Effect of Deuteration on the Phase Transitions and on the Critical Dynamics in Ammonium Hexachlorometallates

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Recent and novel data obtained from chlorine NQR measurements on natural and deuterated $(NH_4)_2MCl_6$ compounds are discussed with special regard to the influence of the ammonium-ion dynamics on the structural stability of these crystals. The temperature dependence (4.2 K to 350 K) of the chlorine NOR frequency v_Q and relaxation rates T_1^{-1}, T_2^{-1} obtained from the natural ammonium salts of Sn, Pd, Os, Pb, Te, Se and from the deuterated salts of Sn, Te and Se are analysed. Slight deviations from the normal temperature behaviour of v_Q and T_1^{-1} are found in Sn, Pd and Os compounds which stay cubic in the whole temperature range. The ammonium compounds of Pb and Te undergo a structural transformation between 80 K and 90 K from the cubic to a trigonal phase which is distinguished by the preservation of the single line spectrum of the chlorine NQR below T_{c1}. The observed divergence of T_1^{-1} at the transition point can be described in terms of a spin-phonon process in the presence of an overdamped soft mode. Deuteration of $(NH_4)_2TeCl_6$ only slightly affects the transition of T_{c1} but leads to new structural changes at lower temperatures. Whereas the natural compound stays trigonal down to 4.2 K the deuterated crystal undergoes two additional structural transformations at $T_{c2} = 48$ K and $T_{c3} = 28$ K which are correlated with a slowing down of the deuteron motion. Approaching T_{c2} from above, the spin-lattice relaxation rate and the spin-spin relaxation rate of the chlorine NQR exhibit distinct anomalies which are attributed to limited jumps of the octahedron in a shallow potential. The barrier height of this potential deduced from the chlorine NQR spin-lattice relaxation rate is 400 K. The transition at T_{c2} is explained by the condensation in one minimum of this potential. At T_{c3} a long range correlation is formed which is accompanied by a rotation of the octahedron about its fourfold axis. A similar mechanism is adopted for the transitions observed in $(NH_4)_2SeCl_6$ at $T_c = 24$ K and in $(ND_4)_2SeCl_6$ at $T_c = 48$ K.

Key words: Nuclear quadrupole resonance; Structural phase transitions; Ammonium-ion dynamics; Hexahalogenometallates; Critical behaviour.

1. Introduction

In the last decade the ammonium hexachlorometallates $(NH_4)_2MCl_6$ have attracted extensive research work which was devoted to the dynamical behaviour of the molecular ions composing this cubic ionic crystal. In the face centred cubic lattice the anions MCl_6^{2-} occupy octahedral lattice sites (Figure 1). At very high temperatures the octahedron undergoes hindered rotations about one of the fourfold molecular axes. This motion has been investigated particularly by its influence on the spin-lattice relaxation rate

of the chlorine nuclear quadrupole resonance [1]. In the low temperature regime librational modes of the octahedron may become soft driving the crystal from the cubic to a lower symmetric structure. The chlorine NQR has been most efficiently applied by several groups to elucidate the structural changes induced by the small angle rotation of the octahedra as well as the critical dynamics associated with the softening of the MCl_6^{2-} librations in hexachlorometallate compounds [2]. Phase transitions have been observed in several alkali metal hexachlorometallates such as K_2SnCl_6 or in ammonium-ion compounds with bromium octahedra, e.g. in $(NH_4)_2SnBr_6$. Until recently, the chlorine-compounds with ammonium-cations have been assumed not to exhibit such rotational displacive transformations [3] and therefore the $(NH_4)_2MCl_6$ compounds are considered to be most
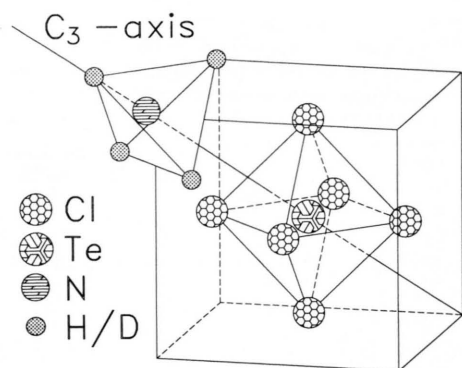
Fig. 1. Part of the unit cell of $(NH_4)_2MCl_6$ showing the orientations of the tetrahedral ammonium-ion NH_4^+ and of the octahedral anion MCl_6^{2-}.

suitable for temperature dependent studies of the ammonium-ion motion.

In the cubic lattice the cations NH_4^+ occupy identical sites of tetrahedral symmetry. The most peculiar property of these molecular ions in the hexachlorometallate crystals is the rather low barrier height to a rotation about their threefold axes of about 600 to 800 K, depending on the metal atom. At ambient temperatures the NH_4^+ molecules already undergo fast classical hindered rotations. Decreasing the temperature below 50 K a crossover to quantum tunnelling motion takes place. The classical motion at elevated temperatures was first studied by specific heat and by proton magnetic resonance experiments [4, 5]. Both methods provided first estimates of the barrier height. Later, these data were improved for several hexachlorometallates by quasi elastic neutron scattering measurements [6]. The neutron scattering experiments also made possible the first direct observation of the tunnelling splitting of the librational ground state at low temperatures [6, 7].

Numerous and thorough studies of the tunnelling motion in ammonium-ion compounds rely on temperature dependent measurements of the spin-lattice relaxation rate of the proton resonance [8, 9]. These latter investigations have also been extended to the deuterated salts, where the expected mass-effect on the tunnelling frequency could be confirmed [10]. Unusual deuteration effects on the spin-lattice relaxation rate of the deuteron magnetic resonance have been observed in $(ND_4)_2SnCl_6$ and $(ND_4)_2TeCl_6$ which were accounted for by limited jumps of the ammonium-ion [11, 12].

Apart from the systems studied in the present work the influence of the ammonium-ion motion on the chlorine nuclear quadrupole resonance is generally rather small. Main effects are deviations from the usual temperature behaviour of the quadrupole resonance frequency and of the spin-lattice relaxation rate. On deuteration these deviations are slightly modified [13, 14].

In the above mentioned research works the physical properties of interest are the peculiarities of the dynamics of either the cation NH_4^+ or the anion MCl_6^{2-}, the mutual perturbation being considered small. In the present contribution those cases will be reviewed and discussed where the dynamics of the MCl_6^{2-} octahedra is measurably affected by the motion of the NH_4^+ tetrahedra. Particular emphasis is devoted to those $(NH_4)_2MCl_6$ crystals, such as M = Te, Se, Pb, where the ammonium-ion dynamics triggers structural transformations. In these systems prominent deuteration effects on the structural transformations and on the chlorine nuclear quadrupole resonance are observed.

The paper is organised as follows. In the next section the important structural and dynamical properties of the cubic $(NH_4)_2MCl_6$ crystals are briefly reviewed. The influence of the ammonium-ion motion on the Cl-NQR frequency and spin-lattice relaxation rate as a function of temperature in natural and deuterated cubic $(NH_4)_2MCl_6$ crystals is discussed in Section 3. Results of Cl-NQR studies of the critical dynamics near the recently discovered rotational displacive phase transitions in $(NH_4)_2TeCl_6$ and $(NH_4)_2PbCl_6$ are described in Section 4. Sections 5 and 6 are devoted to the peculiar observation, the deuteration induced structural transitions in the tellurium compound and the dramatic deuteration effects on the phase transitions in the hexachloroselenate. In Sect. 7 microscopic models are presented to explain the unusual deuteration effects on a microscopic scale.

2. Survey of the Properties of Cubic $(NH_4)_2MCl_6$-Crystals

The ammonium hexachlorometallates $(NH_4)_2MCl_6$ crystallise at room temperature in the cubic antifluorite structure of the K_2PtCl_6-type (space group Fm3m) [15]. In Table 1 only those compounds are listed which have been investigated by Cl-NQR in the context of this work. The face centred cubic unit cell with a lat-

Table 1. Properties of face centred cubic $(NH_4)_2MCl_6$ crystals. Room temperature cubic lattice constant a_0, structure parameter u of the MCl_6^{2-}-octahedra, activation energy E_a for hindered rotations about the threefold axis of the ammonium-ion and the corresponding tunnelling frequency v_T, transition temperatures T_c for structural phase transformations and configuration of outer electron shells of the M^{4+} transition metal ion. The theoretical u-values are calculated using the relation $u = 0.5 - \sqrt{2 \cdot r_{Cl}/a_0}$ [39] where r_{Cl} is the radius of the chlorine ion $r_{Cl} = 0.1838$ nm.

