Chlorine-NQR Relaxation Near the Structural Transitions of Natural and Deuterated $(NH_4)_2TeCl_6$*

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Z. Naturforsch. **47a**, 261–264 (1992); received July 27, 1991

The temperature and isotope dependence of the ^{35,37}Cl-NQR spin-lattice relaxation rate near the cubic to trigonal phase transition at $T_{c_1} \cong 87$ K has been investigated in both $(NH_4)_2TeCl_6$ and $(ND_4)_2TeCl_6$ salts. In the temperature range of ~20 K above and ~10 K below T_{c_1}, the relaxation obeys the relation $(T_1 \cdot T)^2 \propto (T - T_{c_1})$. This behaviour corresponds to a direct relaxation mechanism in presence of a strongly damped rotational soft mode of the $TeCl_6^{2-}$ tetrahedra and is discussed on the basis of cation-anion coupling near the critical region. Below T_{c_1} we observe an extra contribution to the ^{35,37}Cl relaxation rate which is tentatively ascribed to the dynamics of the NH_4^+ tetrahedra.

PACS numbers: 76.60.Gv, 76.60.Es, 64.60.Ht.

Introduction

The natural and deuterated ammonium hexachlorotellurate $(NH_4)_2TeCl_6$ has, at room temperature, the same cubic antifluorite crystal structure as the A_2BX_6 compounds. This structure belongs to the space group O_h^5 (Fm3m) and is characterized by a face-centered cubic arrangement of the BX_6^{2-} octahedra surrounded by a single cubic cage of A^+ ions [1]. Normally, most of the A_2BX_6 hexahalometallates undergo a displacive transition involving a tetragonal distortion accompanied, by the softening of a rotary phonon mode of the BX_6^{2-} octahedra [2]. On the other hand, in the $(NH_4)_2TeCl_6$ and $(ND_4)_2TeCl_6$ crystals studied here, a structural transition at $T_{c_1} \sim 85$ K, associated to a trigonal distortion was found from chlorine-NQR and Raman scattering [3–5]. The distinctive feature of this transition compared to the others occuring in A_2BX_6 antifluorites, is that all halogens remain at equivalent sites below T_c. Thus, a single chlorine-NQR line is observed through the transition, providing an ideal system to investigate the critical dynamics above and below T_c. Furthermore, unusual isotope effects on its structural phase transition have been reported whereby, on deuteration two additional transformations are induced below 80 K, which have been explained by a condensation of the deuteron motion in a triangular shaped potential [6, 7].

Here we report on a detailed study of the critical behavior of the ^{35,37}Cl-NQR relaxation in the vicinity of T_{c_1} aimed at investigating the effect of the coupling between the anion $TeCl_6^{2-}$ octahedra and the cation NH_4^+ tetrahedra on the rotary soft mode, with particular regard to the isotope dependence of this coupling.

Experimental

Measurements of the NQR frequency and relaxation were performed using a modified Bruker SXP-100 spectrometer and an Oxford CF-200 continuous flow cryostat. The temperature of the samples was stabilized to better than 0.1 K. Single crystals and polycrystalline samples of $(NH_4)_2TeCl_6$ and $(ND_4)_2TeCl_6$ were prepared by precipitation in aqueous solutions. Deuterated crystals have been prepared using DCl and D_2O. The degree of deuteration has been monitored by Raman scattering from the internal ammonium ion modes.

Results

The temperature dependence of the ^{35}Cl-NQR frequency ν_Q is shown in Fig. 1 for the natural and deuterated (~95%) compounds. In both cases, the

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* Presented at the XIth International Symposium on Nuclear Quadrupole Resonance Spectroscopy, London, U.K., July 15–19, 1991.

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structural phase transition is marked by a discontinuity in the slope of ν_Q versus T. On deuteration, T_{c_1} is slightly shifted to lower temperature, i.e. from 88 K to 86 K. The absolute values of ν_Q show also only a small isotope effect, indicating that the influence of deuteration on the static average electric field gradient (efg) at the chlorine site is rather small. On the other hand, the dynamical effects of deuteration are more pronounced as evidenced by the temperature dependence of the NQR relaxation rate near T_{c_1} (see Figure 2).

