PHYSICAL REVIEW B VOLUME 41, NUMBER 7 1 MARCH 1990

^{2}D NMR and ^{35}Cl nuclear-quadrupole-resonance study of ammonium-ion motion and phase transitions in natural and deuterated $(NH_4)_2TeCl_6$

C. Dimitropoulos
Institut de Physique Expérimentale, Ecole Polytechnique Fédérale de Lausanne, PHB-Ecublens, 1015 Lausanne, Switzerland

J. Pelzl
Institut für Experimental Physik VI, Ruhr Universität, 4630 Bochum, Federal Republic of Germany

F. Borsa
Dipartimento di Fisica "Alessandro Volta" Unita Gruppo Nazional di Struttura della Materio-Centro Interuniversitario di Struttura della Materio e Istituto Nazionale di Física Nucleare, 27100 Pavia, Italy

(Received 18 September 1989)

The ^{35}Cl nuclear quadrupole resonance (NQR) and the quadrupole perturbed ^{2}D NMR have been investigated in $(ND_4)TeCl_6$ in the temperature range 4.2–85 K. The ^{2}D spin-lattice relaxation rate shows a classical maximum at about 80 K and a broad peak at about 25 K, which is attributed to the influence of a phase transition at the same temperature. An extra contribution to the chlorine NQR spin-lattice relaxation rate is observed near the cubic-to-trigonal transition at 85 K. The disappearance of the NQR signal before the second transition at about 42 K is accompanied by a divergence of the spin-spin relaxation rate. The results are discussed in terms of a localization of the deuterium in a triangle-shaped potential well in the plane perpendicular to the N—D bond direction.

I. INTRODUCTION

From previous investigations[1,2] of $(NH_4)_2TeCl_6$ and $(ND_4)_2TeCl_6$ by Raman scattering and chlorine nuclear quadrupole resonance (NQR) and relaxation it was found that both compounds undergo a structural phase transition at 85 K. On the basis of the ^{35}Cl NQR spectrum and the low-temperature Raman scattering results it was concluded that the transition involves rotations of the $TeCl_6{}^{2-}$ octahedra around a trigonal axis ($\langle 111 \rangle$ pseudocubic axis) leading to a change from a high-temperature cubic structure (space group $Fm3m$) to a low-temperature trigonal phase (space group $R\bar{3}$). Whereas $(NH_4)_2TeCl_6$ shows no indication for further transitions at lower temperature, the appearance of new lines in the Raman spectrum of $(ND_4)_2TeCl_6$ gave a strong indication for additional structural changes occurring below 85 K.[2] This unusual isotope effect indicates that, contrary to the other ammonium hexachlorometallates, there is here a strong coupling between the $TeCl_6{}^{2-}$ octahedra and the orientation of the $ND_4{}^{+}$ tetrahedra. In order to investigate the origin of this coupling and the influence of $ND_4{}^{+}$-ion reorientation on the phase transitions, we have performed additional measurements of ^{35}Cl NQR and spin-lattice relaxation and of ^{2}D quadrupole perturbed spectra and spin-lattice relaxation, with particular emphasis on the temperature region below 85 K.

In Sec. II the correlation time for the "classical" ammonium-ions reorientation process is derived from ^{1}H and ^{2}D spin-lattice relaxation measurements. Furthermore, it is shown that the analysis of the quadrupole perturbed ^{2}D NMR spectrum yields the temperature dependence of the rotational tunneling frequency for the $ND_4{}^{+}$ ion.

The ^{35}Cl NQR and the ^{2}D NMR data presented in Sec. III give clear evidence for a disorder in the orientation of ammonium ions and for additional structural phase transitions at $T < 85$ K, in agreement with the results of Raman scattering and specific-heat data.[3]

II. REORIENTATION AND ROTATIONAL TUNNELING OF AMMONIUM IONS

At sufficiently high temperatures, i.e., $T > 50$K, the reorientation of the ammonium ion in $(NH_4)_2MCl_6$ compounds can be described by a classical random motion characterized by a correlation time. At low temperature the hindered molecular motion must be treated quantum mechanically, introducing the concept of a tunneling frequency.[4]

A. Classical regime of hindered rotation

From the proton spin-lattice relaxation rate T_1^{-1} measurements shown in Fig. 1, one can derive the correlation time τ_H for the reorientation of $NH_4{}^{+}$ ions in $(NH_4)_2TeCl_6$. In fact, the proton relaxation is mainly controlled by H-H intradipolar interaction modulated by $NH_4{}^{+}$ reorientation yielding for T_1 (Ref. 5)

$$T_1^{-1} = \tfrac{2}{3} C_1 \langle \Delta\omega_d^2 \rangle \left[\frac{\tau_H}{1+\omega_0^2\tau_H^2} \frac{4\tau_H}{1+4\omega_0^2\tau_H^2} \right], \qquad (1)$$

where C_1 is a dimensionless constant of order unity that depends on the details of the motion and

