PHASE TRANSITION IN METAL HEXAMMINE COMPLEXES

II - THE EPR SPECTRA OF $Ni(NO_3)_2 6NH_3$ AND

Ni^{++} DOPED $Zn(NO_3)_2 6NH_3$ AND $Cd(NO_3)_2 6NH_3$

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ABSTRACT

The cooperative effect of the ammonias in
$X(NO_3)_2 6NH_3$ (X=Ni,Zn,Cd) was investigated by EPR. In $Ni(NO_3)_2 6NH_3$,
the line width of the single EPR absorption line undergoes a
sudden broadening at Tc=243K. This effect, probably, is a result
of a cooperative freezing of the degrees of freedom of rotation
of the ammonias, giving the appearance of a crystal field on the
Ni^{++} ions. The crystal field does not split the single line,
probably because strong exchange effects assemble the lines. The
crystal field parameter $D=0.425cm^{-1}$ was evaluated by applying the
Anderson and Weiss theory for the exchange narrowing of the line-
width. Small quantities of the Ni^{++} ions in Zn and Cd salts do
not exhibit strong exchange effects. So the single EPR absorption
line above Tc goes to a split line below Tc. For $Ni:Zn(NO_3)_2 6NH_3$,
Tc = 231K and $D=0.606$ cm^{-1}. For $Ni:Cd(NO_3)_2 6NH_3$, Tc=198K and
$D\simeq0.3$ cm^{-1}. Hysteresis in Tc was also observed for all salts.

INTRODUCTION

In this paper we report EPR measurements of Ni^{++} in $X(NO_3)_2 6NH_3$ (X=Ni,Zn and Cd) crystals and attempt to explain the phase transition observed in these salts. In a previous report(I) we have discussed several known properties of these salts and reported the infra-red spectra[1] of $Ni(NO_3)_2 6NH_3$ above and below the phase transition (Tc=243 K). The analysis of vibrational data suggests that the origin of this transition is due to the collective freezing of the degrees of rotation of the ammonias.

In the halogen nickel hexammines, $NiY_2 6NH_3$ (Y=Cℓ, Br and I), which are isomorphous to the present salts, a single EPR line undergoes a sudden broadening below the critical temperature. For these halogen salts Tc depends on the lattice parameter. Bates and Stevens[4,5] have proposed a model where a crystal field appears at Tc, due to a freezing of the rotational degrees of freedom of the ammonias. The effect of this freezing is to remove the zero averaging of the crystal field. This theory was strongly reinforced by observation of the splitting of the single EPR line[6] below Tc for Ni^{++} ions diluted in some non-magnetic, isomorphous, host salts. This model also predicts that Tc is a function of the lattice parameter.

In this paper we report that $X(NO_3)_2 6NH_3$ (X=Ni,Zn,Cd) behaves similarly to the halogen nickel hexammine complexes. We also calculate the crystal field parameter D, based on line-width measurements for concentrated $Ni(NO_3)_2 6NH_3$ and for Ni^{++} ions diluted in $X(NO_3)_2 6NH_3$ (X=Zn,Cd). Finally the Bates and Stevens

model is applied for the salts $X(NO_3)_2 6NH_3$ (X=Ni,Zn,Cd,).

SAMPLE PREPARATION

1. $Ni(NO_3)_2 6NH_3$: Reacting $NiCO_3$ (Baker Analysed Reagent) with HNO_3 (Reagent PA) and adding concentrated NH_4OH (Berzog PA) in excess to the solution, heat is liberated. During cooling to room temperature, powdered crystals are formed. Octahedral crystals of 2mm are easily obtained if the powdered crystals are recristallized slowly at 20°C maintained by a controlled temperature bath. The crystals were dryed in a desiccator over silica gel in an atmosphere of ammonia. Ammonia analysis by a distillation process (micro Kjeldahl apparaturs) indicated the presence of six ammonia molecules in the samples, within 99% of precision.

