Vol. A56 (1979) *ACTA PHYSICA POLONICA* No 4

THERMALLY-DETECTED EPR OF [Ni(NH$_3$)$_6$]I$_2$ AND ITS BEHAVIOUR NEAR THE PHASE TRANSITION

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(Received December 22, 1978)

The thermally detected absorption of the 3d^8 ion Ni^{2+} in the complex Ni(NH$_3$)$_6^{2+}$ iodide was observed at frequencies from 12–18 GHz as a function of temperature in the range 2–21 K and particularly around its phase transition temperature of 20 K. The well known linewidth anomaly was observed and the number of nickel ions participating in the absorption was found to be constant as the transition temperature was traversed. The transition exhibits very small hysteresis (< 0.2 K) and is accompanied by an entropy change as exemplified by the adiabatic heating and cooling curves of the specimen.

1. *Introduction*

This note reports the successful use of thermally-detected TD-EPR [1, 2] at the comparatively elevated temperature of 20 K to study the phase change of [Ni(NH$_3$)$_6$]I$_2$ [3–5]. The purpose of the measurement was to exploit the fact that TD-EPR displays the true EPR absorption signal rather than its derivative. This was done in order to see whether there was any detectable fine structure or anisotropy in the broad EPR line of Ni^{2+} below $T_c = 20$ K as has been predicted [6–8].

2. *Experimental*

The sample holder and the details of the crystal mounting are shown in Fig. 1. The sample was a single crystal of [Ni(NH$_3$)$_6$]I$_2$. The largest dimension, about 3 mm, was fixed to the end of a single crystal quartz rod with GE varnish and it was coated with a thin layer of varnish to prevent loss of ammonia on evacuation of the assembly. At the other

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end of the quartz rod was an Aquadag thermometer whose resistance varied from 500–250 Ω in the range 2–20 K.

The rod and sample passed through thin plastic supporting sheets with negligible thermal conductivity in this temperature range, and its only thermal contact with the liquid helium bath surrounding the brass can was via the aluminium foil leads to the thermometer. Thick copper rods attached to the baseplate of the can ensured that the brass block remained at the bath temperature. The upper surface of the crystal was coated with a thin layer of Aquadag so that the RF microwave field, supplied by a back-wave oscillator, could be used to heat the sample as well as to observe its EPR.

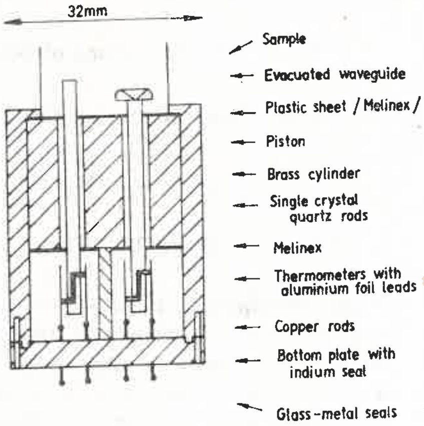

Fig. 1. Sample holder assembly for the TD-EPR of $[Ni(NH_3)_6]I_2$ single crystal. The (left) other quartz rod was not used in this experiment

In order to concentrate the microwave power on the specimen at any desired frequency in the range 12–18 GHz, a sliding stub tuner at room temperature was used to make resonant the length of the waveguide leading to the sample with a Q of about 400. To observe EPR the resistance of the Aquadag thermometer, as measured by an AC Wheatstone bridge, was plotted as a function of the magnetic field, and to vary the sample temperature the thermometer served also as a heater when small DC currents from a high impedance supply were passed through it. The time constant of the thermally isolated rod, sample and thermometer assembly varied from around 1 s at 2 K to about 20 s at 20 K.

A typical lineshape (at 4.2 K) is shown in Fig. 2 as is the fit to a Lorentzian. No fine structure nor anisotropy was observed and the half-height linewidth (0.25 T) was found to remain nearly constant from 2 K to 15 K. There was very little change in linewidth with frequency in the range 12–18 GHz. A rapid narrowing of the line was observed within 1K below T_c (20 K) and just above T_c, the narrow line (half-height width 0.01 T) had the same area as that just below which indicates that all the Ni^{2+} ions are involved in both absorption signals, Fig. 3.

When observing the EPR close to T_c, a DC power of about 10 mW was supplied to the thermometer to heat the rod and the sample and, in addition, the microwave RF field

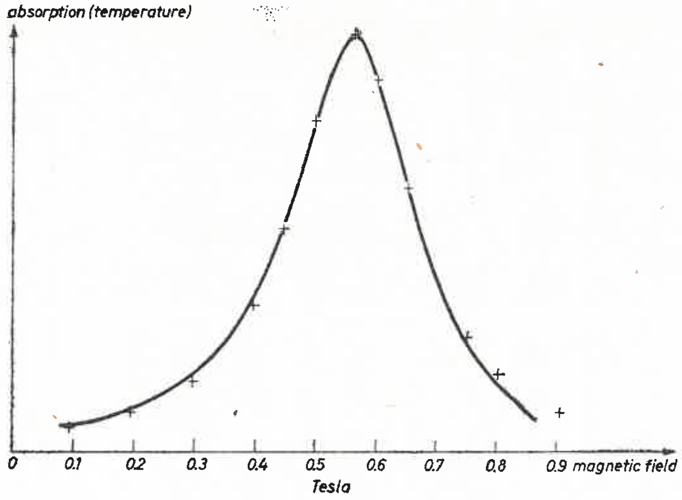

Fig. 2. Thermally detected EPR absorption of the $[Ni(NH_3)_6]I_2$ crystal. The line shape fits to the Lorentzian curve (+) calculated for $\Delta H_{1/2} = 0.24$ T