Compound	a_0 (nm)	u	E_a (K)	v_T (MHz)	T_c (K)	M^{4+}
$(NH_4)_2PdCl_6$	0.9826 [a]	0.234 [b]	308 [b]	13 500 [a]	no	$4d^6 5s^0$
$(NH_4)_2OsCl_6$	0.9881 [a]	0.237 [c]	450 [a]	4 000 [a]	no	$5d^4 6s^0$
$(NH_4)_2SeCl_6$	0.9955 [a]	0.239 [c]	–	–	24 [g]	$3d^{10} 4s^2$
$(NH_4)_2SnCl_6$	1.0060 [n]	0.241 [b]	604 [b]	720 [a]	no	$4d^{10} 5s^0$
$(NH_4)_2PbCl_6$	1.0135 [b]	0.245 [b]	708 [b]	48 [a]	80 [h]	$5d^{10} 6s^0$
$(NH_4)_2TeCl_6$	1.0220 [n]	0.248 [b]	801 [b] 670 [d]	144 [f]	88 [k,l]	$4d^{10} 5s^2$
$(ND_4)_2SeCl_6$	–	–	–	–	48 [g]	$3d^{10} 4s^2$
$(ND_4)_2SnCl_6$	1.0054 [n]	0.241 [c]	750 [d,e]	7.5 [e]	no	$4d^{10} 5s^0$
$(ND_4)_2TeCl_6$	1.0204 [n]	0.245 [c]	790 [d]	1.5 [d]	86 [k,l] 48 [m,d,l] 28 [m,d,l]	$4d^{10} 5s^2$

[a] [16] and works cited therein.
[b] [17] and works cited therein.
[c] calculated.
[d] [12].
[e] [32].
[f] extrapolated to 0 K from [12].
[g] [36].
[h] [21].
[k] [27].
[l] [28].
[m] [30].
[n] [40].

tice constant a_0 of roughly about 1 nm contains 4 formula units. The MCl_6^{2-} octahedra occupy the octahedral lattice sites and are surrounded by eight equivalent NH_4^+ ions centred at tetrahedral sites in positions (1/4, 1/4, 1/4) from the anion (Figure 1). The M–Cl-distance normalised to the lattice constant (u) is slightly smaller than 1/4 (Table 1).

In the cubic phase the ammonium-ions are located in a local field of tetrahedral symmetry (Figure 1). The barrier height to the rotation about the threefold axis is rather small (activation energy $E_a \approx 500$ K) [7]. Therefore the motion in the threefold potential should yield the prominent contribution to the anomalies attributed to the ammonium-ion dynamics in the range between helium and ambient temperatures. Due to the low barrier height the librational modes in the threefold potential are expected to be strongly anharmonic. This conclusion has been confirmed by results of quasi elastic neutron scattering from $(NH_4)_2SnCl_6$ [7]. The splitting of the librational levels is found to increase with increasing energy indicating a box like potential. With increasing temperature the hindered rotations about the threefold axis become more frequent. The probability per unit time for the molecule to perform a hindered rotation about the threefold axis is

$$\tau^{-1} = \tau_0^{-1} \cdot \exp[E_a/kT], \quad \tau_0^{-1} = (2\pi/3)(2I/V_0)^{1/2}.$$

I is the moment of inertia of the ammonium-ion, which is $5.3 \cdot 10^{-47}$ kg · m^2 for NH_4^+ using an N–H distance of 0.103 nm. The moment of inertia of ND_4^+ about its threefold axis is two times larger, as the N–D and the N–H distances are the same within the

given precision. The barrier height V_0 is related to the activation energy E_a (see inset of Fig. 2) by

$$V_0 = E_a + 2\hbar(V_0/2I)^{1/2}.$$

The rather low barrier height for the rotation about the threefold axis (Table 1) also allows a considerable overlap of the wave functions of the librational levels, that gives rise to a tunnelling splitting of the ground state at low temperatures. The tunnelling frequency v_T (Table 1) corresponds to the A-3T-splitting of the tunnelling states. The analysis of the experimental data from the different ammonium hexachlorometallates has indicated a systematic trend of the tunnelling splitting as a function of the cubic lattice constant. The splitting is found to decrease exponentially with increasing a_0 [16]. The corresponding activation energies therefore vary approximately linearly with the lattice constant a_0 (Figure 2). As pointed out by Ottnes and Svare, the parameter u seems to be the crucial property governing the barrier height to a rotation of the ammonium-ion about its threefold axis [17]. The activation energy of the ammonium-ion in the selenium compound has not yet been measured. In the case of $(NH_4)_2PdCl_6$, quasi elastic neutron scattering under hydrostatic pressure revealed a decrease of the tunnelling splitting of proton motion, which has been explained consistently by considering the behaviour of the structural parameter u under pressure [18].

Recent deuteron magnetic resonance studies of $(ND_4)_2SnCl_6$ [11] and of $(ND_4)_2TeCl_6$ [12] provide evidence of an additional tumbling motion of the ammonium-ion in these crystals. The possible micro-
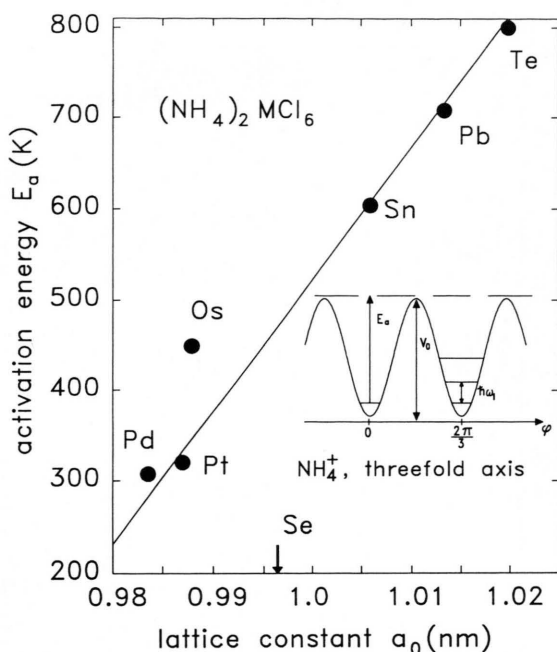
Fig. 2. Activation energy E_a for the rotation about the three-fold axis of the ammonium-ion the different ammonium hex-achlorometallate crystals as a function of the cubic lattice constant a_0 according to the data of Table 1. The inset sketches the threefold potential experienced by the ammonium-ion for rotations about its threefold axis in the cubic phase. ω_1 represents the frequency of the ammonium-ion libration.

scopic origin of this supplementary motion of the ammonium-ion will be discussed in Section 7.

With respect to the lattice stability and the temperature dependence of the electric field gradient at the chlorine site the bonding properties and the librational motions of the MCl_6^{2-}-ion are most important. The barrier height to rotations about the fourfold axis of the octahedron ($E_a = 6000$ K) is slightly smaller than that for rotations about the threefold axis. The probability of hindered rotations according to the relation given above is much smaller and is only detectable by NQR above room temperature. The librational motions are most effective in spin-lattice relaxation processes and in the motional averaging-ranging mechanism of the chlorine NQR. Librations of the MCl_6^{2-}-ion also drive most of the structural transformations observed in the hexachlorometallate compounds [2].

As compared to the isolated ammonium-ion motions which were studied very thoroughly in recent

years only limited research activities have been devoted to the effect of the ammonium-ion dynamics on the crystal properties. In the present work the chlorine NQR has been used as a very efficient tool to investigate the static and dynamic changes of the electric field gradient at the lattice site of the chlorine atom. The influence of the ammonium-ion motion on the MCl_6^{2-}-octahedra has been found to be important for the stability of the crystals against a spontaneous lattice distortion leading to the occurrence of a phase transition (see Table 1). With regard to the occurrence of structural transformations the ammonium hexachlorometallates may be classified into three main categories on the basis of the observed behaviour:

1. The natural as well as the deuterated compounds stay cubic down to liquid helium temperature. In Table 1, where only those compounds are listed which have been investigated in the present work, these are the crystals containing the metal ions Os, Pd, and Sn. In these crystals the frequency and the relaxation rates of the chlorine-NQR show weak deviations from the expected normal temperature behaviour (Figure 3). Only slight effects of deuteration are observed.