2. $Zn(NO_3)_2 6NH_3$ with $\sim$ 5% Ni^{++} dilution. Five grams of $Zn(NO_3)_2 6H_2O$ (Baker Analysed Reagent) in a Pyrex glass tube were kept in a continuous gas flow of ammonia at 70°C, maintained by a water bath during 24 hours. In this process most of the water molecules were substitued by ammonia molecules. Then ammonia was liquified in the same tube, using the same gas, by cooling with nitrogem gas obtained from the evaporation of liquid nitrogen contained in a long dewar. The tube was partially introduced in the dewar and the desired temperature was achieved by regulating the height of the tube relative to the liquid nitrogen surface. The salt was dissolved in the liquid ammonia giving a transparent solution. Evaporation of ammonia above 30°C carried away the remaining water molecules.

Repeating the process of liquefaction and evaporation twice ensured that the samples was free of undesirable water traces. In the final liquefaction, about 0.2 grams of $Ni(NO_3)_2 6NH_3$ were added and a faint blue color was observed. The temperature was kept at -30°C to assure slow evaporation and many octahedral crystals were obtained, the largest about 0.5mm in size. These crystals were transfered carefully to an EPR sample tube at room temperature and one atmosphere of ammonia gas. Ammonia analysis and Zn analysis by ignition at 800°C gave 5.95 ammonia molecules per Zn atom. The crystals of $Zn(NO_3)_2 6NH_3$ are very unstable in air and are highly deliquescent. This is the reason for the special care, as mentioned above in the crystal preparation. It was not possible to obtain good samples simply by cooling a solution (-10°C or 0°C) of the salt in water with excess ammonia.

3. $Cd(NO_3)_2 6NH_3$ with $\sim$ 5% Ni^{++} doping. This salt was prepared in the same way as the preceding $Zn(NO_3)_2 6NH_3$. The initial salt was $Cd(NO_3)_2 4H_2O$ (Carlo Erba Reagent). If the water elimination process described before is applied, liquid ammonia dissolves the salt, giving a transparent solution as for the Zn salt. The crystals of Cd obtained were larger than the Zn crystals, the largest being about 2mm. These crystals were more stable than the Zn crystals. Analysis similar to the one made for the Zn salts gives 6.31 ammonia molecules per Cd atom.

APPARATUS

The EPR spectra of the $Ni(NO_3)_2 6NH_3$ crystals and of the diluted samples were recorded by a Varian 4502-12 X-band spectrometer. Temperature control was performed with a Varian V-4557 variable temperature accessory. Calibration with a thermocouple showed an accuracy of ±2K between 100K and room temperature.

EPR SPECTRA OF $Ni(NO_3)_2 6NH_3$

The EPR spectra of the concentrated single crystals of $Ni(NO_3)_2 6NH_3$ show a single absorption line [2], with behavior quite similar to the one observed for the halogen nickel hexammines.[3,6] Above the transition temperature an isotropic single line, centered at g=2.18, is observed. Its maximum slope line-width (ΔH_{ms}) goes from 600G to 500G as the temperature decreases from room temperature to Tc. At 243K this line undergoes a sudden broadening to about 2000G. Figure 1 shows the variation of line-width (ΔH_{ms}) as a function of temperature.

Insert Figure 1

We verified hysteresis in the transition temperature of about ΔT = 5K, the effect having been observed previously[7] by a dilatometric technique. The line was fit to the Lorentzian curve within an accuracy of 1%. The g value was the same both above and below Tc.

