl}_6$ * $(\text{NH}_4)_2\text{PbCl}_6$ *	

* This work.

the first time in $(\text{NH}_4)_2\text{TeCl}_6$ [7]. As shown in this work, $(\text{NH}_4)_2\text{PbCl}_6$ behaves similarly. A particular feature of this type of transition is the conservation of the single line pattern in the NQR spectrum below T_c . On the basis of a group theoretical analysis, Sutton and Armstrong have shown that among the various subgroups of O_h^5 only a limited number of the ordered phases which can be reached by a rotational distortive transition have all chlorine atoms on equivalent sites [18]. This fact provides the unique advantage that the number of possible space groups for the low temperature phase can be considerably reduced on the basis of the NQR measurements, facilitating the identification by results of Raman and X-ray scattering experiments. In order to rule out a direct influence of proton tunneling or NH_4^+ hindered rotation on the Cl-NQR experiment inducing anomalies in the temperature behaviour of NQR frequencies ν_Q and spin-lattice relaxation rates T_1^{-1} [19], the ^1H -NMR from the ammonium ions has been investigated.

Experimental

Polycrystalline samples of $(\text{NH}_4)_2\text{PbCl}_6$ and $(\text{NH}_4)_2\text{TeCl}_6$ were prepared by precipitation in aque-

ous solution. Mixed crystals of $((\text{NH}_4)_{1-x}\text{K}_x)_2\text{PbCl}_6$ with $x = 0.1$ and $x = 0.2$ have been obtained by the same procedure, starting with the appropriate quantities of the constituents. Single crystals of a size between 1 mm^3 and 5 mm^3 could be grown from aqueous solution of the tellurium salt only.

The $^{35,37}\text{Cl}$ -NQR and ^1H -NMR measurements were carried out using a pulse spectrometer (Bruker SXP-100). The temperature of the sample was stabilized to better than 0.1 K in the range of 4.2 to 300 K , using an Oxford CF-200 flow cryostat. The proton-NMR relaxation rate and the Raman and Brillouin spectra have been investigated on the same samples and in the same temperature range. Details of the inelastic light scattering experiments will be published elsewhere. Here we report on a few selected results only.

Experimental Results

a) Chlorine NQR-Measurements

The temperature variation and isotope dependence of the Cl-NQR frequency ν_Q and the spin-lattice relaxation rate T_1^{-1} for $(\text{NH}_4)_2\text{PbCl}_6$ are shown in Figure 1. For comparison, the corresponding results for $(\text{NH}_4)_2\text{TeCl}_6$ are given in Figure 2. In each compound, both the frequency and the relaxation rate display a distinct anomaly at the same temperature, which has been identified as the phase transition temperature T_c . At T_c , the NQR frequencies $\nu_Q(T)$ vary continuously, whereas their temperature derivatives show a discontinuity. In the vicinity of T_c the spin-lattice relaxation rates strongly increase, forming a cusp at T_c . In the lower parts of Fig. 1 and Fig. 2 these results are shown in the T_1^{-1} versus $(1/T)$ representation. The transition temperatures deduced from the singularities in the $\nu_Q(T)$ and $T_1^{-1}(1/T)$ are: $T_c = 80(1)\text{ K}$ and $T_c = 85(1)\text{ K}$ for the Pb and Te compounds, respectively.

In both crystals the NQR frequencies decrease approximately linearly above T_c , having a temperature coefficient at constant pressure of -0.82 kHz/K in $(\text{NH}_4)_2\text{PbCl}_6$ and -0.45 kHz/K in $(\text{NH}_4)_2\text{TeCl}_6$.

At T_c these coefficients increase abruptly by nearly an order of magnitude (3.0 kHz/K in both compounds) and then again get monotonously smaller with further decreasing temperature.

