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AMMONIA COOPERATIVE PHASE TRANSITION STUDY BY EPR IN $|Ni(NH_3)_6|\ (ClO_4)_2$

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ABSTRACT

A phase transition was observed at T_c=197 K in the complex $|Ni(NH_3)_6|(ClO_4)_2$. The line width of the single EPR absorption line, undergoes a sudden broadening at T_c. The crystal fiel parameter $D=0.1\ cm^{-1}$ was evaluated from the observed line width.

It is our purpose to report the detection of a phase transition in the $|Ni(NH_3)_6|\ (ClO_4)_2$ complex by EPR measurements. This salt has a cubic structure, with the Ni^{++} ions occupying f. c. c. sites and the six ammonia groups forming an octahedron around each Ni^{++} ion. The lattice parameter is $a=11.41$ Å. The $(ClO_4)^-$ groups are located at 1/4 and 3/4 of the body diagonal of the cube, forming another cube of parameter $a/2$[1] around each Ni^{++} ion. The present salt is isomorphous to the complexes $|Me(NH_3)_6|\ X_2$ (Me=Ni, Co, Mn, Zn, Cd, Ca and X=Cl, Br, I, NO_3, BF_4). For many of them phase transitions in the temperature range from 20 K to 250 K have been observed by calorimetric [2-5] and EPR measurements [6-8].

Compounds with Me = Ni show a single EPR absorption line, which undergoes a sudden line broadening at T_c. This effect was proposed to be a result of a cooperative freezing of the degrees of freedom of rotation of the ammonias[9-10], which gives rise to the appearance of a crystal field on the Ni^{++}. This crystal field does not split the single line below T_c probably because of strong exchange effects.

In powdered samples of $|Ni(NH_3)_6|\ (ClO_4)_2$ we found a single EPR absorption line, centered at $g=2.17$, and supposed to be Lorentzian-shaped. The maximum slope line-width, $\Delta H_{ms}=500G$, undergoes a sudden line broadening at $T_c=197$ K to a width $\Delta H_{ms}=2300G$.

The temperature dependence of the EPR maximum sope line-width is shown in figure 1.

INSERT FIGURE 1

The line width ΔH narrowed by exchange interaction was evaluated for a s.c. lattice by Anderson and Weiss[11], using the theory developed by Van Vleck. This theory was recently adapted for the line width evaluation of other cubic lattices[8,13] including the crystal field contribution DS_z^2. An application to $|Ni(NH_3)_6|(NO_3)_2$ gives $D \simeq 0.4\ cm^{-1}$ which agrees reasonably well with the values $D \simeq 0.6\ cm^{-1}$ and $0.3\ cm^{-1}$ observed for the dilute samples $|Ni:Zn(NH_3)_6|(NO_3)_2$ and $|Ni:Cd(NH_3)_6|(NO_3)_2$, respectively.

For the case of our salt, in order to analyse the line-sidth below T_c, we subtract 430G $(\Delta H = (2/\sqrt{3})\Delta H_{ms})$ to separate that part of the line-width due to the phase transition effect. The exchange parameter J was evaluated in the molecular field approximation using the Weiss temperature $\theta = 0.5K$ obtained from magnetic susceptibility measurements[14]. From the effective line width $\Delta H = 1570$ G we obtain

$$D \simeq 0.1\ cm^{-1}$$

In table 1 we compare D, T_c and the hysteresis ΔT at the critical temperature, obtained for a number of hexamine complexes. The EPR spectra of $|Ni(NH_3)_6|(NO_3)_2$, $|Ni(NH_3)_6|Cl_2$, $|Ni(NH_3)_6|(BF_4)_2$ and $|Ni(NH_3)_6|(C\ell O_4)$ show similar temperature dependences. That is, a single line above T_c undergoes a sudden broadening at T_c.

So, the phase transition in $|Ni(NH_3)_6|(C\ell O_4)_2$ is probably due to the cooperative freezing of the degrees of freedom of rotation of the ammonias.

