Temperature and Pressure Variation of the Cl-NQR in A_2PbCl_6-Crystals *

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The ^{35}Cl NQR frequency and spin-lattice relaxation rate in the compounds A_2PbCl_6 (A = Cs, Rb, NH_4, K) have been investigated in the range 4.2 K to 500 K, and as a function of pressure at room temperature. NQR experiments conducted on $(K{:}NH_4)_2PbCl_6$ mixed crystals have been used to complete the NQR-frequency versus temperature diagram of K_2PbCl_6, revealing two structural transitions at $T_{c_1} \cong 358$ K and at $T_{c_2} \cong 333$ K.

1. Introduction

The A_2BX_6 compounds exhibit particular dynamical properties associated with structural transformations or molecular motions. In this context members of the A_2SnCl_6 family have already been investigated most thoroughly [1]. The hexachloroplumbates (A_2PbCl_6) are expected to possess properties closely related to those of the tin compounds as both have a fully occupied d-shell. In this work A_2PbCl_6-crystals with A = Cs, Rb, NH_4 and K are investigated. At room temperature the former three compounds crystallize in the fcc-structure (O_h^5), and no structural changes have been observed for the Rb- and Cs-compounds down to temperatures as low as 4.2 K [2]. Controversial results are reported concerning the appearance of a phase transition in $(NH_4)_2PbCl_6$. Calorimetric analysis seems to indicate a transformation at about 240 K [2] but subsequent IR experiments failed in verifying a structural change [3]. K_2PbCl_6 has a monoclinic structure already at room temperature, and one phase transition had been observed at $T_c \cong 330$ K [2]. Measurements of the chlorine-NQR frequencies at some selected temperatures have been reported for the Cs- and NH_4-compounds [4, 5] but till now no NQR data were available for Rb_2PbCl_6 and K_2PbCl_6.

2. Experimental and Results

^{35}Cl NQR measurements were conducted on powdered samples using a Bruker pulse spectrometer supplied with heads for temperature (4.2 K to 600 K) and pressure dependent studies. Hydrostatic pressures up to 5 kbars were provided by a pressure transmitting liquid [1]. The polycrystalline samples were obtained by precipitation in solution. The preparation of the hexachloroplumbates has always been impeded by hydrolytic reactions causing the most severe problems in the case of K_2PbCl_6. The final chemical composition of the samples has been controlled by Raman scattering and X-ray diffraction analysis.

Cs_2PbCl_6 and Rb_2PbCl_6

The Cs- and Rb-compounds exhibit a single line NQR spectrum which is preserved down to temperatures as low as 4.2 K. In the whole temperature range the NQR frequencies follow a Bayer-Kushida behaviour (Figure 1). Below about 250 K, the spin-lattice relaxation rates are determined by phonon processes leading to T^n ($2 \leqq n \leqq 3$) dependences. A part of these results is shown in Figure 2. Hindered rotations of the $PbCl_6^{2-}$-octahedra start to dominate T_1^{-1} above room temperature. Activation enthalpies ΔH_a deduced from the experimental data are given in Table 1. The values compare well with those obtained for Rb_2SnCl_6 and Cs_2SnCl_6 [1]. Similar correlations do also exist for the hydrostatic pressure coefficients of ν_Q and T_1^{-1}. For completeness,

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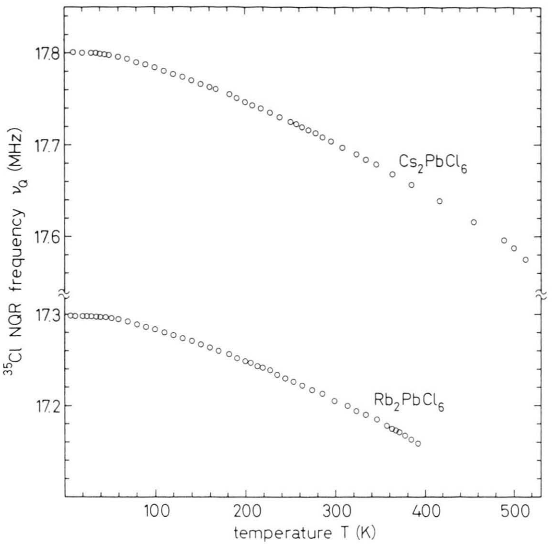

Fig. 1. Temperature dependence of the ^{35}Cl NQR frequency ν_Q in Cs_2PbCl_6 and Rb_2PbCl_6.