2. A structural phase transition from the cubic to a trigonal structure takes place, which has so far only been observed in crystals containing ammonium ions such as $(NH_4)_2PbCl_6$ and $(NH_4)_2TeCl_6$. The transitions which in both systems occur at about 80 K are distinguished by the preservation of the single line NQR-spectrum in the low temperature phase (Figure 3). The phase transformation is only slightly modified if the protons in the ammonium-ions are replaced by deuterons.

3. Phase transformations which most probably are induced or strongly affected by the slowing down of the ammonium-ion motions are observed in $(NH_4)_2TeCl_6$ and in $(NH_4)_2SeCl_6$ at temperatures below 50 K. These transitions exhibit a strong dependence on the degree of deuteration.

In Fig. 3 the temperature dependence of the chlorine NQR frequency and relaxation rate observed in the category 1 and 2 compounds are summarised to demonstrate similarities of the behaviour of the stable crystals and of the systems undergoing a cubic-to-trigonal transition. Details of the temperature dependence of the NQR signal will be described later. In the following chapters our results of recently published
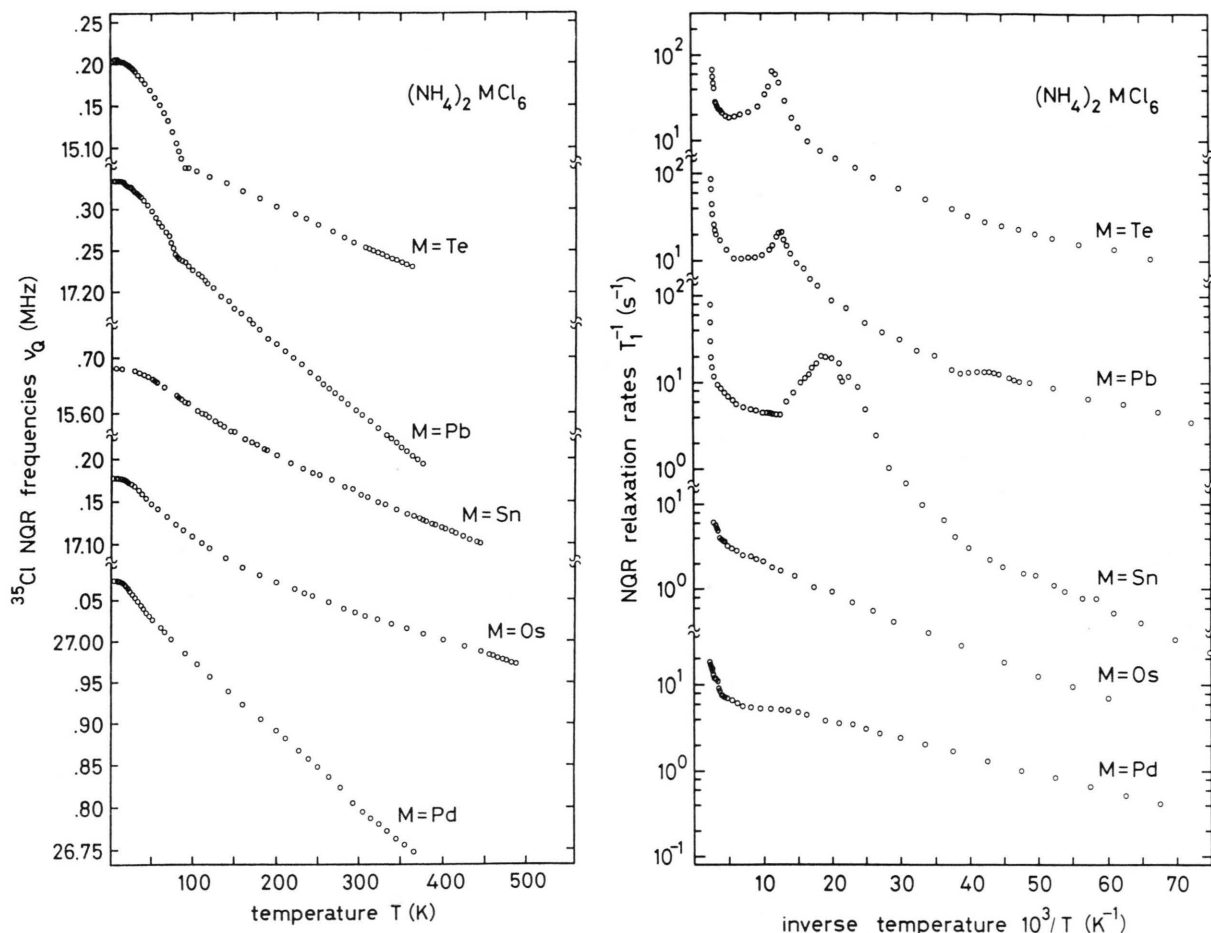
Fig. 3. Temperature dependence of the ^{35}Cl-NQR frequency (left) and spin-lattice relaxation rate (right) observed in $(NH_4)_2MCl_6$ compounds for M = Te [24], Pb [24], Sn [13], Os*, Pd* (*this work).

and also of new unpublished data from Cl-NQR measurements will be presented and a local model will be discussed in terms of the given classification.

3. Ammonium-Ion Motion and Chlorine NQR in Cubic $(NH_4)_2MCl_6$-Crystals

In this section we shall discuss those NQR results that provide information on the influence of the ammonium-ion motion on the static and dynamic NQR parameters measured for the cubic salts $(NH_4)_2PdCl_6$, $(NH_4)_2OsCl_6$, $(NH_4)_2SnCl_6$, and $(ND_4)_2SnCl_6$. The temperature dependencies of the ^{35}Cl-NQR frequency and spin-lattice relaxation rate observed in the ammonium compounds are displayed in Figure 3. Both, fre-

quency and relaxation rate exhibit deviations from the normal quasiharmonic behaviour as observed in Rb_2SnCl_6 [19].

To explain the deviation of the NQR frequency from the Bayer-Kushida temperature dependence Nakamura et al. [14] and Dimitropoulos et al. [13] adopted a model which takes into account the modification of the field gradient due to the jumping ammonium-ion. The model considers the time averaged contribution from the ammonium-ion that dwells a time τ_r in one of the three minima of Fig. 2 and is freely rotating during the time τ_t. The extra contribution to the field gradient then exhibits an Arrhenius-type temperature dependence from which the activation energy E_a has been deduced. Although the value for $(NH_4)_2SnCl_6$ obtained by this procedure is in good
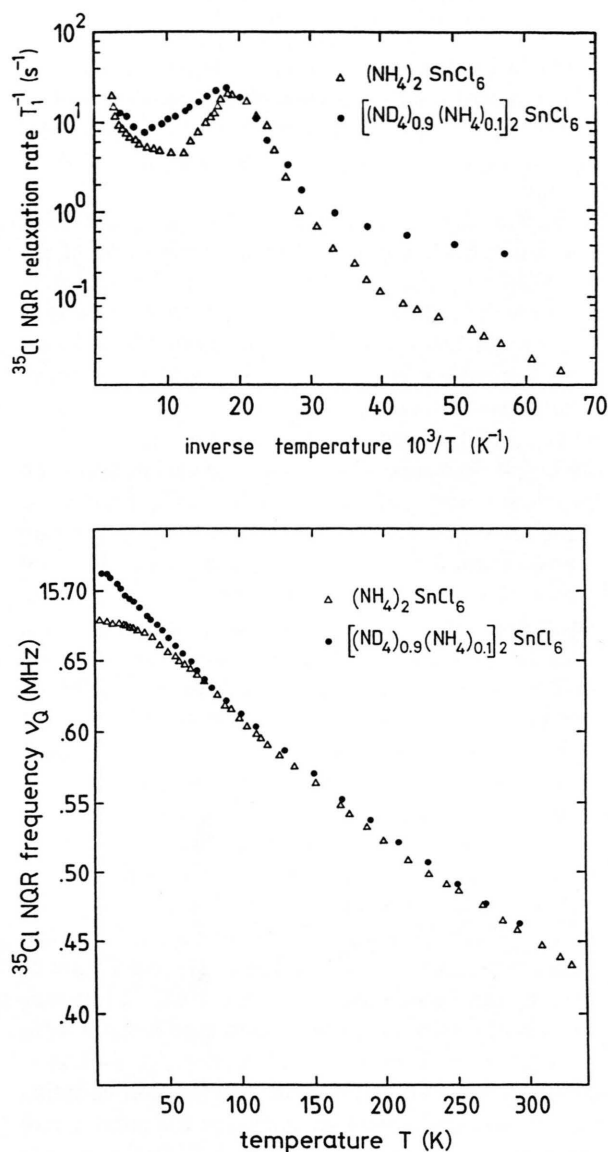
Fig. 4. Temperature dependence of the ^{35}Cl-NQR frequency and spin-lattice relaxation rate in $(NH_4)_2SnCl_6$ (triangles) and $(ND_4)_2SnCl_6$ (full circles). Note the different temperature scales for ν_Q and T_1^{-1}.