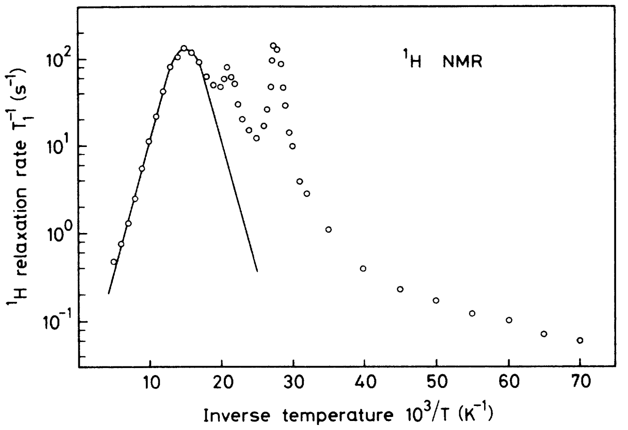

FIG. 1. ^{1}H nuclear spin-lattice relaxation rate vs temperature in $(NH_4)_2TeCl_6$ at the resonance frequency $\nu_0 = 15.07$ MHz. The full line is the theoretical curve according to Eqs. (1) and (2) in the text.

$$\langle \Delta\omega_d^2 \rangle = \tfrac{3}{5}\gamma^4 \hbar^2 I(I+1) \sum_k \frac{1}{r_{jk}^6}$$

is the proton intramolecular dipolar second moment for a crystalline powder that can be estimated to be approximately 3×10^{10} s^{-2} for NH_4^+. By fitting the experimental data with Eq. (1) and assuming

$$\tau_H = \tau_H^o \exp\left[\frac{E_A}{T}\right], \tag{2}$$

one has

$$E_A = 670\pm30 \text{ K}, \tau_H^o = 3.10^{-13} \text{ s},$$

and

$$\langle \Delta\omega_j^2 \rangle = 1.4\times10^{10} \text{ s}^{-2} \quad (C_1 = 1) .$$

The additional peaks in Fig. 1 are due to tunneling assisted relaxation.

The correlation time τ_D for the ND_4^+-ion reorientation can be obtained in the same way from the ^{2}D spin-lattice relaxation data shown in Fig. 2. In this case the relaxation is driven by the coupling of the deuteron quadrupole moment Q with the intramolecular fluctuating electric field gradient (EFG) of the reorienting ND_4^+ group, and T_1 is given by[6]

$$T_1^{-1} = \tfrac{24}{720}\langle \omega_Q^2 \rangle \left[\frac{\tau_D}{1+\omega_0^2\tau_D^2} + \frac{4\tau_D}{1+4\omega_0^2\tau_D^2}\right] . \tag{3}$$

From the fit of the experimental data in Fig. 2 with Eq. (3) and Eq. (2) one has

$$E_A = 790\pm30 \text{ K}, \quad \tau_D^0 = 10^{-13}\text{s} ,$$

and

$$\langle \omega_Q^2 \rangle = 2.15\times10^{12} \text{ s}^{-2}.$$

The effective root-mean-square quadrupole interaction found here, i.e.,

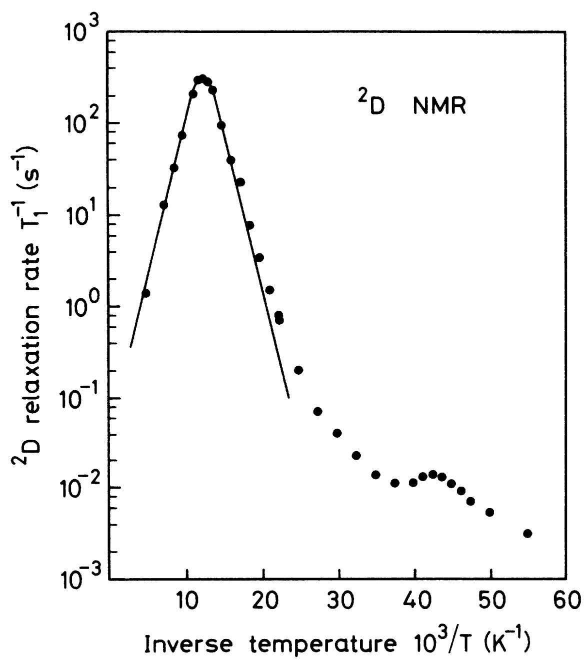

FIG. 2. ^{2}D nuclear spin-lattice relaxation rate vs temperature in $(ND_4)_2TeCl_6$ at the resonance frequency $\nu_0 = 52.4$ MHz. The full line is the theoretical behavior according to Eq. (3) of the text.