The spin-lattice relaxation rate T_1^{-1} exhibits a common temperature but far above or below the transi-

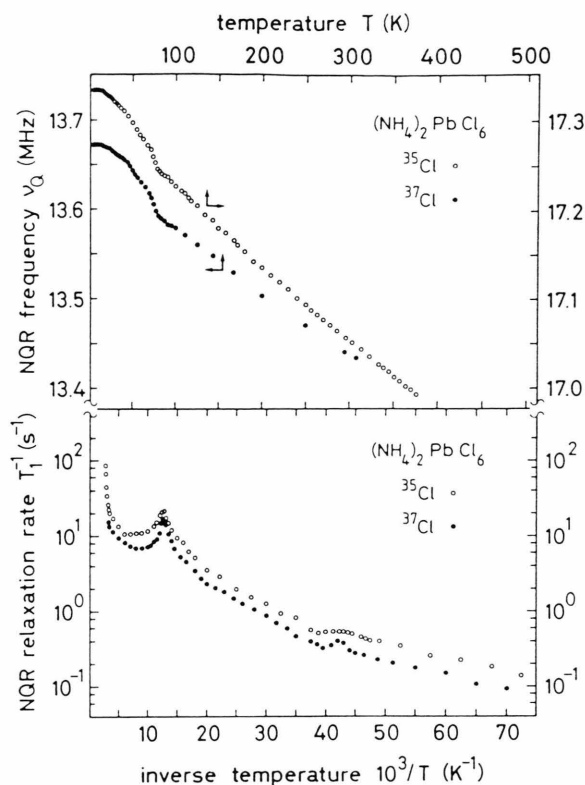


Fig. 1. Temperature and isotope dependence of the chlorine-NQR in $(\text{NH}_4)_2\text{PbCl}_6$. *Upper part*: NQR frequencies of ^{35}Cl (open circles) and of ^{37}Cl (full circles) vs. temperature. *Lower part*: NQR spin-lattice relaxation rates of ^{35}Cl (open circles) and of ^{37}Cl (full circles) vs. inverse temperature. The T -abscissa and the $1/T$ -abscissa are fixed in such a way that at the transition temperatures the abscissas coincide.

tion region. Above room temperature, T_1^{-1} is governed in both salts by hindered rotations of the MCl_6^{2-} octahedra, providing an isotope independent relaxation mechanism [20, 21]. The isotope effects have been probed experimentally only in the case of $(\text{NH}_4)_2\text{PbCl}_6$ (Figure 1). At lower temperatures, except in the transition region, the isotope ratio $R = T_1^{-1}(^{35}\text{Cl})/T_1^{-1}(^{37}\text{Cl})$ is about 1.6. The magnitude as well as the analytical temperature dependence are both in accordance with relaxation processes due to non-resonant phonon interactions. At T_c the isotope ratio has decreased by about 20 per cent. The isotope dependence of the NQR frequencies in $(\text{NH}_4)_2\text{PbCl}_6$ at different temperatures does not display any unexpected behaviour that within the experimental uncertainty would deviate from the normal ratio given by the quadrupole moments.

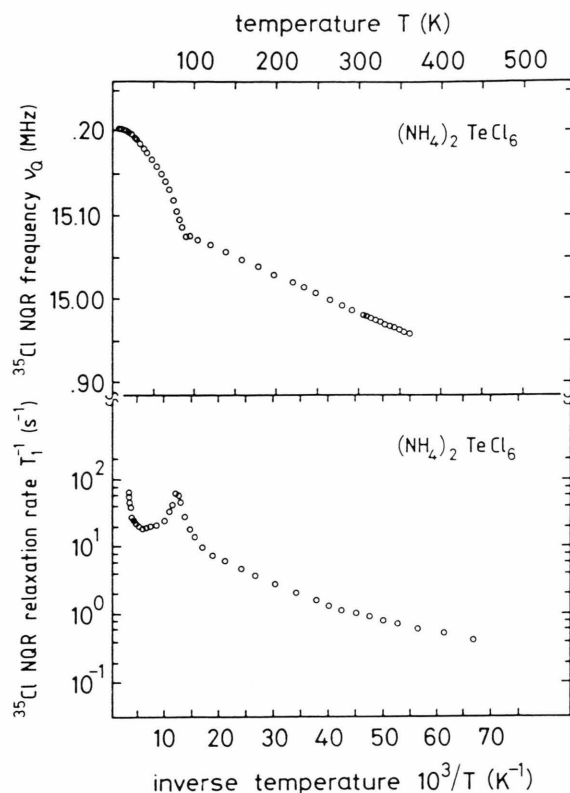


Fig. 2. Temperature dependence of the ^{35}Cl -NQR in $(\text{NH}_4)_2\text{TeCl}_6$. *Upper part*: NQR frequency vs. temperature. *Lower part*: NQR spin-lattice relaxation rate vs. inverse temperature.