agreement with the activation energy determined by other experimental techniques larger deviations are found for the other salts.

As an alternative explanation of the anomalous temperature variation of the chlorine NQR frequency Brown and Segel [20] suggested that the anharmonicity of the MCl_6^{2-}-octahedron libration can account for the appearance of the inflection point in the tem-

perature dependence of the frequency. We have adopted the principal idea but in view of recent experimental data we propose a different effect of the anharmonicity. On the basis of our results we consider the contributions at low temperatures to cause the anomaly. A comparison of the temperature behaviour of the frequencies in Fig. 3 shows the strong similarity between the systems which undergo a structural transformation and those which stay cubic. The increase of the frequency in $(NH_4)_2PbCl_6$ and $(NH_4)_2TeCl_6$ below the transition temperature scales with the order parameter, which is a rotation of the octahedron about its threefold axis [21]. This shift, however, has two contributions. (i) The change of the field gradient due to the small angle rotation of the octahedron with respect to the surrounding lattice ions. (ii) The increase of the electric field gradient due to the development of a volume strain accompanied by an expansion of the lattice.

Evidence for a coupling of the order parameter to a negative homogenous volume strain comes from our Raman data of $(NH_4)_2TeCl_6$ where the totally symmetric vibration of the octahedron displays a positive temperature coefficient below T_{c1}. We assume that the anomalous increase of the chlorine NQR frequency in the cubic salts of Sn, Os, and Pd, which is qualitatively similar to that observed in the tellurium and lead compounds is due to the growing of this volume strain in the course of the slowing down of the ammonium-ion motion. The microscopic origin of this effect will be discussed in more detail in Section 7.

A further support of the given interpretation comes from the deuteration effects (Figure 4). Above 80 K the chlorine NQR frequencies of $(ND_4)_2SnCl_6$ and $(NH_4)_2SnCl_6$ are nearly identical, but decreasing the temperature towards 0 K the frequency of the deuterated crystal increases more rapidly than that of the natural compound. In the scope of the present model this difference is explained by a slightly smaller lattice constant of the deuterated salt. The spin-lattice relaxation rate is also most strongly affected by deuteration at low temperature (Figure 4). Below 55 K the relaxation rate of the natural tin salt exhibits a Raman-T^5 dependence [23]. In the deuterated salt the relaxation rate is enhanced by an order of magnitude at very low temperature. In addition there is a crossover from a T^5 to a linear T-dependence below 30 K. An intriguing feature of the chlorine NQR in both $(ND_4)_2SnCl_6$ and $(NH_4)_2SnCl_6$ is the appearance of the maximum in the spin-lattice relaxation rate at about 55 K. In the
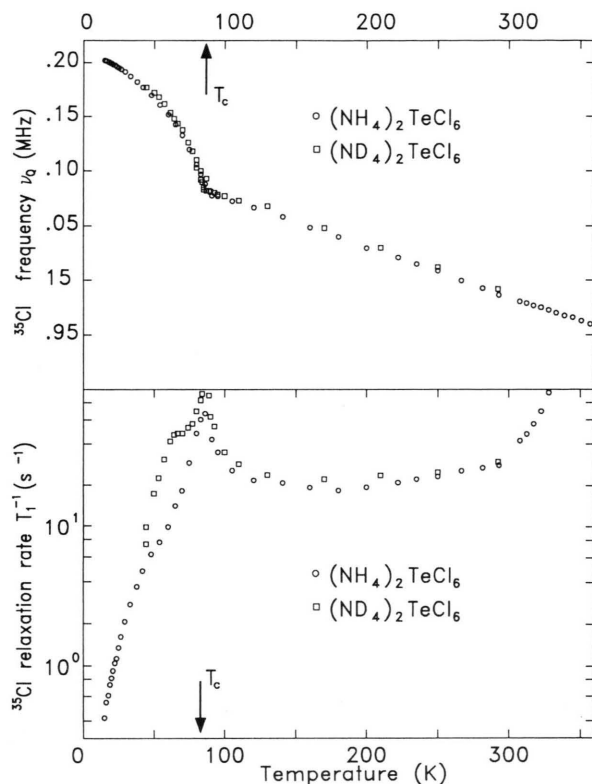
Fig. 5. Temperature dependence of the ^{35}Cl-NQR frequency and spin-lattice relaxation rate in $(NH_4)_2TeCl_6$ (open circles) and $(ND_4)_2TeCl_6$ (squares) from [24].

tellurium and lead compounds (Fig. 3) the peak in the relaxation rate is associated with the critical dynamics at the structural transition (next chapter). As the tin compound stays cubic, the anomaly has been attributed to cross-relaxation with tunnelling splittings of the ammonium-ion [22]. A thorough investigation of the effect of deuteration on this relaxation peak could not provide further evidence for the cross relaxation mechanism [23]. Therefore, the problem of the microscopic origin of this maximum in the tin compound remains still open. In the context of the present explanation one may think of an incipient phase transition that is suppressed by the quantum mechanical motion of the ammonium-ion below 60 K.

4. Cubic-to-Trigonal Phase Transitions in $(NH_4)_2PbCl_6$ and $(NH_4)_2TeCl_6$

$(NH_4)_2PbCl_6$ and $(NH_4)_2TeCl_6$ exhibit a phase transition between 80 K and 90 K different to those

already observed in the other hexachlorometallates, and which was first discovered by chlorine NQR [24]. The temperature dependence of the frequency and of the spin-lattice relaxation rate observed in the natural and deuterated tellurate compound is displayed in Figure 5.

At the transition temperature T_{c1} at about 88 K there is a discontinuous change of the slope of the Cl-NQR frequency shift as a function of temperature in both the natural and deuterated crystal. There is no line splitting below T_{c1} indicating that all chlorine sites remain equivalent in the low symmetry phase. The same behaviour has also been observed in $(NH_4)_2PbCl_6$ where the transition occurs at $T_{c1} = 80$ K [24]. The preservation of the single line spectrum provides a very important reliable indication of the structure below T_{c1}: The basis vector of the displacive transformation must be a rotation about the threefold axis leading to a trigonal structure. As the Raman-scattering data indicate a unit-cell conserving transition the space group of the low temperature structure could be assigned as C_{3i}^2 for the plumbate and tellurate crystals in the scope of Landau's theory [24]. The space group has later been confirmed by elastic neutron scattering experiments performed on both $(NH_4)_2PbCl_6$ [25] and $(NH_4)_2TeCl_6$ [26].