$$\langle \omega_Q \rangle^{1/2} = 1.5\ 10^6 \text{ s}^{-1}$$

compares very well with the static quadrupole coupling frequency

$$\omega_Q = \frac{3}{2}\frac{e^2qQ}{\hbar} = 1.7\times10^6 \text{ s}^{-1}$$

typically found in ND_4^+ groups.[7,8] It should be noted from Fig. 2 that neither an anomaly is observed in the ^{2}D relaxation rate at the phase transition temperature 85 K nor a noticeable change in the activation energy for the ND_4^+ reorientation for $T < 85$ K.

B. Tunneling regime

The effect of rotational tunneling on the ^{1}H spin-lattice relaxation in ammonium salts has been widely investigated.[9] The tunneling frequency can be determined from T_1^{-1} measurements in two limiting cases: (a) $\bar{\nu}_t \gg \nu_0$: a frequency-independent maximum or hump is observed from which one can derive a very qualitative estimate of $\bar{\nu}_t$; (b) $\bar{\nu}_t = \nu_0$ or $\bar{\nu}_t = 2\nu_0$: a distinct peak in T_1^- can be observed as a function of measuring frequency; furthermore, in the temperature region in which ν_t is a rapidly varying function of T, a frequency dependent peak can be observed as a function of temperature when the condition $\nu_t(T) = \nu_0$ or $2\nu_0$ is fulfilled. From the data in Fig. 2 it appears that this is the case in $(ND_4)_2TeCl_6$. Then from the two peaks in Fig. 1 we obtain

$$\nu_t \cong \nu_0 = 15 \text{ MHz} \quad \text{at } T \cong 47 \text{ K},$$

$$\nu_t \cong 2\nu_0 = 30 \text{ MHz} \quad \text{at } T \cong 37 \text{ K} .$$

The above values can be compared with the exact tunneling frequencies obtained by inelastic neutron scattering in $(NH_4)_2SnCl_6$, namely, $\nu_t = 720$ MHz at $T = 0$ K and $\nu_t \cong 500$ MHz at $T = 40$ K. The values found in the Te compound are 1 order of magnitude smaller, in qualitative agreement with the fact that the activation energy for the NH_4 reorientation in the Te compound is higher than in the Sn compound (see Table I). For the case of $(ND_4)_2TeCl_6$ the orientation tunneling frequency is too small to be derived from ^{2}D T_1 data. However, as will be shown later, the tunneling frequency can be measured in this case from the analysis of the quadrupole perturbed ^{2}D NMR powder spectrum by using recent theoretical calculations.[10] Let us start by recalling that, when the reorientation correlation frequency τ_D^{-1} for ND_4^+ becomes smaller than the intramolecular quadrupole interaction frequency ω_Q, one should normally observe a powder pattern with two peaks at $\pm\nu_Q/4$ symmetrically located with respect to the Larmor frequency ν_0.[6] From the preceding estimate of τ_D one expects $\tau \cong \omega_Q^{-1}$ for $T \cong 50$ K. In agreement with this, starting just below 70 K the ^{2}D NMR signal loses intensity because of the broadening associated with the slowing down of the ND_4^+ reorientations. However, for $T < 40$ K the quadrupole perturbed ^{2}D powder spectrum is not observed, because quantum-mechanical motional narrowing takes over and the spectrum is typical of rotational tunneling effects (see Fig. 3). These effects have been recently analyzed for ^{2}D NMR spectra in powders of $(ND_4)_2SnCl_6$.[10] It has been shown that from the splittings of the inner doublets of the ^{2}D NMR spectrum (see Fig. 3) as a function of temperature one can derive the tunneling frequency ν_t. In $(ND_4)_2TeCl_6$, the splitting of the otherwise degenerate rotational tunneling T levels is probably larger than in the Sn compound because of the trigonal distortion occurring below 85 K. Thus the ^{2}D NMR spectrum in powders is not well resolved except for the two A doublets coming from the A symmetry species. The experimental values of the splittings (Fig. 3) were fitted to the theoretical results for the separations S between doublets of A and E symmetry species in the ^{2}D NMR spectra in high fields. (See Ref. 10, Figs. 2 and 3). From this comparison, we have estimated the temperature dependence of the tunneling frequency as shown in Fig. 4. In this figure values obtained in $(ND_4)_2TeCl_6$ are also compared with those obtained in the $(ND_4)_2SnCl_6$ salt.[11] The temperature dependence is remarkably the same in both systems, while the tunneling frequency in the Te compound is five times smaller than in the Sn compound, in agreement with the fact that the energy barrier for reorientation is larger in the first case (see Table I).