Mixed crystals of $((\text{NH}_4)_{1-x}\text{K}_x)_2\text{PbCl}_6$ had already been prepared in connection with a study of the phase transition in K_2PbCl_6 , of which the results have been published recently [19]. For this reason we have also chosen the plumbate compound to inspect the effect of substitution of potassium for ammonium. Figure 3 shows the NQR results obtained from a mixed crystal containing 10 mol% K^+ . In the doped sample the discontinuity occurring in the frequency behaviour and the cusp in the spin lattice relaxation rate are shifted both by about 5 K to higher temperatures. Satellite lines are also observed at frequencies lower than that of the main cubic line. The intensities of these extra lines are rather small and their behaviour has been pursued only in a limited temperature range around 300 K.

The estimated concentration dependence of the transition temperature is considerably smaller at the

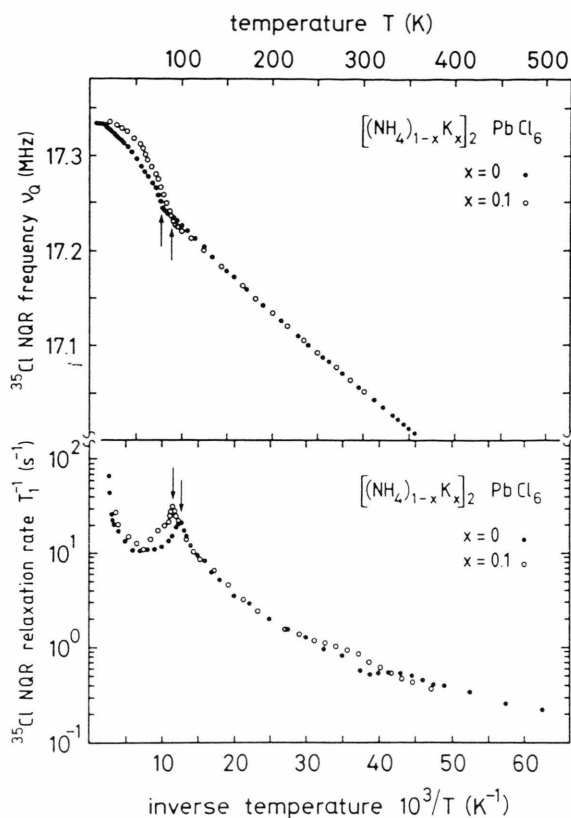


Fig. 3. Effect of substitution of K^+ for NH_4^+ on the ^{35}Cl -NQR in $(\text{NH}_4)_{1-x}\text{K}_x)_2\text{PbCl}_6$. Results are shown for $x = 0.1$ (open circles) and $x = 0$ (full circles). Temperature dependences of the NQR frequency and the NQR spin-lattice relaxation rate are displaced in the upper and lower part, respectively.

ammonium rich side ($dT_c/dx \cong +50 \text{ K/mol}$) than at the potassium rich side, where substitution of NH_4^+ for K^+ leads to an initial slope of $dT_c/dx = -273 \text{ K/mol}$ [21]. This asymmetry in the concentration dependence has already been observed in other solid solutions of A_2MX_6 compounds [22]. The microscopic origin of this concentration dependence remains still unexplained.

b) ^1H -NMR Measurements

The low barrier to rotation of the ammonium ion in $(\text{NH}_4)_2\text{MX}_6$ compounds admits at low temperatures for a quantum motion of the protons by tunneling. This tunneling process opens a further channel for relaxation. Therefore T_1^{-1} of the protons increases when the Larmor frequency is e.g. equal to the split-