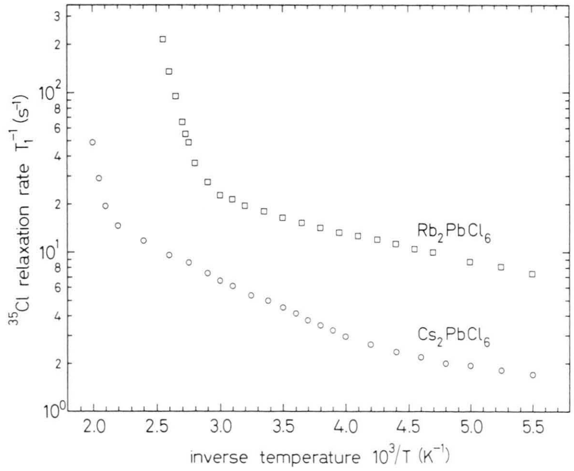

Fig. 2. Lattice relaxation rate T_1^{-1} as a function of the inverse temperature in Cs_2PbCl_6 and Rb_2PbCl_6.

the room temperature coefficients of $(NH_4)_2PbCl_6$ and K_2PbCl_6 are listed in the same table although these data do not serve for a direct comparison because of the influence of the NH_4^+-motion and soft librational modes, respectively.

$(NH_4)_2PbCl_6$

The ammonuim salt maintains a single line spectrum in the covered temperature range (Figure 3a).

Table 1. ^{35}Cl NQR data of A_2PbCl_6 compounds: temperature and hydrostatic pressure coefficients of the NQR frequency (ν_Q) and of the spin-lattice relaxation rate (T_1^{-1}) at $P = 1$ bar and $T = 300$ K. ΔH_a is the activation enthalpy of hindered rotation.

Cation	Cs	Rb	NH_4	K *
$\left(\frac{\partial \nu_Q}{\partial T}\right)_P$ /kHz K^{-1}	− 0.6	− 0.4	− 0.75	− 5.8
$\left(\frac{\partial \nu_Q}{\partial p}\right)_T$ /kHz $kbar^{-1}$	− 1.1	− 9.1	− 8.6	− 18.0
$\left(\frac{\partial \ln T_1^{-1}}{\partial p}\right)_T$ /$kbar^{-1}$	− 0.2	− 0.05	− 0.07	− 0.4
ΔH_a/K	15 000	9 000	9 000	7 000

* Values corresponding to line α (see Figure 4a).

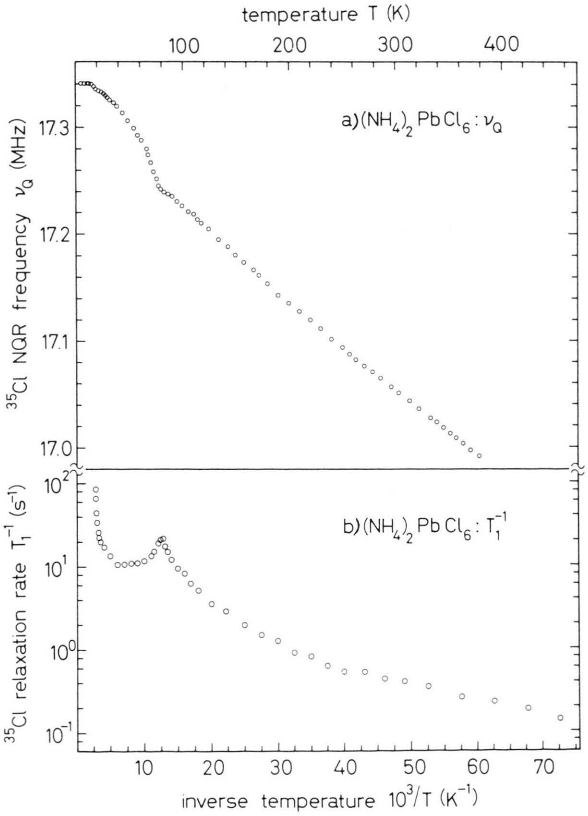

Fig. 3. Temperature dependence of the ^{35}Cl NQR frequency (a) and of the spin-lattice relaxation rate (b) in $(NH_4)_2PbCl_6$.

In contrast to the Rb- and Cs-compounds the NQR frequency and spin-lattice relaxation rate display anomalous temperature behaviours which we attribute to the influence of the NH_4^+ motion. Hindered rotations are expected to dominate above 150 K giving rise to an extra NQR frequency shift like in the case of $(NH_4)_2SnCl_6$ [6]. The step-like features appearing in the frequency diagram at low temperatures (Fig. 3a) account for the influence of NH_4^+ tunneling. A detailed analysis of this ammonium motion effect will be given elsewhere. Modifications of the NQR spin-lattice relaxation rate due to the tunneling process, which have already been reported for $(NH_4)_2SnCl_6$ [7], seem also to exist in $(NH_4)_2PbCl_6$ (Figure 3b).