TABLE I. Summary of parameters for ammonium ions reorientation and tunneling.

System	E_A (K)	$\bar{\nu}_t(T)$ (MHz)	τ_0 (s)
$(NH_4)_2TeCl_6$	670±30	30 (37 K)	3×10^{-13}
$(ND_4)_2TeCl_6$	790±30	1.5 (0 K)	1×10^{-13}
$(NH_4)_2SnCl_6$	600±30[a,b]	720[a] (0 K)	2.6×10^{-13}
$(ND_4)_2SnCl_6$	750±30[c]	7.5[c] (0 K)	0.6×10^{-13}

[a] M. Prager, W. Press, B. Alefeld, and A. Müller, J. Chem. Phys. **67**, 5126 (1977).

[b] J. Strange and M. Terenzi, J. Phys. Chem. Solids **33**, 923 (1972).

[c] Reference 11.

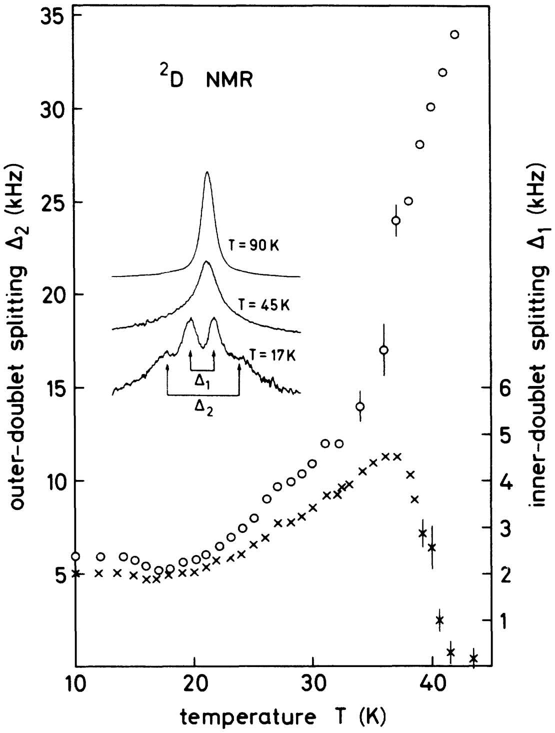

FIG. 3. ^{2}D quadrupole perturbed NMR spectrum at 52.4 MHz in polycrystalline $(ND_4)_2TeCl_6$. The splittings Δ_1 (×) and Δ_2 (○) of the two resolved doublets are plotted as a function of temperature.

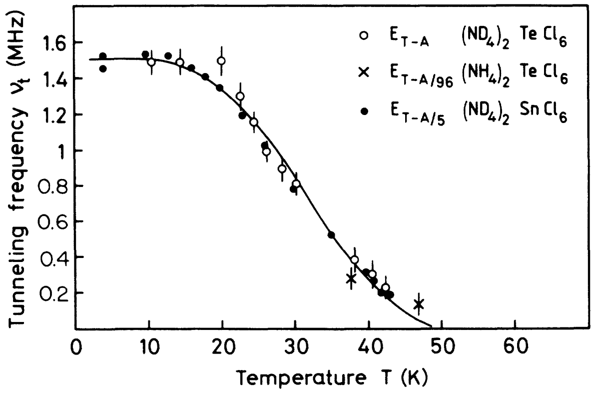

FIG. 4. Tunneling frequency ν_t vs temperature in various samples. The frequency measures the energy separation between the A level and the average position of the T levels in the rotational tunneling spectrum. In order to facilitate the comparison of the data from the different samples, they have been normalized to the values of ν_t for ND_4^+ in $(ND_4)_2TeCl_6$. Note that the normalization factor 96 corresponds to the isotopic effect factor.