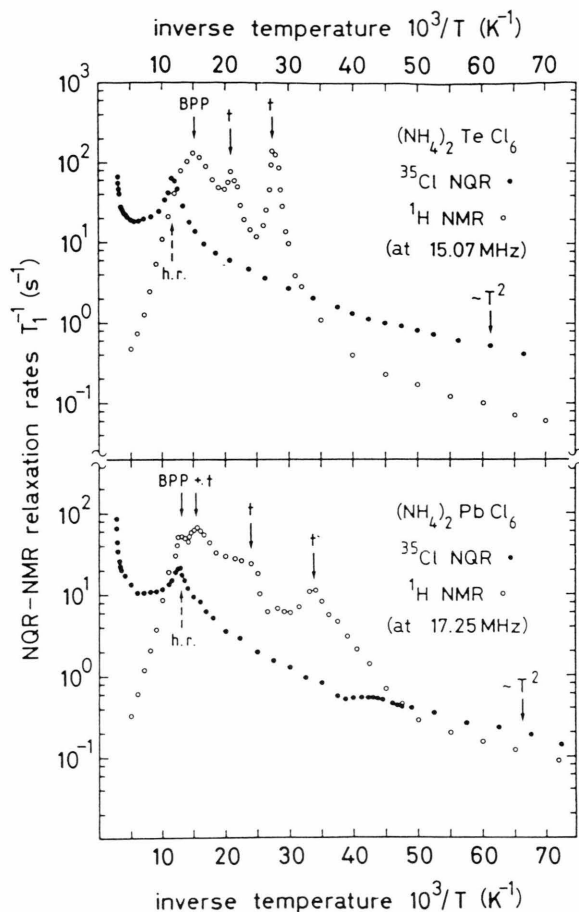


Fig. 4. Spin-lattice relaxation rates of the protons from ^1H NMR (open symbols) and T_1^{-1} of the ^{35}Cl -NQR (full symbols) measured in $(\text{NH}_4)_2\text{TeCl}_6$ (upper part) and $(\text{NH}_4)_2\text{PbCl}_6$ (lower part). The ^1H -NMR was tuned to the corresponding ^{35}Cl -NQR frequency, which is 15.07 MHz in the Te salt and 17.25 MHz in Pb salt, respectively.

ting of the tunneling levels with the appropriate symmetry [3–5]. This relaxation path can also be accessible to the chlorine nuclei via a cross relaxation mechanism producing a cusp in the $T_1^{-1}(1/T)$ behaviour in the $^{35,37}\text{Cl}$ -NQR measurement. The cross relaxation between ^1H and $^{35,37}\text{Cl}$ nuclei has already been detected by NMR-NQR in $(\text{NH}_4)_2\text{SnCl}_6$, where a maximum in $T_1^{-1}(\text{Cl-NQR})$ around 55 K has been observed [23].

We have investigated the proton spin lattice relaxation in $(\text{NH}_4)_2\text{PbCl}_6$ and $(\text{NH}_4)_2\text{TeCl}_6$ with the ^1H -NMR transition tuned to the ^{35}Cl -NQR splitting in the critical region. Figure 4 displays the temperature variation of the proton spin lattice relaxation

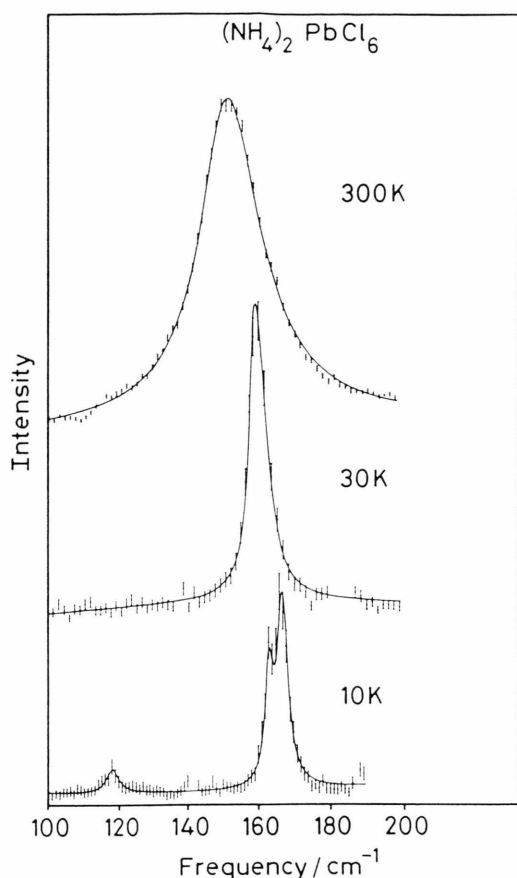


Fig. 5. T_{2g} -internal mode of the PbCl_6^{2-} -octahedron in $(\text{NH}_4)_2\text{PbCl}_6$ at three temperatures above and below the phase transition at $T_c = 80$ K (after [26]). The line at about 118 cm^{-1} corresponds to the external T_{2g} -vibration, that emerges from the background only at very low temperatures.

