

X-RAY ABSORPTION SPECTROSCOPY FOR PARTIALLY DEUTERATED AMMONIUM HEXACHLOROPALLADATE

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Ammonium hexachloropalladate belongs to the family of ammonium hexachloro-metallates $(\text{NH}_4)_2\text{MCl}_6$, where M is 3d metal *eg.*: Pd, Pt, Ir, Os or *p*-elements *eg.*: Se, Sn, Te, Pb. The compounds with 3d elements exhibit a stronger covalent M-Cl bonding and a smaller unit cell, compared to the *p*-elements [1]. First NMR observations show a decrease of the spin-lattice relaxation time (T_1) at the order-disorder phase transition, which is related to ordering of the ammonium cations [2]. Additionally, the deuteration can induce a transition from the cubic phase to the low symmetry phase [3].

In this paper, we present EXAFS data, together with NMR T_1 relaxation time data, for ammonium hexachloropalladate samples deuterated at 30%, 50% and 70%, labelled as D30, D50 and D70, respectively. XAS experiments have been done at beamline C at HASYLAB at DESY, Hamburg, Germany in the fluorescence mode at

the Pd K-edge. NMR experiments had been done at the Department of Magnetic Resonance Spectroscopy at Institute of Nuclear Physics PAN, Krakow, Poland.

XANES experiments clearly show that all deuterated samples have a Pd:K edge position shifted by +2.0(2) eV compared to the metallic Pd (used as a reference) edge position 24350 eV. EXAFS experiments reveal clearly that the first shell Cl peak is observed at 2.189(5) Å, 2.196(5) Å and 2.195(5) Å for 30%, 50% and 70% deuterated samples, respectively (Fig. 1). The full-width-half-maximum (FWHM) of this line was derived: 0.33(1) Å, 0.32(1) Å and 0.32(1) Å, for D30, D50 and D70, respectively. The change of position and the change of the full-width-half-maximum for the first shell Cl peak do not depend on temperature (Fig. 2). Peaks of next-neighbour shells are also visible: N at 4.3(2) Å and Cl at 5.4(3) Å and will be later analysed.

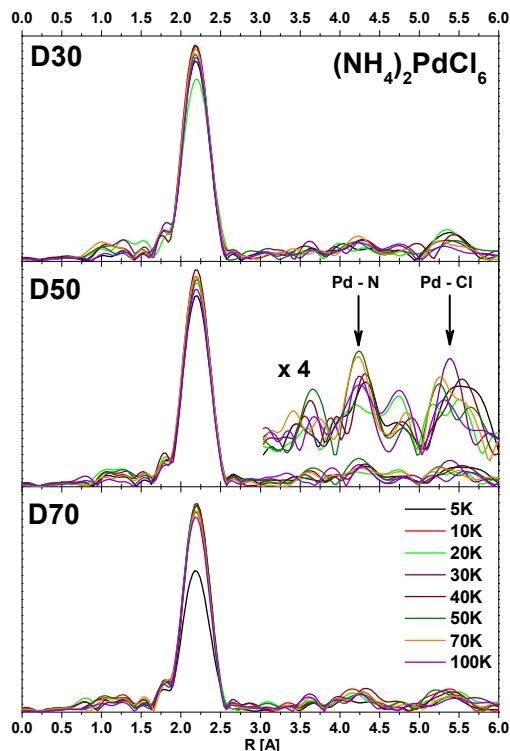


Figure 1. EXAFS spectra of 30% (D30), 50% (D50) and 70% (D70) deuterated ammonium hexachloropalladate. The enlarged region of higher R is presented for 50% deuteration.