Moving from the natural to the deuterated ammonium hexachlorotellurate crystal, a small reduction of the transition temperature from 88 K to 86 K is observed [27, 28]. The critical dynamics near the transition temperature is also modified [27] (see Figure 6). Passing through the transition, the ^{35}Cl/^{37}Cl-isotope ratio of the spin-lattice relaxation rate remains constant at a value of about 1.5, indicating a phonon assisted relaxation mechanism in the weak coupling limit. This conclusion is supported by the temperature dependence of the relaxation rate T_1^{-1} in the vicinity of the transition point. Approaching T_{c1} from above and from below the relaxation rate fairly well follows a law given by

$$T_1^{-1} = \hat{A}T/(T - T_{c1})^{1/2}.$$

This behaviour is expected for a direct spin-phonon process in the presence of an overdamped soft mode [29], where $\hat{A}$ is the coupling constant. In addition, the one over square root dependence is an indication of an isotropic interaction which is consistent with the displacive rotation about the threefold axis. The coupling constants $\hat{A}$ deduced from the experimental data of the natural and deuterated crystal are about two times
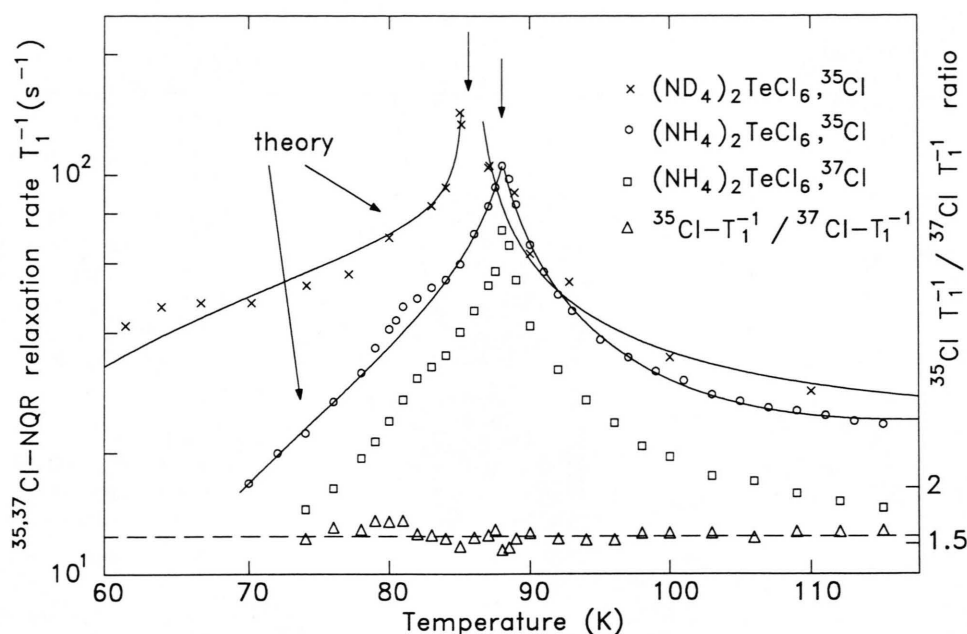
Fig. 6. Temperature dependence of the ^{35}Cl- and ^{37}Cl-NQR spin-lattice relaxation rate in the vicinity of the cubic-to-trigonal phase transitions in $(NH_4)_2TeCl_6$ (open circles and squares) and $(ND_4)_2TeCl_6$ (crosses). In addition the ratio of the relaxation rates of the two chlorine isotopes is shown, from [27].
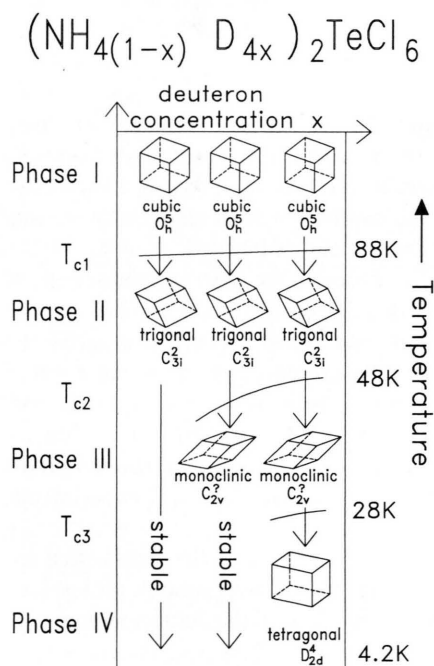

Fig. 7. Diagram showing schematically the phase transitions in natural, in partially deuterated and in completely deuterated $(NH_4)_2TeCl_6$.

larger for the temperature region below T_{c1} as compared to those above T_{c1}. On deuteration the coupling constant is enhanced by about 20% [27]. This latter observation can be explained by an increased soft mode damping in the deuterated salt which, on the other hand, should also shift the transition to higher temperatures. The measured decrease of T_{c1} upon deuteration is therefore attributed to a competing mechanism which could be a slightly larger lattice constant of $(ND_4)_2TeCl_6$. Indeed, with decreasing temperature a rising positive volume defect of the deuterated salt has been deduced from elastic neutron scattering obtained below T_{c1} [28].

5. Phase Transitions Induced by Deuteration in $(NH_4)_2TeCl_6$

Cooling further below T_{c1} dramatic deuteration effects are observed in $(NH_4)_2TeCl_6$. Whereas the natural compound stays trigonal down to temperatures as low as 4.2 K the deuterated crystal undergoes two additional structural transformations at $T_{c2} = 48$ K and $T_{c3} = 28$ K. Details of the structure of these new
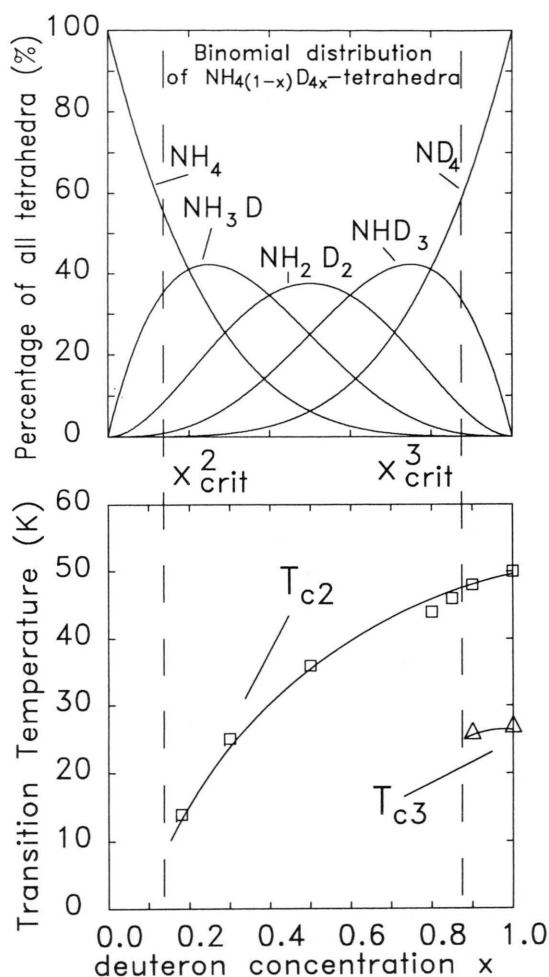
Fig. 8. Phase transition temperatures T_{c2} and T_{c3} in $(NH_{4(1-x)}D_{4x})_2TeCl_6$ as functions of the deuteron concentration x (bottom) [31]. The diagram at the top shows the concentration of the differently deuterated tetrahedra if a binomial distribution of the deuterons is assumed.