together with T_1^{-1} of the ^{35}Cl NQR for these compounds. The peaks (marked “t”) in the proton spin lattice relaxation rates are attributed to transitions between the tunneling states of the ammonium ion. The “classical” BPP maxima are also shown. Although the resonance frequencies are the same, there is no correlation between anomalies occurring in the proton NMR and chlorine NQR- T_1^{-1} relaxation rate patterns.

c) Brillouin and Raman Scattering

Raman scattering has been observed from the same powdered samples used in the NQR experiments. Brillouin scattering requires single crystals, which were available only for $(\text{NH}_4)_2\text{TeCl}_6$.

From the measured Brillouin shift the temperature variation of the three cubic elastic constants of $(\text{NH}_4)_2\text{TeCl}_6$ has been determined [7, 8, 24]. A discontinuity observed at about 83 K is accounted for by the structural transition. Similar to the elastic behaviour observed in other A_2MX_6 compounds [25], in the high temperature cubic phase of $(\text{NH}_4)_2\text{TeCl}_6$ the shear elastic constant ($C_{11}-C_{12}$) softens when T_c is approached from above. Details of the Brillouin scattering results will be published elsewhere.

The most obvious features provided by the Raman spectra are the splitting of the $T_{2g}-\text{MCl}_6^{2-}$ internal mode observable at low temperatures in $(\text{NH}_4)_2\text{PbCl}_6$ (Fig. 5) and in $(\text{NH}_4)_2\text{TeCl}_6$ [8, 27]. In both compounds and below T_c , new but very weak lines emerge from the background in the external mode region below 100 cm^{-1} . The total number of Raman lines in the low temperature phase of $(\text{NH}_4)_2\text{PbCl}_6$ as shown in Fig. 5 points towards a transition due to a Γ -point distortion.

Discussion

a) Symmetry Considerations

The most unique feature of the structural transformation observed in $(\text{NH}_4)_2\text{PbCl}_6$ and $(\text{NH}_4)_2\text{TeCl}_6$ relies on the absence of any line splitting in the NQR spectrum of the lower symmetry phase. Phase transitions that preserve the single line pattern of the Cl-NQR in A_2MX_6 compounds have been predicted on group theoretical grounds by Sutton and Armstrong [18]. Considering the distortion of the high temperature cubic structure (space group O_h^5) due to the condensation of a normal mode at the zone center or at the X, L, and W points of the Brillouin zone, the authors showed that only a few transitions would preserve a single line NQR pattern. According to their tables, Γ -point and L-point distortions which lead to the space groups D_{3d}^5 , C_{3i}^2 , D_3^7 and D_{3d}^6 are not associated with an NQR line splitting. The elaborated tables are incomplete as far as zone boundary distortions are concerned because the analysis has been restricted to the order parameter having the smallest number of components. For the case of the $\text{X}-\text{A}_{2g}$ representation space we have already published a complete set [16] which is incorporated in Table 1.

Two further experimental observations can be used to narrow the number of possible space groups. At first, the NQR frequency varies continuously at the

transition (Figs. 1 and 2) indicating a second order type transition. Secondly, the low temperature Raman spectra of $(\text{NH}_4)_2\text{PbCl}_6$ display a splitting into a doublet for the T_{2g} -internal mode of the MX_6^{2-} -octahedron, but no additional lines are discoverable, which would point towards a cell-doubling at the transition. Both these experimental observations are in favour of a T -point transition from O_h^5 to C_{3i}^2 as indicated in Table 1.