III. ORIENTATION OF $ND_4{}^+$ IONS AND PHASE TRANSITIONS IN $(ND_4)_2TeCl_6$ BELOW 85 K

In the previous section we have discussed the data regarding the dynamics of $NH_4{}^+$ ions that do not bear directly on the problem of the phase transitions present in the deuterated compound below 85 K. In this section we concentrate on the data that give clear evidence for such phase transitions, and a model is suggested for the unusual isotope effect observed in the hexachlorotellurates.

A. ^{35}Cl NQR and spin-lattice relaxation

The ^{35}Cl NQR line was detected near 15 MHz. The temperature dependence of ν_Q display a slope discontinuity at about 85 K in both natural and deuterated hexachlorotellurates. At the same temperature a peak is observed in the relaxation rates. The relevance of these results with respect to the trigonal distortion have been already discussed.[1]

At even lower temperature an isotope effect was observed, whereby in $(ND_4)_2TeCl_6$ (but not in the natural compound) the signal broadens and T_2 becomes very short until about 42 K, where the ^{35}Cl signal disappears altogether. The temperature dependence of the ^{35}Cl spin lattice, T_1^{-1}, and spin spin T_2^{-1}, relaxation rates are shown in Fig. 5. Another distinctive feature of the deuterated compound is the shoulder displayed in the T_1^{-1} versus T curve just below T_c (see Fig. 5). We argue that both the relaxation rate behavior and the disappearance of the ^{35}Cl NQR signal can be explained in terms of a disorder in the $ND_4{}^+$ ion orientations of the type of the one observed in cubic $(NH_4)_2SiF_6$ by inelastic neutron scattering[12] and later confirmed by NMR.[13] The relative orientation of the $ND_4{}^+$ tetrahedra and the $TeCl_6^{2-}$ octahedra is sketched in Fig. 6. If the interchange of D atoms due to the reorientations around the four three-fold axes C_3 were among positions lying on the $\langle 111 \rangle$ cubic diagonal, the EFG at the ^{35}Cl site would be the same for all 12 equilibrium positions. Then the only modulation of the EFG would be during the transit time. An estimate of the contribution to relaxation from this mechanism is given in Ref. 14, and it turns out to be negligible in the present case. On the other hand, if one assumes, as in $(NH_4)_2SiFe_6$, that the $ND_4{}^+$ ions have their stable positions on a triangular shaped region of about 1 Å on the surface of a sphere perpendicular to the N–D bond direction, then reorientations of the $ND_4{}^+$ ions leading to interchange of D atoms among the different equilibrium positions would produce a modulation of the EFG at the ^{35}Cl site. The corresponding intermolecular contribution to relaxation can be described approximately by

$$T_1^{-1} = \langle \Delta\omega_Q^2 \rangle \frac{\tau_D}{1+\omega_Q^2\tau_D^2} \ . \qquad (4)$$

The difference between the ^{35}Cl T_1^{-1} in $(ND_4)_2TeCl_6$ and $(NH_4)_2TeCl_6$ is also plotted in Fig. 5 and compared with the fit according to Eq. (4). The parameters ob-

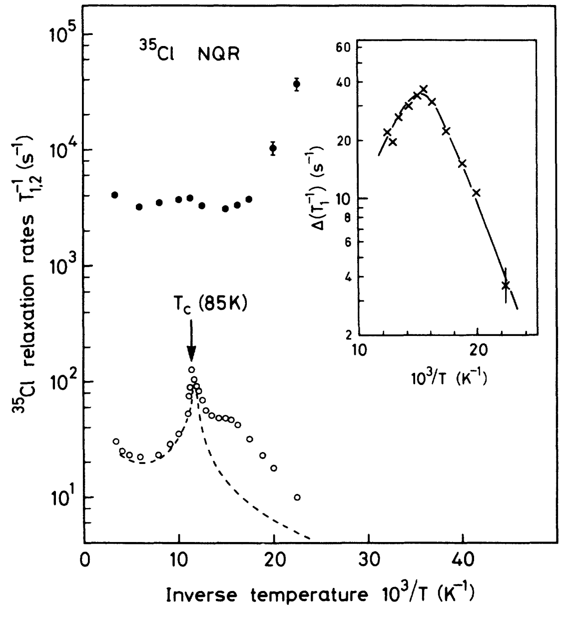

FIG. 5. ^{35}Cl NQR nuclear spin-lattice (○) T_1^{-1} and spin-spin (●) T_2^{-1} relaxation rates vs temperature in $(ND_4)_2$ $TeCl_6$. The dashed line corresponds to the results in the natural $(NH_4)_2TeCl_6$ compound. In the inset we have plotted the difference $\Delta(T_1^{-1})$ (×) between the values in the natural and deuterated compound. The full line is the theoretical behavior according to Eq. (4) in the text.