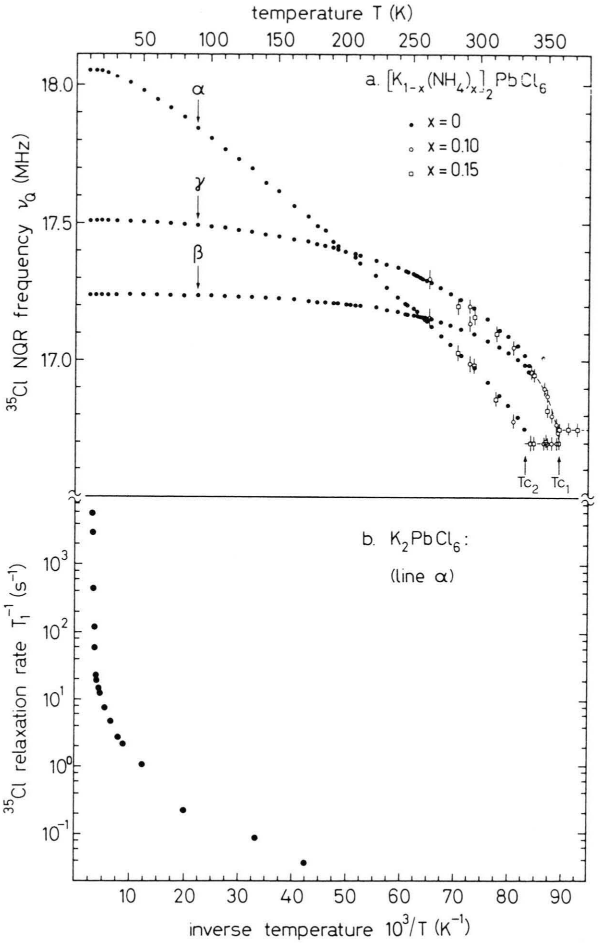

Fig. 4. a) Temperature dependence of the ^{35}Cl NQR in K_2PbCl_6. Data from the pure matrix (full points) and from $(NH_4{:}K)_2PbCl_6$ mixed crystals (open symbols). – b) Spin-lattice relaxation rate of pure K_2PbCl_6 (line α in Fig. 4a) versus inverse temperature.

K_2PbCl_6

Among the hexachloroplumbates investigated in this work only the potassium compound was expected to undergo a structural transformation at about 330 K [2]. Apart from the difficulty to prepare the sample, an NQR investigation of the phase transition is faced by a further severe experimental problem: Because of the rather high relaxation rates in the hindered rotation regime, the chlorine NQR signal can only be perceived just below T_c and the NQR remains undetectable in the cubic phase. The full points in Fig. 4a show the evolution of the NQR frequency as observed in pure K_2PbCl_6 below the phase transition. The resonance pattern consists of three distinctly resolved lines compatible with e.g. a monoclinic structure at room temperature. Within the experimental error the three lines have nearly equal spin-lattice relaxation rates, therefore only one trace has been reproduced in Figure 4b. Near room temperature, the relaxation rates in K_2PbCl_6 are already two orders of magnitude faster than in the other three plumbates. Again, these observation compare well with the behaviour found for the homologous tin compounds A_2SnCl_6 [1]. However, in the case of K_2SnCl_6 the phase transition takes place fairly below room temperature whereas in K_2PbCl_6 the structural transformations coincide with the fast relaxation regime. To render the temperature range in the vicinity of T_c accessible to an NQR investigation, we have conducted NQR studies on the mixed compounds $(K_{1-x}(NH_4)_x)_2PbCl_6$ ($x = 0.10-0.15$). Substitution of ammonium for potassium reduces the transition temperature ($dT_c/dx = -273$ K/mol), shifting the region of interest to lower temperatures. The NQR line pattern observed in the mixed crystals clearly reveals the appearance of two successive transitions. Proceeding from the data measured in the doped crystals and taking into consideration the concentration dependences of T_c and of the NQR frequencies we have constructed an extrapolated frequency-temperature diagram for the pure K_2PbCl_6 salt (Figure 4a). A most convincing result is the agreement between the extrapolated values determined from the different compositions. According to this diagram, K_2PbCl_6 undergoes two phase transitions at $T_{c_1} \cong 358$ K and at $T_{c_2} \cong 333$ K. The structure of the intermediate phase ($T_{c_1} > T > T_{c_2}$) is most probably tetragonal. In the cubic phase the NQR frequency (ν_Q) shows no noticeable temperature dependence: $\nu_Q = 16.76$ MHz at 373 K.

3. Conclusion

The temperature and pressure variation of the chlorine NQR in the A_2PbCl_6 compounds shows many similarities with the behaviour observed in A_2SnCl_6 crystals. A feature peculiar to $(NH_4)_2PbCl_6$ is an extra NQR frequency shift below 80 K which is attributed to the influence of the proton tunneling motion of the ammonium ion. Relaxation effects prevent NQR analysis of the phase transition in pure K_2PbCl_6. It has been demonstrated that in such a case detailed information can be obtained from the investigation of impurity doped crystals.

Acknowledgement

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