Microscopically, the transition from O_h^5 to C_{3i}^2 would involve an in-phase rotation of the MCl_6^{2-} -octahedra about their threefold axis. The phase transitions in the other A_2MX_6 compounds are generally induced by a rotation about one of the fourfold axes. The different behaviour observed in $(\text{NH}_4)_2\text{PbCl}_6$ and $(\text{NH}_4)_2\text{TeCl}_6$ may arise from the steric links between the octahedra which are provided by the tetrahedrally shaped NH_4^+ ions.

b) Temperature Dependence of the Cl-NQR

Generally, the occurrence of a rotational displacive phase transition becomes recognizable in the temperature behaviour of both the NQR frequency and relaxation rate already above and below T_c . On approaching the transition temperature from above, the NQR frequency and the relaxation time can decrease due to the influence of the soft librational mode. Below T_c the fluctuations of the soft mode components of the ordered phase may cause similar effects, but with increasing distance from T_c the frequency variation will be dominated by the developing expectation value of the order parameter. The soft mode effects on the NQR have to be discussed according to two temperature regimes: the critical regime, which is confined to the nearest vicinity of the transition, and the Landau or mean field regime, which extends a few tenth K above and below T_c .

The cusps displayed by the spin-lattice relaxation rates near T_c in $(\text{NH}_4)_2\text{PbCl}_6$ as well as in $(\text{NH}_4)_2\text{TeCl}_6$ are attributed to the order parameter fluctuations. A similar anomaly in NaNO_2 has been investigated experimentally and theoretically by Bonera et al. [28]. On the basis of their models Armstrong et al. have been able to analyse the temperature dependence of the spin-lattice relaxation rates in K_2OsCl_6 [29]. The temperature behaviour near T_c in $(\text{NH}_4)_2\text{PbCl}_6$ and $(\text{NH}_4)_2\text{TeCl}_6$ deviates from that found in K_2OsCl_6 . In the whole range only a single exponential recovery of

the nuclear magnetization is observed, but the isotope ratio R varies from a value of 1.2 at T_c to a value of about 1.6 at temperatures $T < T_c - 5$ K and $T > T_c + 5$ K. The decrease of R to a value near unity in the neighborhood of T_c points toward an additional relaxation mechanism through very infrequent jumps of the MX_6^{2-} -octahedra [20, 21] occurring in the critical region.

The renormalization effects of the soft mode on the NQR frequency in the mean field regime (which is 10–50 K above T_c in other A_2MX_6 systems) seem to be rather small in both ammonium compounds. In the whole temperature range above T_c , $\nu_Q(T)$ varies essentially linearly with the temperature, as one would expect from a normal Bayer-Kushida behaviour, in contrast e.g. to the marked softening of the NQR frequency in K_2ReCl_6 [30]. It seems to be a reasonable assumption that for both ammonium compounds the soft mode contributions are also negligible in the ordered phase below T_c and that consequently the measured increase of the NQR frequency is correlated with the increasing amplitude of the order parameter $\Delta\Phi$, which would be an in-phase rotation of the octahedra about their threefold axis in the case of C_{3i}^2 .

The extra contribution $\Delta\nu_Q$ due to the developing order parameter amplitude has been determined by subtracting the background frequency ν_Q^C from the measured frequency (Fig. 6), where ν_Q^C is defined as the NQR frequency of the cubic phase extrapolated to temperatures below T_c , adopting a one mode Bayer-Kushida mechanism:

$$\nu_Q^C(T) = \nu_0^C - \nu_0^C \coth\left(\frac{h\omega_R}{2kT}\right). \quad (1)$$

Estimates of the rotational mode frequency, which is the most effective vibrational mode in the motional averaging process, have been deduced from Raman scattering results [26, 27]: $h\omega_R$ is approximately 45 cm^{-1} and 50 cm^{-1} in $(\text{NH}_4)_2\text{PbCl}_6$ and $(\text{NH}_4)_2\text{TeCl}_6$, respectively. Inserting this value into (1), and making use of the measured linear high temperature coefficients of the NQR frequency, which are -0.82 kHz/K in the lead compound and -0.45 kHz/K in the tellurium compound, the parameters $\Delta\nu_Q^C$ and ν_0^C could be determined. In Fig. 6 (dashed line), ν_Q^C calculated with (1) for the temperature range of the ordered phase of $(\text{NH}_4)_2\text{TeCl}_6$ compound is displayed. The increment $\Delta\nu_Q$ also shown in Fig. 6 is obtained as the difference between the measured frequency (full circles)