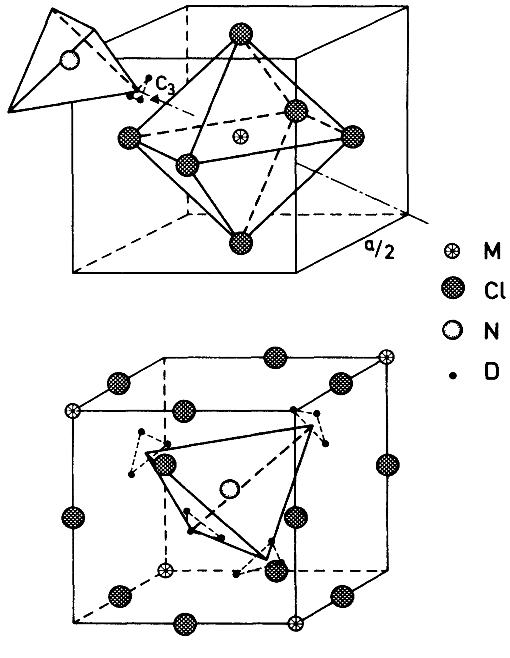

FIG. 6. Sketch of the relative orientation of $ND_4{}^+$ tetrahedra and $TeCl_6{}^{2-}$ octahedra, with the three equivalent positions of H (D) atoms characterizing the dynamic disorder.

tained from the fit are

$$E_A \cong 400\text{K}, \quad \tau_D^0 = 2.5\times 10^{-11}\ \text{s} ,$$

and

$$\langle \Delta\omega_Q^2 \rangle = 6.3\times 10^9\ \text{s}^{-2}.$$

These values are consistent with a model of small rotations of the $ND_4{}^+$ groups over the triangular-shaped region. In fact, it is quite likely that there are three equilibrium positions of the $ND_4{}^+$ groups corresponding to the D atom pointing more towards one near neighbor Cl ion (see Fig. 6) with shallow potential minima and low-energy barriers in between. It should be noted that the effective intermolecular quadrupole interaction $\langle \omega_Q^2 \rangle$ derived earlier corresponds to a static quadrupole frequency $\nu_Q \cong 10$ kHz, which is too small to justify the dramatic shortening of T_2^{-1} (see Fig. 5) and the disappearance of the NQR signal. In fact, a careful search for an inhomogeneously broadened ^{35}Cl NQR spectrum ($\gtrsim 10$ kHz wide) at low temperature was unsuccessful.

Thus we are led to conclude that a large intramolecular change in the EFG must take place at $T \cong 42$ K, with a concommittant nonuniform distribution of EFG at the ^{35}Cl site. This conclusion points towards a nonuniform distortion of the $TeCl_6{}^{2-}$ octahedra, with a modulation of the order parameter that must encompass several lattice units.

It should be noted that around the same temperature at which the ^{35}Cl NQR signal disappears, new Raman lines can be observed both in the spectrum of the internal tetrahedral and of the octahedral modes.[3]

B. ^{2}D spin-lattice relaxation rate

As we have shown in Sec. II, the ^{2}D relaxation rate (see Fig. 2) is dominated over much of the temperature range by the fluctuations of the intramolecular EFG due to the reorientations along the four C_3 axes. No effect can be detected of the phase transition at 85 K or of the disorder of the $ND_4{}^+$ group. Furthermore, the temperature dependence of the tunneling frequency (Fig. 4) is the same in $(ND_4)_2TeCl_6$ and in $(ND_4)_2SnCl_6$, suggesting that the rotational tunneling is not affected appreciably by the exact position of the D in the equilibrium position. On the other hand, a secondary maximum in T_1^{-1} at about 25 K is evident in the data of Fig. 2. This maximum cannot be ascribed to the reorientation motion of $ND_4{}^+$ groups because at 25 K this is already too slow. Also, a tunneling maximum can be ruled out because it would imply a very high tunneling frequency.

IV. DISCUSSION

Recent Raman scattering studies and x-ray diffraction measurements have proved the occurrence of two additional transitions in $(ND_4)_2TeCl_6$.[3] The diagram in Fig. 7 outlines the actual knowledge on the transformations in the natural and deuterated hexachlorotellurates. The anomaly of the ^{35}Cl NQR relaxation rates at about 40 K (Sec. III A) and the maximum in the deuteron spin-lattice relaxation rate at about 25 K (Sec. III B) have already been related to the two transitions leading to phase III and phase IV, respectively. Whereas the space group of phase II could be identified on the basis of the NQR (Ref. 2) and inelastic light scattering results,[1] the symmetries of the two low-temperature phases in the deuterated compound are still unknown. But there are strong indications by the ND_4 Raman spectra and the present ^{35}Cl NQR data that the ordering of the ammonium ions are involved in these phase transitions.