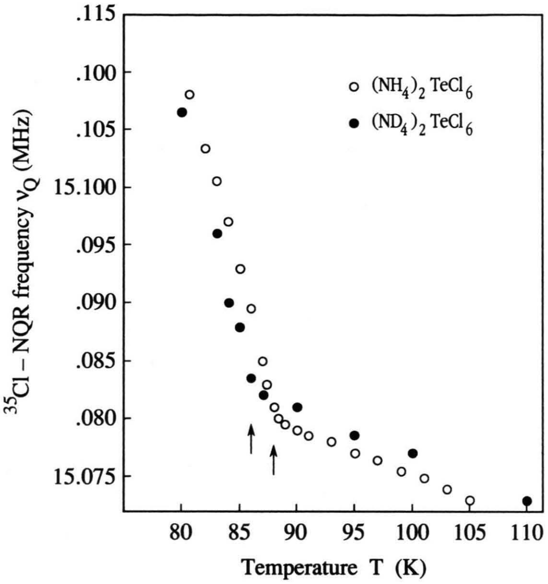

Fig. 1. ^{35}Cl-NQR frequency ν_Q vs. temperature in natural and deuterated hexatellurates. The arrows indicate the temperatures of the structural transition.

Below T_{c_1}, a shoulder appears, which is not directly related to the rotary soft mode as will be discussed further on. The ratio of the relaxation rate for the two chlorine isotopes is constant through the transition and very close to the ratio ($\cong 1.6$) of the squares of their quadrupole moments Q, indicating that the relaxation mechanism is driven by small fluctuations of the quadrupole interaction.

Discussion and Conclusions

The enhancement of the relaxation rate near T_{c_1} is normally related to the anomalous temperature dependence of generalized unstable lattice modes near a structural ferro-distortive phase transition [3, 6]. Since the relaxation rates of the ^{35,37}Cl isotopes scales as Q^2 (see Fig. 2), a perturbative approach which relates the relaxation transition probabilities to the nuclear spin-phonon-scattering, is appropriate near T_{c_1} (weak collision limit). This sitation is to be compared to the one occuring at temperatures above 300 K, where an enhancement of T_1^{-1} is observed, due to sudden and slow 90° reorientations of the $TeCl_6^{2-}$ octahedra. In this case the relaxation rates are identical for both chlorine isotopes, since the mechanism involves a change of the total quadrupole hamiltonian (strong

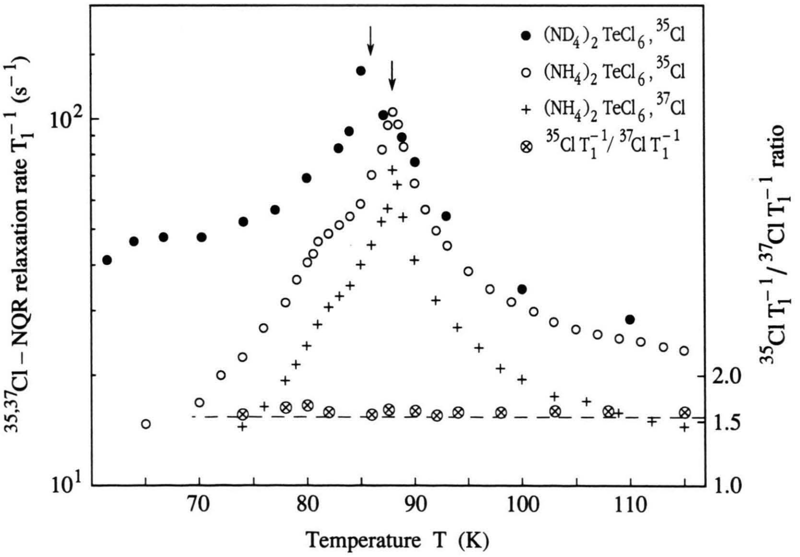

Fig. 2. ^{35,37}Cl-NQR relaxation rate vs. temperature in hexatellurates. The arrows indicate the temperature of the structural transition. The dashed line corresponds to the ratio of the square of the quadrupole moments for the two Cl isotopes.