Fig. 9. ^{35}Cl-NQR spin-spin (top left) and spin-lattice (bottom left) relaxation rates as measured in $(ND_4)_2TeCl_6$ [12]. The dashed line represents the experimental result obtained on $(NH_4)_2TeCl_6$. In the inset the difference of the spin-lattice relaxation rates of the deuterated and natural compound is plotted.

phases have been deduced from Raman-scattering data [12, 30] and from elastic neutron scattering experiments [28]. The main results are summarised in the diagram of Figure 7. In partially deuterated $(NH_{4(1-x)}D_{4x})_2TeCl_6$ the transition temperatures T_{c2} and T_{c3} decrease gradually with decreasing deuterium content x in order to disappear abruptly at a critical concentration x_c which is different for the two transitions [31]. Figure 8 (bottom) shows the results of a Raman scattering investigation on mixed crystals. When the protons in the ammonium ion are gradually substituted by the deuterons the binomial formula can be used to determine the deuteron distribution on the
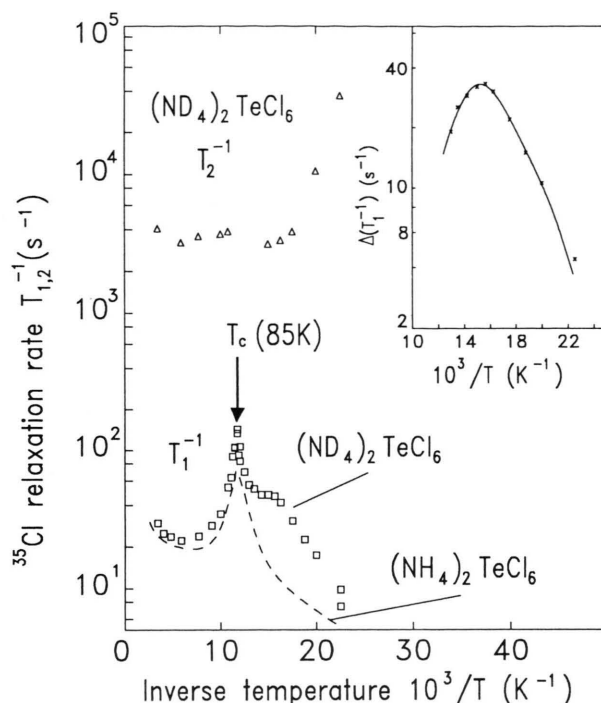
tetrahedra. From the comparison in Fig. 8 one can conclude that the transition T_{c2} is already induced when one proton in NH_4^+ is replaced by D whereas the transition T_{c3} requires at least that every second tetrahedron is completely deuterated.

Obviously, the considerably different behaviour of the natural and deuterated tellurium crystals at low temperatures implies a large impact of the ammonium-ion dynamics on the lattice stability of these compounds at low temperatures (Figure 7). Information on the microscopic mechanism of this deuteration effect is provided by the proton and deuteron magnetic resonance studies and the chlorine NQR experiments [12].

The temperature dependence of the spin-lattice relaxation rates of the proton magnetic resonance at 15 MHz in $(NH_4)_2TeCl_6$ and of the deuteron magnetic resonance at 52 MHz in $(ND_4)_2TeCl_6$ reveal both a maximum at about 80 K which is attributed to an intramolecular relaxation mechanism effected by the hindered rotation of the ammonium-ion. The activa-
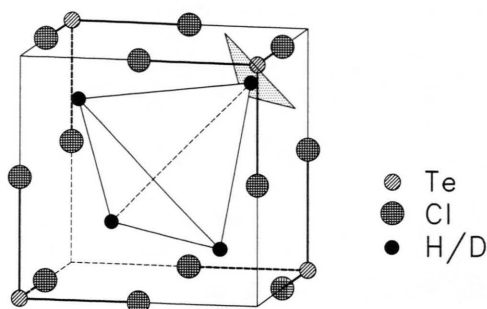
Fig. 10. Sketch of the path of the proton or deuteron when the ammonium-ion performs limited jumps in the threefold shallow potential perpendicular to the threefold cubic axis

tion energies for the rotation of the ammonium-ions about their threefold axis deduced from these measurements are given in Table 1. The ^{1}H-nuclear spin-lattice relaxation rate shows two additional maxima at lower temperatures which were explained by tunnelling assisted relaxation processes providing an estimate of the tunnelling splitting of NH_4^+ in $(NH_4)_2TeCl_6$ [12]. This procedure is not applicable to $(ND_4)_2TeCl_6$, as the separation of the tunnelling levels is about two orders of magnitude smaller. Instead, the tunnelling splitting of ND_4^+ in $(ND_4)_2TeCl_6$ as a function of temperature could be deduced from a detailed investigation of the quadrupole perturbed line shape of the deuteron nuclear resonance [12]. However, the ^{2}D nuclear spin-lattice relaxation exhibits a second maximum at 24 K which is assumed to be due to a supplementary motion of the ND_4^+-molecular ion in the lattice which is a tumbling motion of the ammonium-ion around the threefold crystallographic axis (Figure 10). Support of the existence of this motion is provided by the results of a thorough investigation of the ^{2}D nuclear spin-lattice relaxation rate in $(ND_4)_2SnCl_6$ [32]. The authors observed an extra minimum in the temperature dependence of the spin-lattice relaxation time at about 15 K. This feature is interpreted as a reorientation related minimum due to a motion where the N–D bonds are not parallel to the cubic [111] crystal axis. Direct evidence for a trifurcated bonding potential between the proton or deuteron and the nearest halogen-ions in ammonium-ion hexahalogenometallates comes from elastic neutron scattering. In $(NH_4)_2SiF_6$, Schlemper et al. [33] found a threefold disorder of the protons in a region of about 0.1 nm. Similar results were also obtained on $(NH_4)_2SnCl_6$ [34]. The activation energy for the lim-

ited jumps of the deuterons in $(ND_4)_2SnCl_6$ deduced from the D-NMR is 17 K [23]. On the basis of their model treatment we estimate a slightly higher value of about 25 K for $(ND_4)_2TeCl_6$ using our deuteron resonance data.

Approaching T_{c2} from above the chlorine NQR signal fades out and does not recover at all below this transition temperature. The broadening of the NQR signal is associated with a diverging spin-spin-relaxation rate at T_{c2} (Fig. 9, top left). In the same temperature range the spin-lattice relaxation rate in the deuterated salt exhibits a shoulder which is absent in the protonated sample (Fig. 9, bottom). The difference between the spin-lattice relaxation rates in the deuterated and the natural crystal displays the temperature dependence of a thermally activated process. Fitting the data (Fig. 9, inset) with the relation

$$\Delta T_1^{-1} = \langle \Delta \omega_Q^2 \rangle \frac{\tau_D}{1 + \omega_Q^2 \tau_D^2}, \quad \tau_D = \tau_D^0 \exp[E_a/kT]$$

yields an activation energy $E_a = 400$ K and a pre-exponential factor $\tau_D^0 = 2.5 \cdot 10^{-11}$ s. The deduced activation energy is much lower than that for the rotation of the ND_4^+-ion about its threefold axis (Table 1) and much larger than the activation energy for the already discussed limited jumps of the ammonium-ion. But also the pre-exponential factor rules out a direct contribution to the extra relaxation channel from an ammonium-ion motion. The moment of inertia deduced from τ_D^0 is $4.0 \cdot 10^{-43}$ kg m^2 for a threefold and $1.8 \cdot 10^{-43}$ kg m^2 for a twofold rotational potential. These values are three orders of magnitude larger than the moment of inertia of the ammonium-ion but very near to that of the $TeCl_6^{2-}$, which is $1.5 \cdot 10^{-44}$ kg m^2 for a rotation about the threefold axis of the octahedron.

Therefore, the extra-contribution to the spin-lattice relaxation of the chlorine NQR in $(ND_4)_2TeCl_6$ is attributed to limited rotational jumps of the $TeCl_6^{2-}$-octahedron. The potential minima for these jumps are anticipated to be formed in the course of the slowing down of the deuteron motion (see Section 7).

6. Deuteration Effects
on the Structural Phase Transitions in $(NH_4)_2SeCl_6$

When Daiyu Nakamura and his co-workers for the first time measured the chlorine NQR in $(NH_4)_2SeCl_6$ they were not able to observe a structural transition
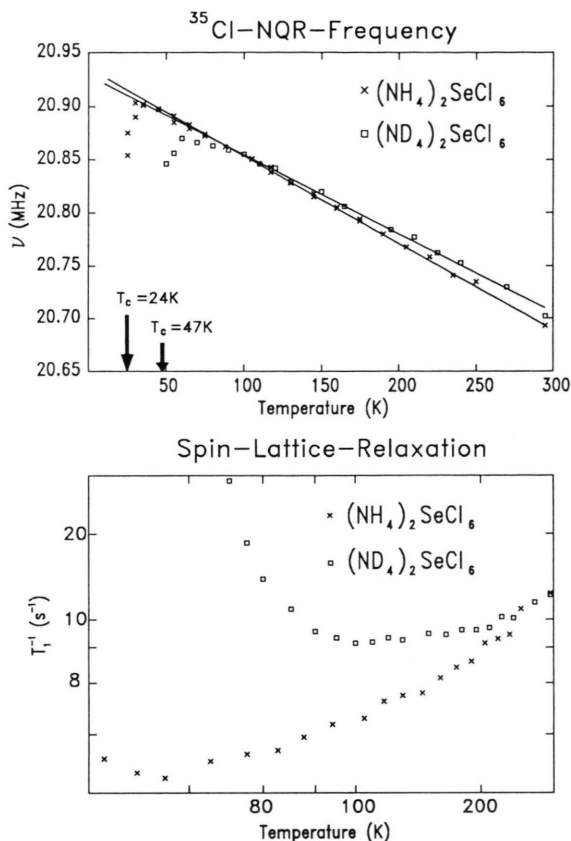
Fig. 11. Temperature dependence of the ^{35}Cl-NQR frequency (top) and spin-lattice relaxation rate (bottom) in $(NH_4)_2SeCl_6$ (crosses) and $(ND_4)_2SeCl_6$ (squares). Note the different temperature scales for ν_Q and T_1^{-1}.