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TABLE 1

T_c, D and T for a number of $Me(NH_3)_6\ X_2$ type complexes

COMPLEX	T_c(K)	D(cm^{-1})	ΔT(K)	REFERENCES
$\vert Ni(NH_3)_6\vert C\ell_2$	76	0.3	5	15
$\vert Ni(NH_3)_6\vert (NO_3)_2$	243	0.4	5	8,13
$\vert Ni:Zn(NH_3)_6\vert (NO_3)_2$	231	0.6	5	8
$\vert Ni:Cd(NH_3)_6\vert (NO_3)_2$	198	0.3	10	8
$\vert Ni(NH_3)_6\vert (C\ell O_4)_2$	197	0.2	5	present work
$\vert Ni(NH_3)_6\vert (BF_4)_2$	140	—	—	7

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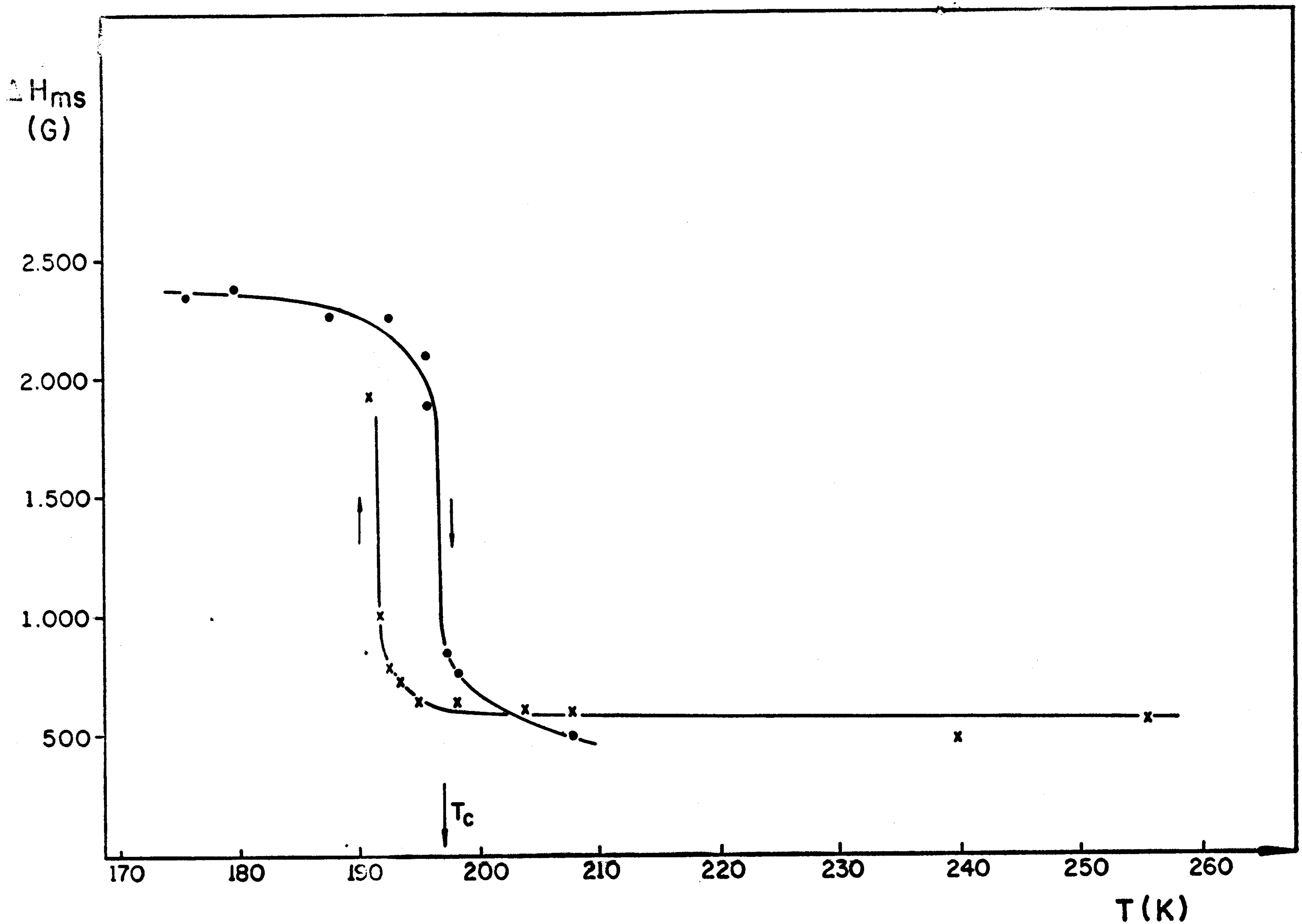
FIGURE CAPTION

Figure 1. Temperature dependence of the EPR maximum slope line width, ΔH_{ms} (Gauss), of powdered samples of $|Ni(NH_3)_6|\ (C\ell O_4)_2$.



ΔHms
(G)
2.500
2.000
1.500
1.000
500
Tc
170
180
190
200
210
220
230
240
250
260
T(K)