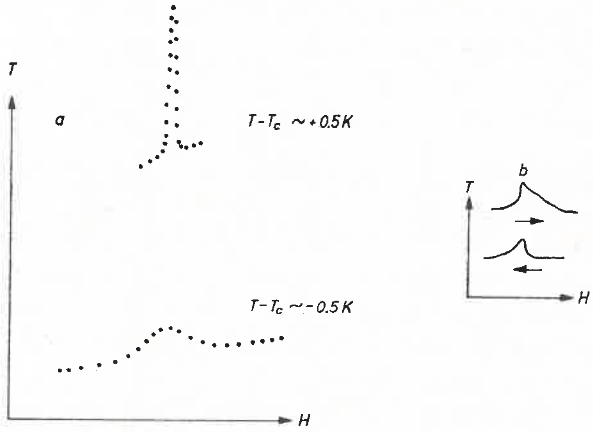

Fig. 3. TD-EPR of $[Ni(NH_3)_6]I_2$ near the phase transition temperature T_c. a) absorption line-shape above and below T_c (magnetoresistance of the thermometer is seen as a side effect on both curves); b) an effect of traversing through T_c due to resonant heating of the sample. The arrows indicate the direction in which the resonance condition is approached

supplied about 1 mW of heating by its effect on the resistive Aquadag layer on top of the sample.

As the DC power was adjusted to take the specimen through T_c, the effect of switching the microwave power off and on in a zero magnetic field was observed (Fig. 4). As can be seen, the effect of this procedure when the temperature is well below or above T_c is an approximately exponential change in the specimen temperature. However, if while heating or cooling T_c is traversed, a pronounced waiting period is observed which clearly indicates

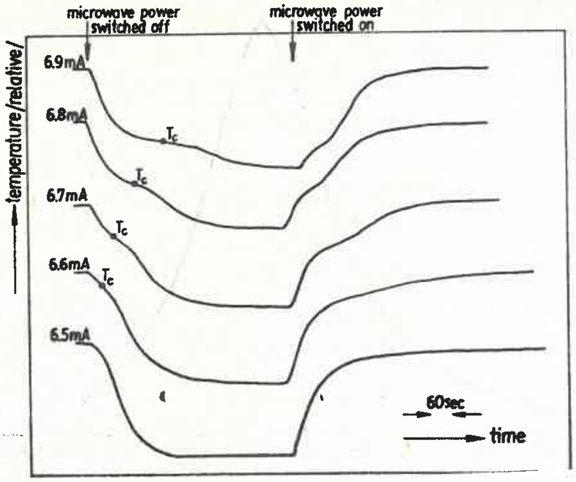

Fig. 4. The effect of switching the microwave power off and on in a zero magnetic field: five different transients correspond to various DC power settings within the range 6.75–6.90 mA. The resistance of the heater is 250 ohm

the phase change and the associated entropy change. The fact that the anomaly occurs at the same position for both rising and falling temperature shows that the hysteresis in T_c is less than 0.2 K.

3. *Discussion*

The structural phase transition [9, 10] in the nickel hexammine halides is thought to be due to cessation of the free rotation above T_c of the six NH_3 groups by a cooperative electrostatic interaction [11]. Below T_c, the large linewidth could be due to the $S = 1$ Ni^{2+} ion having a variety of zero field splittings depending on the configurations that the clusters occupy in the distorted cubic (Fm3m) lattice. The absence of observable fine structure indicates that there must be sufficient broadening of each of these configuration spectra to produce the smooth lineshape. Such a broadening could be due to the dipolar interaction between Ni atoms approximately 8 Å distant [12] and to the residual librational motion of the six NH_3 groups. The narrowing of the broad line just below T_c leading to the much narrower line above T_c could then be due to the onset of free rotation of the NH_3 groups and the consequent change to a time-averaged cubic environment for the $S = 1$ ion. An order of magnitude calculation based on temperature vs time dependence (Fig. 4) yields an entropy change exceedingly larger than the value of 8.2 J $mol^{-1}K^{-1}$ quoted after specific heat measurements [13]. The anomaly of thermal conductivity similar to that observed for some nickel hexammine halides [14] may lead to an overestimation of the amount of heat absorbed by the sample thus causing the discrepancy. Diluted diamagnetic systems of some of these hexammine complexes have been obtained in powder and single crystal form [15, 16] and show single values of the zero field splitting for the Ni^{2+} ion. This is difficult to reconcile with the results suggested by all measurements including ours. However since the non-magnetic hexammines have very different transition temperatures from their magnetic counterparts, it is by no means impossible that the ammonia groups orientation in the diamagnetic compounds could be ordered whereas in the magnetic case they could be disordered as suggested here.

We thank the SRC for providing a grant and a research studentship to M.G. We also thank the British Council for providing a travelling grant to P.B.S. The useful discussions with Drs A. R. Bates and J. R. Fletcher are also gratefully acknowledged as well as the valuable comments of Professor J. Stankowski to whom P.B.S. is particularly indebted. Thanks are also due to Mr L. Ferris for providing the unique crystals of nickel hexammine iodide.

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