INTERPRETATION FOR THE $Ni(NO_3)_2 6NH_3$ LINE-WIDTH

1.   The Dipole-Dipole Contribution

To explain the behavior of the line width we assume that the broadening is caused by the onset of an axially distorted field created by the transition of the ammonias. Above the transition, the NH_3 groups are rotating and so the neighborhood of the Ni^{++} ion is a perfectly octahedrical environment. Only two $\Delta m = 1$ transitions occur at the same field. Below Tc the freezing of the degrees of freedom of rotation produces a field distortion at the Ni^{++} positions. This introduces the term DS_z^2 to the spin Hamiltonian and so some splitting to the EPR line should be observed. However, in concentrated crystals of $Ni(NO_3)_2 6NH_3$ this splitting was not observed. In this case we are induced to adopt the assumption that effect of the exchange interaction is to assemble the lines giving a single line. This line is Lorentzian shaped, as predicted by the Anderson and Weiss[8] theory of exchange narrowing of lines. This first condition on the line shape was fullfilled by the experimentally observed line within 1%, as pointed out above ($\Delta H = \sqrt{3} / 2 \Delta H_{ms}$) .

The line width ΔH^o narrowed by exchange interaction was evaluated for a s.c. lattice by Anderson and Weiss using Van Vleck's theory,[9] giving

$$\Delta H^0 = H_p^{o2} / H_e$$

with
$$H_p^{o2} = 5.1(g\beta n)^2 \; S(S+1)$$

$$H_e = \frac{J}{g\beta} \left[2.83 \; S(S+1) \right]^{1/2}$$

where   n   is the density of spins and   J   is the exchange parameter.   The above formulas can be applied to other   cubic structures by rewriting H_e as

$$H_e = (z/6)^{1/2} \frac{J}{g\beta} \left[2.38 \; S(S+1) \right]^{1/2}$$

where   z   is the number of nearest neighbors.

For $Ni(NO_3)_2 6NH_3$,   z = 12, and by substituting   g=2.18, $\beta = 0.9273 \times 10^{-20}$ erg/G, $n=3.3 \times 10^{21}$ spins/cm^3 and   S = 1 we have

$$H_p^o \simeq 150 \; G$$

The parameter   J   is evaluated from the expression for the Weiss temperature,   θ

$$K\theta = \frac{2}{3} \; J \; z \; S(S+1)$$

where   K   is the Boltzmann constant.   J   is calculated using   θ = 3.3 K obtained from magnetic susceptibility measurements [10]   and H_e is evaluated using this values.   The results are

$$J = 1.163 \times 10^{-17} \; erg$$

$$H_e = 10.400 \; G$$

Then

$$\Delta H^0 = 2.06 \; G$$

This ΔH^o value is negligible when compared with the experimental $\Delta H^n = 430$ G ($\Delta H^n = \sqrt{3}/2 \ \Delta H^n_{ms}$; $\Delta H^n_{ms} = 500$ G).

2. The Crystal Field Contribution

The predicted value of $\Delta H^o = 2$ G above Tc is much lower than the experimental value $\Delta H^n = 430$. This large discrepancy between the dipolar and the experimental broadening suggests that we have many unknown sources of line broadening. That is

$$\Delta H^n = \Delta H^o + \Delta H^u$$

where ΔH^u is from unknown sources of broadening and is supposed to be independent from the exchange interaction. If a crystal field contribution is included we have

$$\Delta H = [(H^o_p)^2 + (H^D_p)^2] / H_e + \Delta H^u$$

or

$$\Delta H^D = \Delta H - \Delta H^n = (H^D_p)^2 / H_e$$

That is, for the purpose of the line-width analysis below Tc , we have to subtract 430 G to obtain that part of the width due to the phase transition effect.

Below Tc we have to introduce the crystal field. We can write the crystal field Hamiltonian by .

$$\hat{H}_D = D \sum_i (\vec{S}_i \cdot \vec{n}_i)^2$$

where $\vec{n}_1$ is the direction of the distortion in the unit cell.

The second moment is given by

$$(\omega_p^D)^2 = \frac{1}{\hbar^2} \frac{T_r \{ [A_D , [A_D , s^-]] s^+ \}}{T_r \{s^- , s^+\}}$$

where $s^{\pm} = S_x \pm i S_y$ and D is the cubic crystal field parameter.