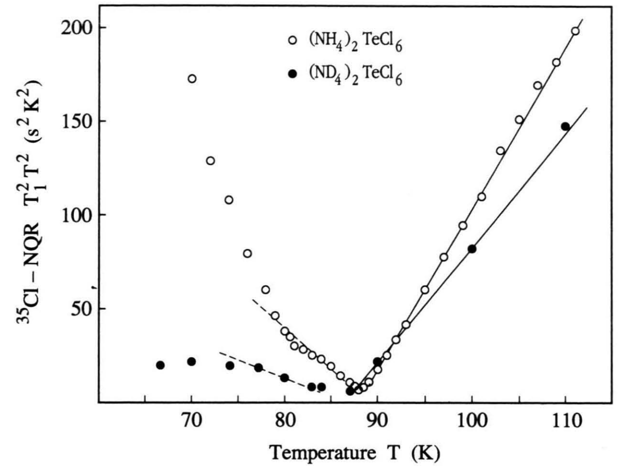

Fig. 3. Plot of $(T_1\,T)^2$ vs. temperature for the hexatellurates. The straight lines correspond to the fit to the critical behavior $T_1^{-1} \propto (T-T_{c_1})^{1/2}$.

collision limit) leading to a relaxation rate T_1^{-1} which yields directly the reorientation rate τ^{-1} [8].

The analysis of the experimental results in Fig. 3 indicates that the relaxation rate diverges at $T \rightarrow T_c$ according to a power law

$$T_1^{-1} = AT/(T-T_c)^{1/2}. \qquad (1)$$

The coupling coefficient A is different in the cubic and the trigonal phases and depends on the degree of deuteration. The power law of (1) corresponds to the theoretical prediction obtained by considering a dominant relaxation mechanism due to a direct spin-phonon process in presence of overdamped generalized soft mode [10]. The square root singularity is characteristic of an isotropic interaction as one would expect in the present case, if the efg at the chlorine site were modulated by rotational vibrations of the $TeCl_6^{2-}$ octahedra around each of the three equivalent pseudo-cubic [1, 0, 0] axes with equal probability. A generalized soft mode made up of linear combination of equal amplitude rotational vibrations around any of the [1, 0, 0] axes is consistent with the trigonal symetry of the frozen-in phase below T_{c_1}. It should be emphasized that in the K_2OsCl_6 salt, where the soft mode is only weakly damped, the divergence of T_1^{-1} at T_c, is found to obey a $(T-T_c)^{-1}$ law as predicted for a Raman two-phonon relaxation mechanism appropriate in the case of underdamped soft modes [10, 11]. Thus one can conclude that the coupling between the $TeCl_6^{2-}$ octahedra and the NH_4^+ tetrahedra causes an enhanced damping of the rotary soft mode. This conclusion is strongly supported by recent Raman scattering measurements, showing an overdamping of the librational soft mode of the $TeCl_6^{2-}$ octahedra near the critical region [12]. The values of the constant A in (1) as deduced from the reciprocal of the slopes of the straight lines in Fig. 3 are: $A = 0.34$ ($sec^{-1}\,K^{-1/2}$) for $(NH_4)_2TeCl_6$ and $A = 0.4$ ($sec^{-1}\,K^{-1/2}$) for $(ND_4)_2TeCl_6$. If one assumes that the dominant effect on the coefficient A comes from the width Γ of the rotary soft mode, $A \propto \Gamma$ [10], one can tentatively conclude that the effect of deuteration is on increasing the damping of the soft mode.

We consider now briefly the origin of the shoulder displayed in the T_1^{-1} versus T curve just below T_{c_1} which is particularly pronounced for the deuterated compound. At is was argued previously [7], this shoulder is due to an extra contribution to the chlorine-NQR relaxation rate, associated with the modulation of the efg during the tumbling motion of the NH_4^+ tetrahedra among three equivalent positions in a triangular shape potential. It is plausible, that the less pronounced shoulder observed in the natural salt is due to the same mechanism. The fact that this extra contribution to the relaxation is dependent upon deuteration both in magnitude and in the temperature position of the maximum, is in agreement with an isotope dependence of that triangle-shaped potential well.

Acknowledgements

The authors thank S. Müller for preparing the crystals used in this work.

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