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PHASE TRANSITION OF $(NH_4)_2PdCl_4$ STUDIED BY NUCLEAR MAGNETIC RESONANCE

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The phase transition of $(NH_4)_2PdCl_4$ was confirmed at 132 K by the proton T_1. A thermal hysteresis in T_1 was observed, indicating that the transition is of a first-order. The transition is probably accompanied by the order-disorder change of an ammonium ion, but this is not effective for the transition temperature.

Ammonium ions in $(NH_4)_2PdCl_4$ are, like those in NH_4Cl, surrounded by eight Cl atoms and disordered between two orientations.[1)] Adams and Berg suggested a phase transition at about 150 K from their far-IR results.[2)] The subsequent neutron diffraction experiments on $(ND_4)_2PdCl_4$ showed no change in the crystal structure at 295 and 125 K.[1)] We have studied the molecular motion of an ammonium ion in this palladate by means of the pulsed NMR technique for comparison with that in NH_4Cl[3)] and α-NH_4HgCl_3,[4)] and obtained some evidence on the phase transition.

The sample was obtained by slow evaporation of an aqueous solution containing NH_4Cl and $PdCl_2$ in the mole ratio of 2:1. It was identified by powder X-ray diffraction. The spin-lattice relaxation time, T_1, of ^1H nuclei was measured with a Bruker B-KR 322s pulsed spectrometer on a sequence of $180°-\tau-90°-\tau'-90°_{90°}$. The temperature of the sample was varied from 77 to 300 K and controlled within ±0.05 K.

In Fig. 1 the T_1 measured at 20.00 MHz was plotted against T^{-1}. A T_1 minimum with a value of 11 ms was observed at 112 K. This minimum was analyzed in terms of the 90°-reorientational motion of the ammonium ion about a diad axis. The observed values of T_1 were fitted to the following equation,

$$T_1^{-1} = (27/80)(\gamma^4\hbar^2/r^6)[\tau_c/(1+\omega_0^2\tau_c^2) + 4\tau_c/(1+4\omega_0^2\tau_c^2)] \quad (1)$$

with motional parameters of $\tau_0 = 12\pm2$ fs and $E_a = 12.0\pm0.1$ kJ mol^{-1}. It was, therefore, concluded that the disordered structure of the ammonium ion given by neutron diffraction are of a dynamical nature.

The existence of the phase transition was indicated in the log T_1 - $1/T$ curve and confirmed by DTA. Figure 2 shows the T_1 around the transition temperature, T_t. When the sample was heated, it transformed at 132 K only with a change in the slope of the T_1 curve. In a cooling run, however, the transformation occurred at 129 K with a small jump of T_1. Because the thermal hysteresis was observed, the phase transition is of a first-order. By applying Eq. 1 and the same T_1^{min} value to both phases, the correlation time was calculated. Above T_t, the Arrhenius relation

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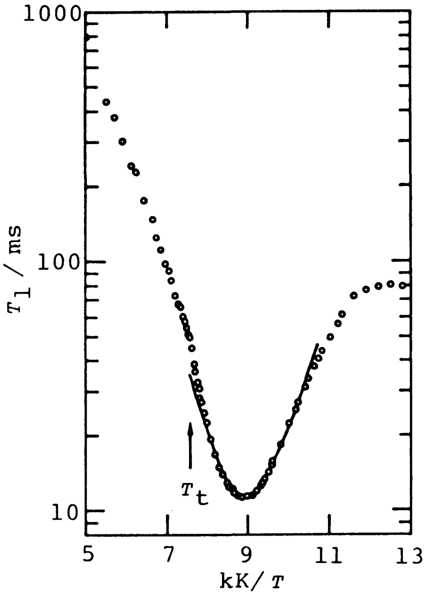

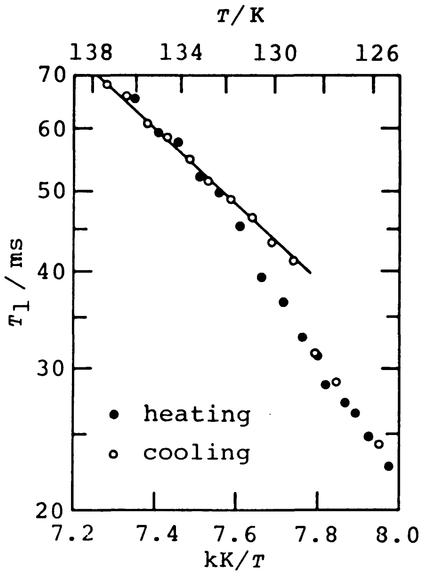

Fig. 1 (left) and Fig. 2 (right)

The solid lines show the best fit to Eq. 1.

holds well within the experimental error; τ_0 = 100±21 fs and E_a = 9.4±0.2 kJ mol^{-1}. In the low-temperature phase, this relation holds only below 120 K with parameters of τ_0 = 35±8 fs and E_a = 11.1±0.2 kJ mol^{-1}. As the temperature approaches T_t from below, the correlation time becomes shorter and shorter than the extrapolated one. These features are very similar to those of NH_4Cl.[3)]

The assignment of the T_1 minimum together with the T_1 behavior around T_t indicates that an order-disorder change of the ammonium ion is associated with the phase transition of $(NH_4)_2PdCl_4$. If this orientational change is most effective to the phase transition, T_t can be estimated from both the statistical theory for a three-dimensional Ising lattice and the octupole-octupole interaction between the nearest-neighbor ammonium ions.[5,6)] It is 63.3 or 50.0 K, depending on a reference material for the octupole moment, NH_4Cl or α-NH_4HgCl_3. The poor agreement between the observed and the estimated T_t means that the change of the ammonium orientation plays, in fact, a minor role in the phase transition. Therefore, some kind of change in the crystal structure, such as displacement of cations and anions, may be present in the phase transition, as was pointed out by Adams and Berg from the comparison between the IR results of ammonium and potassium tetrachloropalladates.

The full experimental data and the details of an analysis of the molecular motion will be published elsewhere.

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