Fig. 12. *Top:* Part of the A_2MCl_6 lattice showing the two important overlap interactions between nearest neighbours governing a rotative displacive transition. *Bottom:* Sketch of the overlap-repulsion potentials between chlorines and neighbouring cations (U^{A-Cl}) and chlorines of next nearest octahedra ($U^{Cl-Cl'}$) and the total potential as a function of the rotation angle φ of the MCl_6^{2-}-octahedron above and below the phase transition.

because of the experimental restriction to temperatures above 77 K [35]. Extending the range to lower temperatures we recently discovered structural transformations in the natural as well as in the deuterated selenium compound [36]. The most intriguing feature is the large shift of the transition when hydrogen is replaced by deuterium.

The temperature dependence of the Raman spectrum and of the chlorine NQR frequency and relaxation rate (Fig. 11) provides conclusive evidence for a structural transition at 24 K in $(NH_4)_2SeCl_6$ and at 48 K in $(ND_4)_2SeCl_6$ [36]. Approaching T_c from high temperatures, in both compounds the chlorine NQR frequency first increases linearly and starts to soften a few tens of degrees above the transition. Simultaneously with the softening of the frequency the spin-lattice relaxation rate and the line width increase. The line broadening is purely inhomogeneous because in
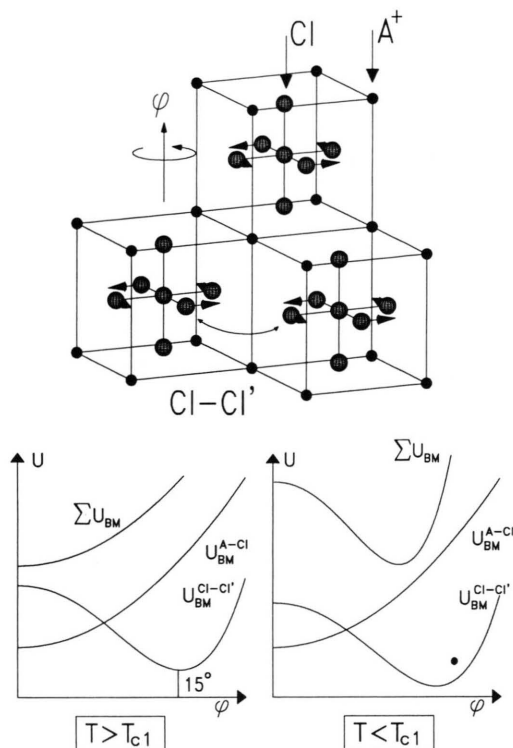
the same temperature range the spin-spin-relaxation rate of the chlorine NQR signal remains essentially constant. These effects are more pronounced and are covering a larger temperature range in the deuterated selenate. The low temperature phases show similarities with the phase below $T_{c3} = 28$ K in $(ND_4)_2TeCl_6$. The chlorine NQR signal in the selenium compounds also fades out at the transition and does not recover at lower temperatures [36, 37]. The appearance of a multi-line pattern in the Raman spectrum particularly in the E_g mode frequency region points towards a tetragonal distortion associated with a considerable strain. Despite the strain coupling, the transitions are predominantly of second order. The evolution of the strain field is considered as the main cause of the inhomogeneous broadening of the NQR-line and of the disappearance of the signal below T_c.

7. Model Considerations

In this section we shall sketch the concept of a microscopic model in order to describe the mentioned three categories of behaviours in the $(NH_4)_2MCl_6$ compounds. In the frame of this model the observed chlorine NQR data and deuteration effects are discussed on the line of the given classification. The model is based on two general but essential assumptions.

1. The structural stability of the A_2MCl_6-compounds is governed by the competition of the nearest neighbour A–Cl and Cl–Cl' overlap interactions.
2. In the $(NH_4)_2MCl_6$ and $(ND_4)_2MCl_6$ compounds the A–Cl interaction potential is modified by the rotational dynamics of the NH_4^+ and the ND_4^+-ion, respectively.

The first assumption basically corresponds to the steric model developed by I.D. Brown thirty years ago [38]. In his purely geometrical approach Brown considered the separations of the anions and cations. By minimising the occupied volumes he proposed geometrical limits for the occurrence of cubic or lower symmetric structures. The approach used in the context of this work corresponds to a mean field approximation where the molecular-ions are treated in the mean local interaction field of the surrounding ions. In the context of this local model two competing repulsive interactions are governing the onset of the rotational displacive transition (Figure 12): the overlap repulsion of next neighbour chlorines located at different octahedra ($U^{Cl-Cl'}$) and the overlap repulsion of the chlorine with the surrounding cations (U^{A-Cl}). The Coulomb interaction between the different point charges is only slightly changed by the small angle rotation and can be neglected in the context of this treatment. Using the Born-Mayer-approximation the two overlap interactions are expressed by simple exponentials:

$$U^{A-Cl} = B_1 \exp (r_{A-Cl}/\varrho_1)$$

and

$$U^{Cl-Cl'} = B_2 \exp (r_{Cl-Cl'}/\varrho_2).$$

Figure 12 (bottom) shows schematically the variation of the two interaction potentials as a function of rotation angle φ about the fourfold axis of the octahedron. For simplicity this rotation is assumed to induce the transformation. U^{A-Cl} increases continuously with increasing rotation angle φ stabilising the system at

$\varphi = 0$, whereas $U^{Cl-Cl'}$ is passing through a minimum which in a hard sphere model appears at a φ-value of about 15°. The location of the minimum of the total interaction potential obviously depends on the relative contributions of the two overlap interactions. This very simple picture demonstrates the outstanding importance of the interaction potential between the ammonium-ion and the chlorines for the appearance of a lattice instability in the $(NH_4)_2MCl_6$ crystals. As this interaction sensitively depends on the effective charge distribution at a given temperature, in the case of a "delicate balance" between A–Cl and Cl–Cl' interaction the ammonium-ion dynamics must be a crucial property for both the structural stability and the temperature behaviour of the chlorine NQR particularly near a phase transition point.

The condition of "delicate balance" is evidently governed by the geometrical distances (Brown's condition) and by the electron distribution on the octahedron. The latter property seems also of particular importance for the behaviour of the ammonium hexachlorometallates. Rössler and Winter have shown that the phase transition temperatures in alkali-ion hexahalogenometallate compounds scale with the ligand-field stabilisation energy of the transition-metalion [3]. With increasing number of d-electrons the transition temperature is reduced.

A systematic behaviour that follows a similar trend of bonding properties can be attributed to the natural ammonium-ion hexachlorometallate compounds $(NH_4)_2MCl_6$. For metal-ions M^{4+} containing an incomplete d-shell such as Re, Os, Ir, Pt, Pd, the chlorine compounds stay cubic down to helium temperature (Table 1). Closed d-shell metal-ion compounds can undergo a transition such as $(NH_4)_2PbCl_6$ (Pb^{4+}: $5d^{10}$) or the transition is just suppressed as in $(NH_4)_2SnCl_6$ (Sn^4: $4d^{10}$). Octahedra with metal-ions carrying s-valence-electrons (Se^{4+}: $4s^2$, Te^{4+}: $5s^2$) exhibit structural transformations which, in addition, behave markedly different for natural and deuterated ammonium-cations. It should be noted that the barrier height to the ammonium-ion motion as a function of the lattice constant (see Fig. 2) also fits into the already discussed systematic trend based on bonding properties with the possible exception of the selenium compounds.