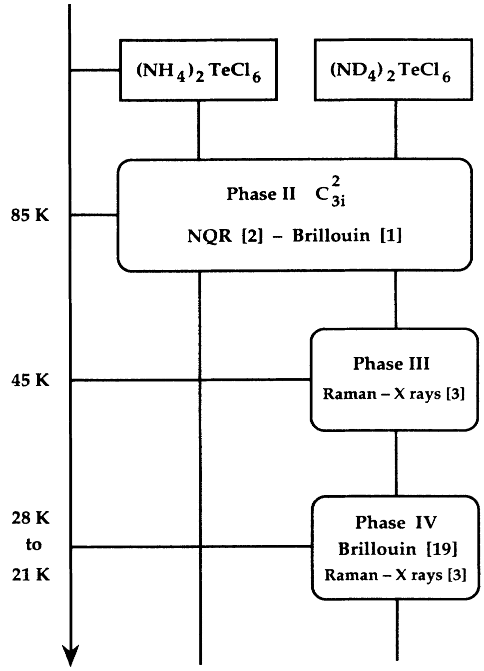

FIG. 7. Diagram showing the phase transitions in natural and deuterated ammonium hexachlorotellurate as identified by different techniques (references indicated).

At the transition at about 45 K new Raman lines in the internal and external mode spectrum appear and the splitting and the intensities gradually increase as the temperature is lowered.[1,3] The Raman observations point towards a second-order type transition at 45 K leading to a considerably enlarged unit cell or an incommensurate structure. Between 21 and 28 K the Raman pattern changes abruptly and exhibits a hysteresis in accordance with a first-order transition.[3]

In view of the present results, we propose the following interpretation of the two transitions in the scope of the model already sketched in Sec. III A and Fig. 5: The hydrogen or deuterium that is associated with three chlorine atoms at the corners of an equilateral triangle experiences a trifurcated hydrogen bond.[15] With increasing lattice constant and decreasing temperature the effective free space available for the hydrogen in the chlorine triangle becomes larger, enhancing the tendency for a directed hydrogen bond that would be accompanied by a transition to a lower symmetry involving a small rotation and probably also a deformation of the $TeCl_6^{2-}$ octahedra. In the $(NH_4)_2MCl_6$ family the lattice constant and the barrier to rotation of the ammonium increase in the sequence from $M = \mathrm{Pd}$ to $M = \mathrm{Te}$.[16] The trifurcation may be considered as a dynamical disorder of the hydrogen moving in the triangle shaped potential and the transition as the localization of the hydrogen at one of the three shallow potential minima. In $(NH_4)_2TeCl_6$ and in the other chlorometallates this localization is prevented by a fast classical and quantum motion of the hydrogen or deuterium, respectively. Only the case of the tellurium compound with heavy ammonium-ion localization becomes possible. Therefore the isotope effect in $(NH_4)_2TeCl_6$ seems to be due to the slower motion of the deuterium as compared to that of the hydrogen. As a consequence the probability for tunneling at low temperatures or for classical rotation at more elevated temperatures between the three minima is reduced, giving rise to the anomalies in the chlorine NQR relaxation rates (Sec. III). The underlying mechanism of perturbation could be the forming and breaking of the hydrogen bond.[17]

With further decreasing temperature the free space of the deuterium becomes larger favoring the directed hydrogen bond. The transition at 45 K in $(ND_4)_2TeCl_6$ (Fig. 7) is interpreted as a result of the localization of the deuterium in a shallow minimum near one of the chlorines but no long-range correlation is developed. This disorder could give rise to the already mentioned incommensurate structure and the strong perturbation of the NQR signal. A long-range correlation of the ND_4^+ induced local distortions is established at the transition at about 25 K. The Raman spectra indicate that in phase IV the inversion symmetry has been lost. The broad peak in the ^{2}D relaxation rate occurring at the same temperature (see Fig. 2) yields indication that the transition to phase IV is accompanied by critical collective fluctuations in the dynamics of deuterons.[18]

V. CONCLUSION

Natural and the deuterated $(NH_4)_2TeCl_6$ behave very similar at temperatures above 50 K. Both compounds undergo the same structural transformation at 85 K from the cubic to a trigonal symmetry. But at lower temperatures a distinct isotope effect is observed. In the deuterated compound at least two additional transitions at about 45 K and about 25 K had been identified by inelastic light scattering. Quadrupole perturbed ^{2}D NMR and the chlorine 35 NQR have been applied in this work to study the origin of these isotope induced phase transitions in $(ND_4)_2TeCl_6$. The anomalies observed in the ^{35}Cl NQR lead to a model of a hydrogen moving in a triangle shaped shallow potential well formed by the adjacent chlorine ions. The phase transitions occurring only in the deuterated compound are accounted for a localization of the deuterium in one of the wells, whereas the hydrogen in the same crystal rests still trifurcated down to the lowest temperature because of its fast classical and quantum motion.