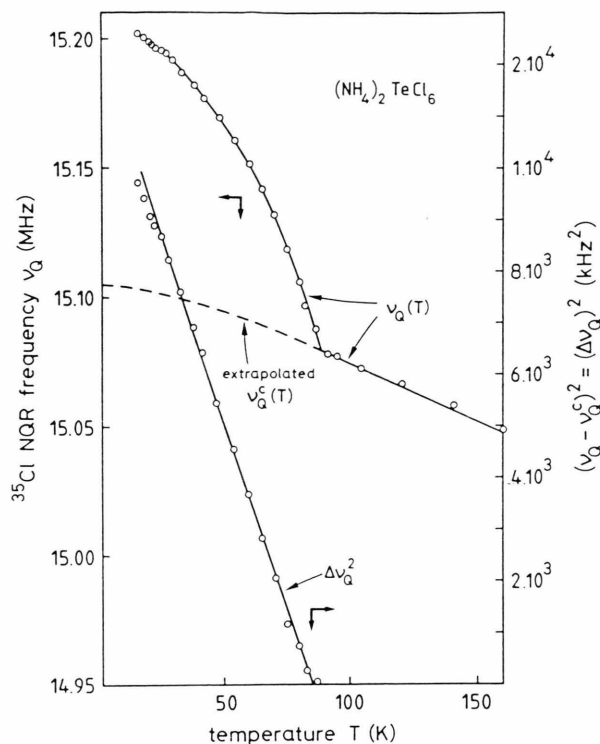


Fig. 6. Temperature behaviour of the NQR frequency increment $(\Delta\nu_Q)^2$ in $(\text{NH}_4)_2\text{TeCl}_6$ at $T \leq T_c$. $\Delta\nu_Q$ is obtained from the measured frequency $\nu_Q(T)$ (full circles) by subtracting the value extrapolated from the high temperature behaviour $\nu_Q^C(T)$ (dashed line).

and the extrapolated cubic behaviour indicated by the dashed line. For $(\text{NH}_4)_2\text{TeCl}_6$, $\Delta\nu_Q^2$ varies linearly with the temperature increment $(T_c - T)$. In the context of the Landau theory, the square of the order parameter $\Delta\Phi^2$ is expected to show the same behaviour. Therefore we have

$$\Delta\nu_Q \sim \Delta\Phi \sim (T_c - T)^{1/2}. \quad (2)$$

On a microscopic scale, small displacements of the surrounding charges cause a change of the electric field gradient. To lowest order we consider the distance changes of the nearest and next nearest neighbours relative to a chlorine atom on a rigid MCl_6^{2-} -octahedron on the basis of a simple point charge approximation. A rotation of the octahedron about its

threefold axis by an angle $\Delta\Phi$ would then give rise to an NQR frequency shift which is proportional to $\Delta\Phi^2$. A trigonal distortion of the point charge lattice associated by steric hindering with the small angle rotation of the octahedra would also be proportional to $\Delta\Phi^2$. These power laws do not depend on the phase relation between the rotating octahedra. Different behaviours are expected only for the field gradient at the lattice site of the cation [31]. Consequently, the observed increment $\Delta\nu_Q$ has to be accounted for by a different mechanism e.g. charge redistributions due to overlap distortion of the octahedron below T_c .

Conclusion

The phase transitions occurring in $(\text{NH}_4)_2\text{PbCl}_6$ at 80 K and $(\text{NH}_4)_2\text{TeCl}_6$ at 85 K show several features distinctly different from those observed in other hexachlorometallates. First of all, the transformation is induced by a rotation of the octahedra about their threefold axis, leaving all chlorine sites equivalent. As a consequence, the chlorine NQR resonance line does not split into components when the crystal passes through the transition point. Secondly, below T_c the increment of the NQR frequency displays the same temperature dependence as the order parameter, which is the angle of rotation about the threefold axis. This observation can not be explained in a point charge model by the rotation of the octahedra. Thirdly, in the mean field regime of the high temperature phase the renormalization effects due to the soft mode on the NQR frequency are less pronounced than in other A_2MX_6 -compounds. This difference might be due to the steric links between the MCl_6^{2-} -octahedra provided by the tetrahedral shaped NH_4^+ -ions.

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