Assuming the distortion in the direction (111) we obtain

$$(\omega_p^D)^2 = \frac{10}{3} \frac{D^2}{5\hbar^2} \qquad \text{or} \qquad (H_p^D)^2 = \frac{2}{3} (\frac{D}{g\beta})^2$$

Then we have

$$\Delta H^D = (2/3)(D/g\beta)^2 / H_e$$

By using the experimentally observed ΔH reduced by 430 K to account for the unkown sources of broadening, we have

$$D = 0.425 \text{ cm}^{-1}$$

EPR SPECTRA OF Ni: $Zn(NO_3)_2 6NH_3$

$Zn(NO_3)_2 6NH_3$ is expected to be quite similar to $Ni(NO_3)_2 6NH_3$ because the Ni^{++} and the Zn^{++} are expected to have almost the same radius. However we do not have measurements of the lattice parameter of the Zn salt. Above Tc the Ni diluted in the Zn salt shows an isotropic single line with $\Delta H = 430$ G, like

the one observed in the concentrated salt, although we have now
crystals mixed with powder. Tc is 231 K which is 12K below
the transition temperature for the Ni salt. Hysteresis in Tc
was about 5K, as for the Ni salt. Below Tc the single line splits
into several lines. The characteristic features of the lines
below Tc are shown in figure 2.

For the spectra interpretation we use the Wasserman
and Blombergen method.[11] As the number of line is greater than
expected for the powdered samples, we adopt as primary assigment
the strong absorption line at 5250G. The Hamiltonian is assumed
to be

$$\bar{H} = g\ \beta\ \vec{H}.\vec{S}. + DS_z^2$$

The intense assymetrical line at 5250G was assigned as $H_{\perp 2}$ and
so we must have $h\nu < D$. If this assigment is assumed, there are
two other lines with small intensity and assigned to $H_{||1}$ and
$H_{||2}$ transitions. Experimentally these lines were observed at
3000G and 9050G and have small intensities. An indication that
this assigment is correct is the 6000G separation between the
two lines, as expected for $H_{||1} - H_{||2}$ and $h\nu < D$. The values
of g and D were obtained from

$$h\nu = D - g\beta H_{||1}$$

$$h\nu = g\beta H_{||2} - D$$

$$h\nu = \left[(D/2)^2 + (g\beta H_{\perp 2})^2 \right]^{1/2} - D/2$$

At   225K   we have

$$g = 2.17$$
$$D = 0.606 \text{ cm}^{-1}$$

in good agreement with values given for undiluted $Ni(NO_3)_2 6NH_3$.

The number of lines present in the observed spectra is greater than the set of three lines mentioned above. The extra lines are probably due to magnetic impurities, such as Co, Fe and others. But to assure our assigment we also discuss the temperature behavior of the spectra. When the temperature was lowered we observed that a number of lines moved slowly to higher magnetic fields, suggesting that D increases as the temperature decreases. For $h\nu < D$, if D increases, the values of the fields of the lines assigned to $H_{||1}$, $H_{||2}$ and $H_{\perp 2}$ must increase, as was observed (see figure 2).

If the assign $h\nu > D$, the line at 5250G must be assigned as $H_{||2}$. In this assigment we would expect lines at

$$H_{\perp 2} = 4000G \qquad .$$

$$H_{\perp 1} = 1500G$$

$$H_{||2} = 750G$$

and $D \simeq 0.2$ cm^{-1} . Lines were not found in the expected positions and intensities, which confirms the above adopted assigment.

EPR SPECTRA OF Ni: $Cd(NO_3)_2 6NH_3$

The EPR spectra of Ni: $Cd(NO_3)_2 6NH_3$ is different from that observed for Ni:$Zn(NO_3)_2 6 NH_3$. The values of Tc are also different, with Tc=231 K for Ni:Zn salt and Tc=198 K for Ni:Cd. The single line at g=2.17 breaks down at Tc and several lines appear and the behavior of the spectra of these salts is different, as can be seen by comparing figures 2 and 3. A very weak line at 6000G and a broad line near H = 0 indicates

Insert Figure 3

that $D \simeq h\nu$ By assigning the 6000G line to $H_{||2}$, we have

$$D \simeq 0.3 \text{ cm}^{-1}$$

The hysteresis is about 10K, twice larger than the one observed for $Ni(NO_3)_2 6NH_3$ and $Ni:Zn(NO_3)_2 6NH_3$. The values of D in the Ni:Zn salt is greater than in the Ni:Cd salt. This observation can not yet be explained from the present available experimental data.