---

[1] U. Kawald, S. Müller, J. Pelzl, and C. Dimitropoulos, Solid State Commun. **67**, 239 (1988).

[2] C. Dimitropoulos and J. Pelzl, Z. Naturforsch. Teil A **44**, 109 (1989).

[3] S. Müller, U. Kawald, J. Pelzl, and C. Dimitropoulos, Proceedings of Phonons **89**, Heidelberg, Germany, 1989 (unpublished).

[4] M. M. Pintar, *NMR Basic Principles and Progress* (Springer-Verlag, Berlin, 1976), Vol. 13; see also M. Punkkinen, J. Magn. Res. **19**, 222 (1975).

[5] D. E. O'Reilly, E. M. Peterson, and T. Tsang, Phys. Rev. **160**, 333 (1967).

[6] A. Agragam, *Principles of Nuclear Magnetism* (Oxford University Press, New York, 1961).

[7] D. E. O'Reilly and T. Tsang, J. Chem. Phys. **46**, 1291 (1967).

[8] R. R. Kispel, H. E. Petch, and M. M. Pintar, J. Chem. Phys. **56**, 676 (1970).

[9] I. Svare, J. Phys. C **10**, 4137 (1977); I. Svare, A. M. Raaen, and G. Thorkildsen, *ibid.* **11**, 4069 (1978).

[10] L. P. Ingman, E. Koivula, Z. T. Lalowicz, M. Punkkinen, and E. E. Ylinen, J. Chem. Phys. **88**, 58 (1988).

[11] L. P. Ingman, E. Koivula, Z. T. Lalowicz, M. Punkkinen, and E. E. Ylinen, Z. Phys. B **66**, 363 (1987).

[12] E. O. Schlemper, W. C. Hamilton, and J. J. Rush, J. Chem. Phys. **44**, 2499 (1966).

[13] R. Blinc and G. Lahajnar, J. Chem. Phys. **47**, 4146 (1967).

[14] C. Dimitropoulos and J. Pelzl, J. Mol. Struct. **58**, 107 (1980).

[15] O. Knop, I. A. Oxton, and M. Falk, Can J. Chem. **57**, 404 (1979).

[16] M. Prager, A. M. Raaen, and I. Svare, J. Phys. C **16**, L181 (1983).

[17] K. Negita, N. Nakamura, and H. Chihara, Chem. Phys. Lett. **63**, 187 (1979).

[18] A. Rigamonti, Adv. Phys. **33**, 115 (1984).

[19] U. Kawald (private communication).

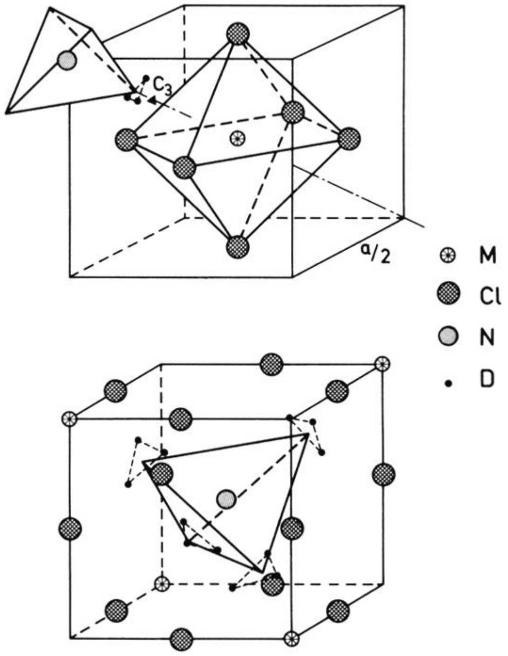

FIG. 6. Sketch of the relative orientation of ND_4^+ tetrahedra and $TeCl_6^{2-}$ octahedra, with the three equivalent positions of H (D) atoms characterizing the dynamic disorder.