Proceeding from the supposition of a "delicate balance" between the A–Cl and the Cl–Cl' overlap interactions we now consider the influence of the ammonium-ion dynamics on the lattice stability and chlorine

NQR in the different categories treated in the preceding chapters.

The ammonium-ions in the category 1 compounds experience a low barrier height to rotation. As a consequence NH_4^+ or ND_4^+-ions undergo fast classical or quantum mechanical rotations in the whole temperature range. The effects of the charge distribution of this rotating molecule on the $A-Cl$ overlap interaction is comparable to that of a large alkali cation such as Rb^+. The anomalies observed in the temperature behaviour of the chlorine NQR frequency v_Q and spin-lattice relaxation rate T_1^{-1} can be explained on the same grounds. At high temperatures v_Q and T_1^{-1} are expected to behave similar to normal alkali hexachlorometallates. Deviations from the normal behaviour at low temperatures are attributed to the release of the overlap pressure. The observed increase of the frequency and of the relaxation rates are in agreement with the negative pressure coefficient of both parameters [19]. In addition, as the deuterated ammonium hexachlorometallate has a slightly smaller lattice parameter the measured positive shift of v_Q and of T_1^{-1} on deuteration can at least partially be explained by the same effect.

The ammonium hexachlorometallates which belong to the category 2 are distinguished by the occurrence of a cubic-to-trigonal structural transition. So far only the ammonium-ion compounds with Pb and Te have been found to show this particular transition. In a lattice with spherically shaped cations the most favourable transition from an energetic point of view involves the rotation of the octahedron about one of its fourfold axes as sketched in Figure 12.

This displacement leaves two chlorine-atoms unaffected. Therefore the preference of a rotation about the threefold axis required for the transition to a phase with trigonal symmetry must be related to the presence of the ammonium-ion. We suppose that the steric hindering of the tetrahedral molecule prevents the octahedra from undergoing a rotation about the fourfold axis. This rotation would require either a distortion of the ammonium-tetrahedron or a distortion of the surrounding lattice, which finally occurs at T_{c3} in $(ND_4)_2TeCl_6$. At present we are not able to quantify this hindering potential of the ammonium-ion. Although according to the systematic trend displayed in Fig. 2 the occurrence of a transition to the trigonal phase seems to be related to the barrier height the absence of any remarkable deuteration effect on T_{c1} rules out a mechanism which is based only on the

slowing down of the hindered rotations. The observed anomalies of the chlorine NQR frequency and relaxation rates which are caused by the cubic-to-trigonal transition can be explained on the basis of Landau's theory by a coupling to the order parameter and to soft mode fluctuations as discussed in the Sections 4, 5, and 6.

An unequivocal influence of the ammonium-ion motion on lattice stability must be adopted for the category 3 systems where a strong deuteration effect exists. The deuteration induced phase transitions in $(NH_4)_2TeCl_6$ and $(NH_4)_2SeCl_6$ are attributed to the modification of the $A-Cl$ interaction by the condensation of the deuteron motion. In contrast to our earlier interpretation [12] the tumbling motion of the ammonium-ion around its threefold axis is not further considered to represent the main mechanism. The barrier height for this motion of about 25 K as estimated from the deuteron NMR data is too low to play a significant role in the interesting temperature region. Therefore, the deuteration dependent effects have to be related to the slowing down of the reorientional rotation of the ammonium-ion about its threefold axis. At the third tansition in $(ND_4)_2TeCl_6$ at T_{c3} the localising deuterons may enable the rotation of the octahedron around its fourfold axis. This rotation, which leads to a long range ordered tetragonal structure, must be associated by a considerable c/a lattice distortion in order to reduce the $A-Cl$ overlap interaction. The driving mechanism for the transitions in $(ND_4)_2TeCl_6$ is again the reduction of the $Cl-Cl'$ overlap interaction which is most efficient for a rotation about the fourfold axis. In $(ND_4)_2SeCl_6$ and $(NH_4)_2SeCl_6$ the phase transitions seem to be induced by a similar mechanism as in $(ND_4)_2TeCl_6$. This is probably due to the smaller lattice constant in the selenium compound which leads to a comparatively larger $Cl-Cl'$ interaction potential. The reduction of the $A-Cl$ contribution to the interaction energy by the condensation of the proton or the deuteron then allows a direct transition associated with a rotation of the octahedron about its fourfold axis. We consider the transition at $T_{c3} = 28$ K in $(ND_4)_2TeCl_6$ and that at $T_c = 48$ K in $(ND_4)_2SeCl_6$ to be of the same kind. The structural transition at $T_c = 24$ K in $(NH_4)_2SeCl_6$ is also assumed to be effected by the rotation of the octahedron triggered by the condensation of the protons of the ammonium-ion. The corresponding transformation may possibly exist in $(NH_4)_2TeCl_6$ below liquid helium temperatures.

The situation is more complicated and therefore less clear for the second transition at T_{c2} in $(ND_4)_2TeCl_6$. The anomaly of the spin-lattice and spin-spin-relaxation rate of the Cl-NQR near T_{c2} undoubtedly point towards a supplementary motional effect. The deduced quantitative values of the activation energy and moment of inertia are in favor of additional limited jumps of the $TeCl_6^{2-}$-octahedra. This limited jumps could take place between two minima involving a small angle rotation about one axis of the octahedron. At T_{c2} the system condenses in the minimum of the low temperature phase. A main difficulty is to understand on the basis of this hypothesis the observed deuteration dependence of T_{c2} [31]. The slowing-down of the rotational motion of the ammonium-ion alone cannot account for the large difference between the behaviours of the protonated and deuterated salt and for the existence of deuteration effects at low deuteron concentrations. A possible explanation could be the homogeneous strain field that builds up with deuteron content. The microscopic origin of this strain field is still unknown and its investigation is devoted to the future research work.

8. Conclusions

The influence on the lattice stability of the rotational dynamics of the ammonium-ion in $(NH_4)_2MCl_6$ compounds is analysed on the basis of the results of chlorine NQR investigations. Particular attention has been devoted to the effect of deuteration on the physical properties accessible by the NQR measurement. The intermolecular effects caused by the motion of the ammonium-ion have been discussed in the framework of three main categories of behaviour: Ammonium hexachlorometallate compounds which stay cubic down to liquid helium temperature, systems undergoing a cubic-to-trigonal structural transition, and compounds where deuteration strongly affects the appearance of structural transitions. The first category comprises the $(NH_4)_2MCl_6$ compounds containing the transition metal ions Sn, Pd, Os. In these crystals the chlorine NQR shows deviations from the normal behaviour, particularly at low temperatures, which are explained by the modification of the internal pressure due to the motion of the ammonium-ion. The distinguishing feature of the compounds of the second category is the occurrence of a cubic-to-trigonal phase transition where the single-line chlorine NQR spectrum is retained in the low temperature phase. This type of transition, which has so far been observed only in the tellurium and lead compounds, is attributed to the steric hindering of the ammonium ion which at this temperature prevents the MCl_6^{2-}-octahedra from a rotation about the fourfold axis. The critical behaviour in the vicinity of the transition temperature T_{c1} as investigated by the chlorine NQR can be satisfactorily described on the basis of Landau's theory. A question that still remains open concerns the rather small effect of deuteration on this transition. The category 3 compounds are characterised by a strong influence of deuteration which either induces new phase transitions as observed in $(NH_4)_2TeCl_6$ or leads to a considerable influence on the transition in $(NH_4)_2SeCl_6$ associated with a large shift of the transition temperature. Although the chlorine NQR signal fades out in both compounds when these low temperature transitions are approached from above, the spin-spin and spin-lattice relaxation data provide further information on the microscopic mechanism triggering these transitions. In the scope of a simple model the dramatic effect of deuteration is explained by the influence of the ammonium-ion motion on the delicate balance between the cation-chlorine and chlorine-chlorine overlap interaction which controls the lattice stability of the $(NH_4)_2MCl_6$ crystals.

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