DISCUSSION

The observation that the line width ΔH^n is the same in both undiluted and doped salts of $Ni(NO_3)_2 6NH_3$ above Tc

indicates that ΔH^n is the natural line width arising from unknown sources of broadening. The dipolar contribution to the line width was shown to be negligible. The value used in the evaluation of the dipolar contribution $H_e = 10400G$ is in good agreement with the experimentally observed exchange field of about 13000G.[12]

The sudden broadening of the line in the undiluted salt and the splitting of the single isotropic line in the doped salts at Tc were interpreted as due to the appearance of an observable crystal field. This supports the hypothesis of the collective freezing of degrees of freedom of the ammonias in the skeleton $| X(6NH_3)_6 |^{++}$.

The values of D were assigned as

$$D = (0.425 \pm 0.003) \text{ cm}^{-1} \qquad Ni(NO_3)_2 6NH_3$$

$$D = (0.606 \pm 0.003) \text{ cm}^{-1} \qquad Ni: Zn(NO_3)_2 6NH_3$$

$$D \simeq 0.3 \text{ cm}^{-1} \qquad Ni: Cd(NO_3)_2 6NH_3$$

The mean value of D for the diluted salts, $D = 0.45 \text{cm}^{-1}$, is in good agreement with the value obtained from line width data.

The values of Tc were observed to be

$$Tc = 243K \qquad Ni(NO_3)_2 6NH_3$$

$$Tc = 231K \qquad Ni:Zn(NO_3)_2 6NH_3$$

$$Tc = 198K \qquad Ni:Cd(NO_3)_2 6NH_3$$

that is, Tc(Ni) > Tc(Zn) > Tc(Cd).

The present observed behavior for the line width is very similar to the one observed for the halogen hexammine salts. The Bates and Stevens model, developed for the halide salts, fails when applied to nitrate salts. The lattice parameter of

$Ni(NO_3)_2 6NH_3$ is a = 10.96Å , which is between the lattice parameters of $NiBr_2 6NH_3$ (a=10.46Å) and $NiI_2 6NH_3$ (a=11.01Å). So we might expect that the transition temperature of $Ni(NO_3)_2 6NH_3$ will be between the Tc's of these salts, i.e., between 45K and 24K. But for $Ni(NO_3)_2 6NH_3$ we have Tc=243K larger than the expected. This high value of Tc was discussed previously[1] and attributed to the contribution of an extra potential on the hydrogens of the NH_3 by the nitrate radicals. Including the effect of the nitrate radical in the Bates and Stevens model it is possible to predict that Tc increases as the lattice parameter decreases in the $X(NO_3)_2 6NH_3$ salts.

The lattice parameters of Zn and Cd salts are unknown. The lattice parameter of the Zn salt is expected to be sligthly greater than the lattice parameter of the Ni salt, because Zn has a larger atomic radius than Ni. In the same way we expect the parameter of the Cd salt to be the largest one, that is

a(Ni) < a(Zn) < a(Cd)

This correlation between the lattice parameter gives

Tc(Ni) > Tc(Zn) > Tc(Cd)

by using the Bates and Stevens modified model. This is now in agreement with the experimentally observed correlation. It may be assumed that this procedure is correct since we are comparing crystals assumed to be of the same structure.

ACKNOWLEDGMENT:

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Figure 1.   The EPR   maximum slope line-width, ΛH_{ms}, versus

temperature of the $Ni(NO_3)_2 6NH_3$.