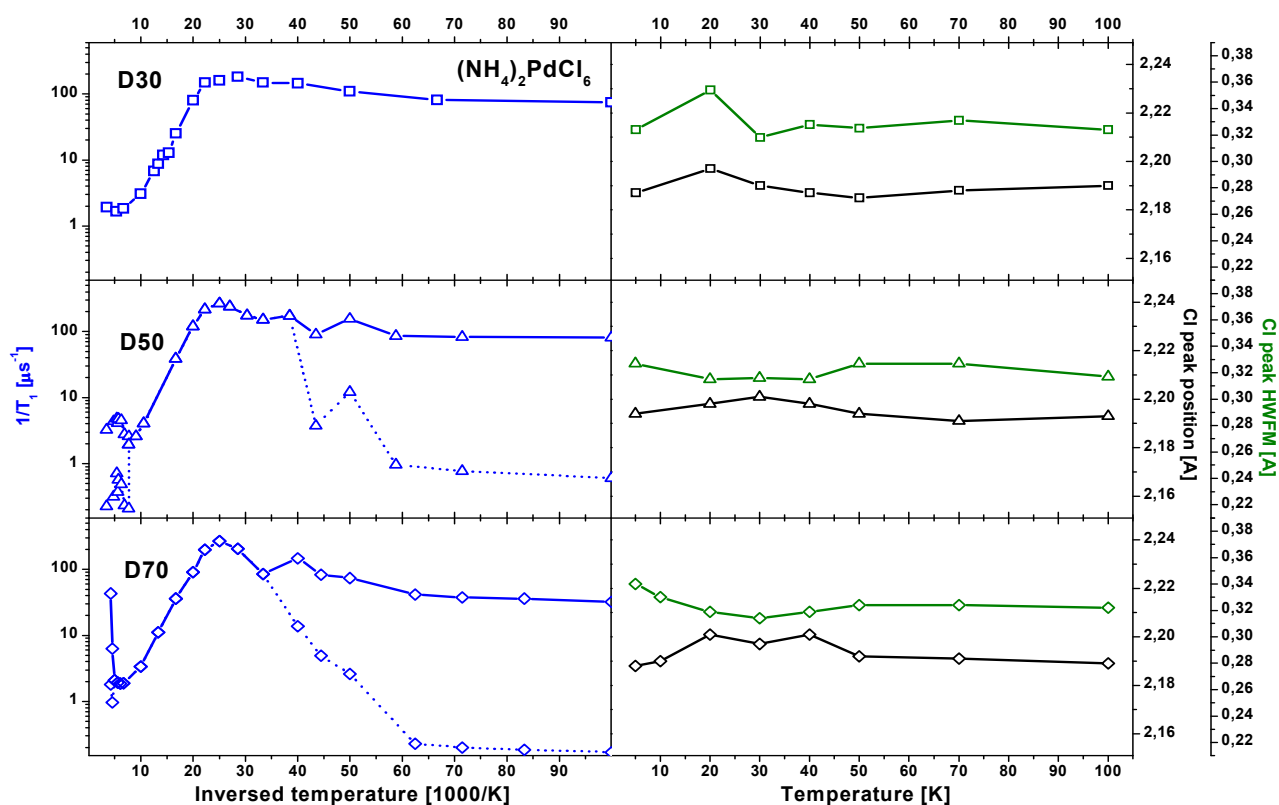


Figure 2. Deuteron relaxation rate (left, blue line), the centre of the first neighbour Cl peak (right, black line) and FWHM of this peak (right, green line) for 30% (squares), 50% (triangles) and 70% (diamonds) deuterated ammonium hexachloropalladate.

The maximum of the spin-lattice relaxation rate can be explained by rotation of the ammonium tetrahedrons about threefold symmetry axes. For 50% and 70% deuterated samples two exponential behaviour of T_1 is also observed. The unchanged position of the first Cl peak together with unchanged FWHM indicates that the ammonium ion rotation has a local character and does not affect the Pd and Cl crystallographic sublattice. Only between about 25 K and 50 K there are small shifts in both values which may be related to a correlation frequency of ammonium ions of the order of 10^8 s^{-1} in this range.

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References

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