Figure 2.   The   EPR   spectra of the $Ni:Zn(NO_3)_2 6NH_3$.
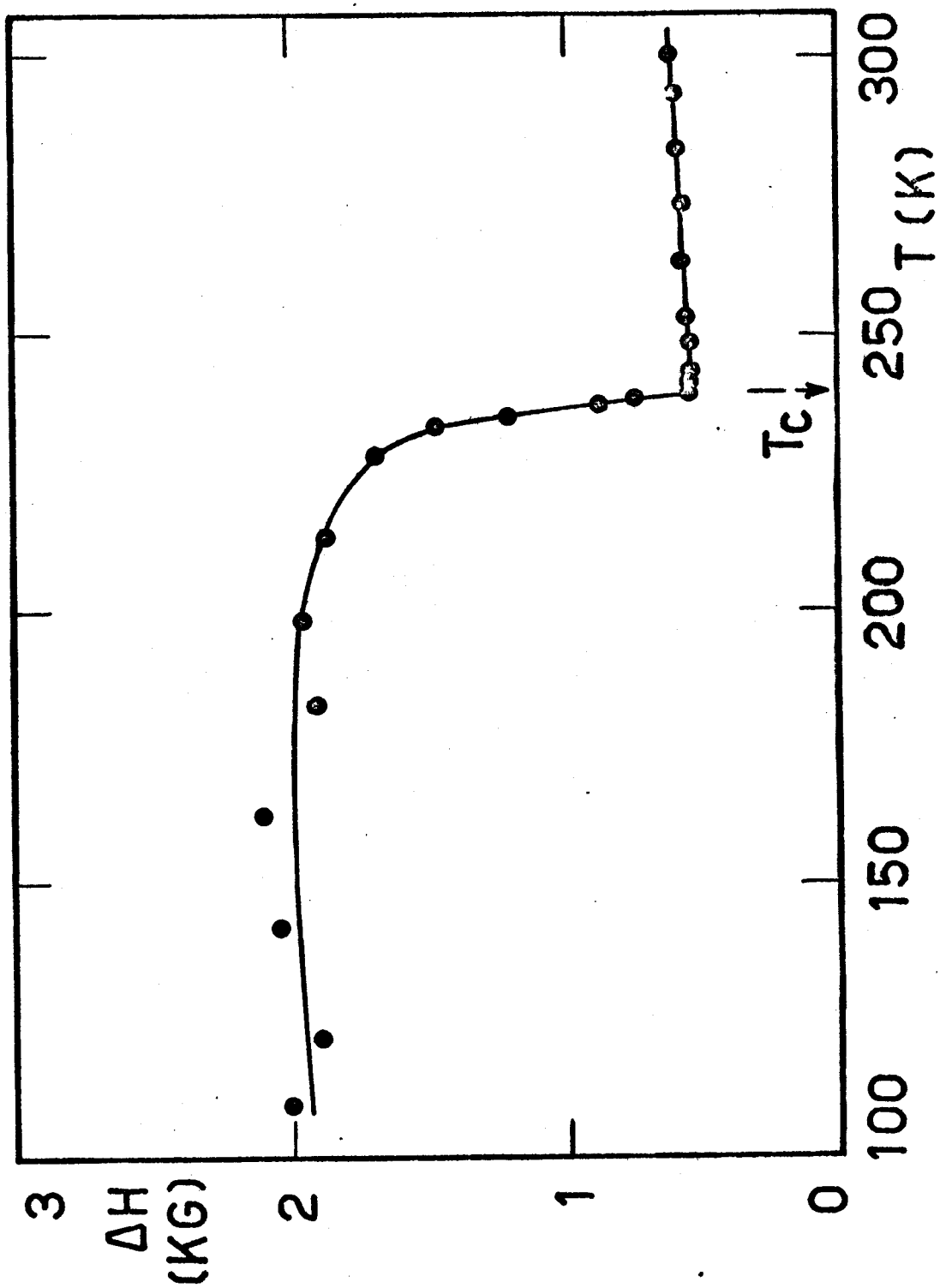
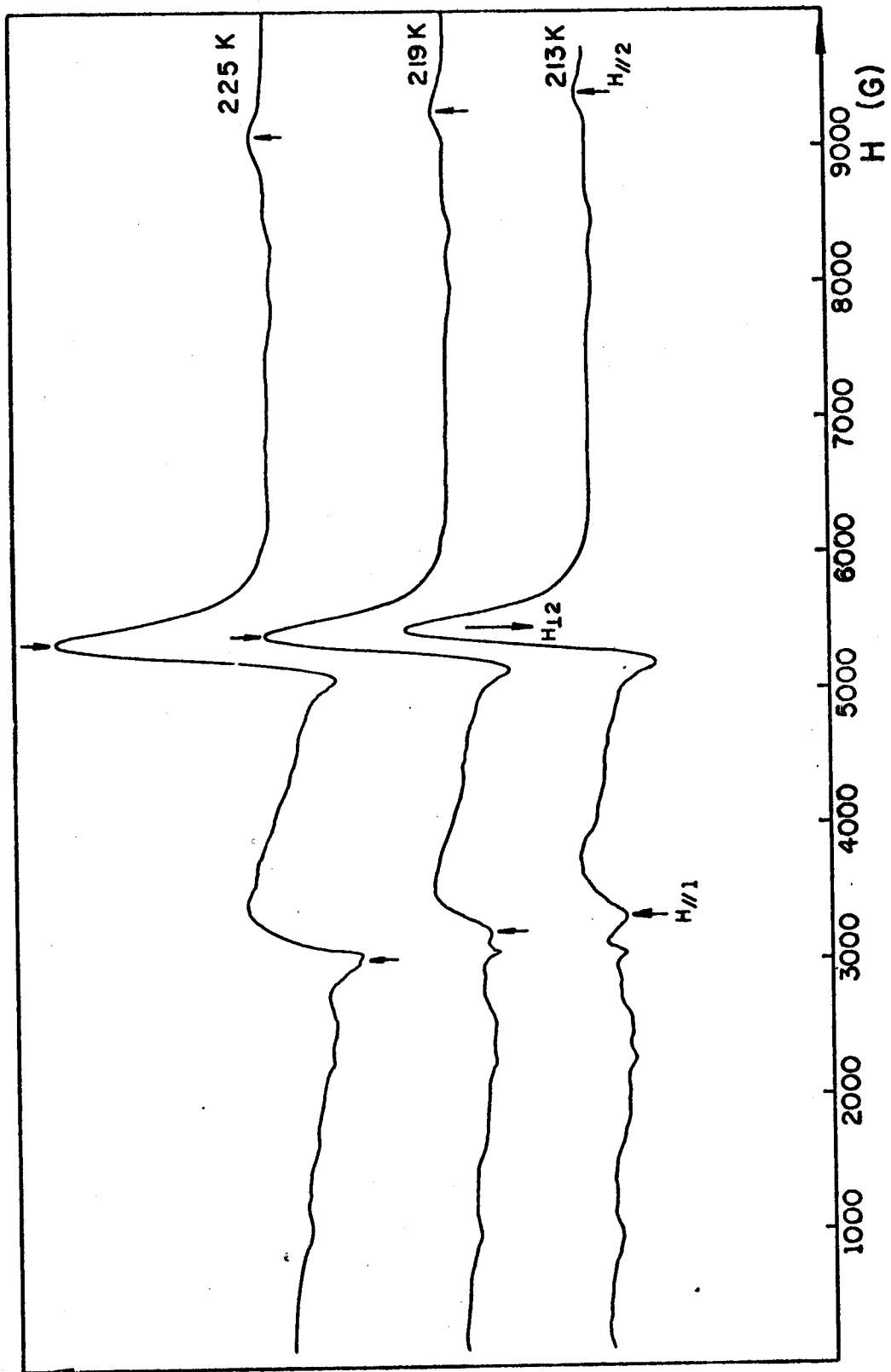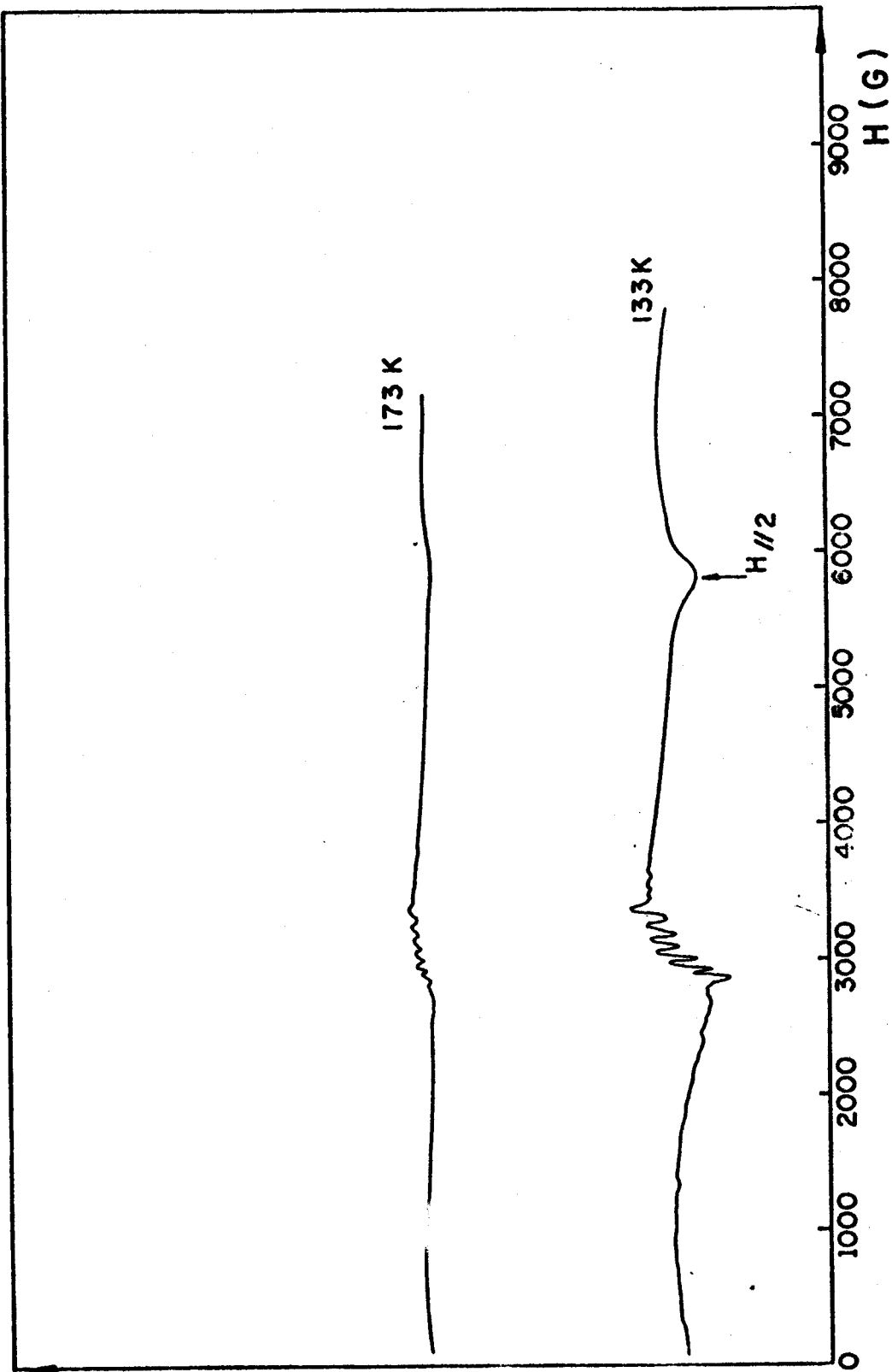Figure 3.   The   EPR   spectra of the $Ni:Cd(NO_3)_2 6NH_3$.

Figure 1

Figure 2

Figure 3