

# TEMPERATURE DEPENDENCE OF THE EPR SPECTRA OF [Ni(NH<sub>3</sub>)<sub>6</sub>]<sup>2+</sup> COMPLEXES IN CADMIUM HEXAMMINE FLUOROBORATE AT THE PHASE TRANSITION

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(Received March 27, 1976)

In powdered samples of [Cd(NH<sub>3</sub>)<sub>6</sub>](BF<sub>4</sub>)<sub>2</sub> containing 0.1 to 5% Ni, the temperature-dependence of the EPR spectrum of the Ni<sup>2+</sup> ion is studied from 77 to 290 K. The single line observed at room temperature for which  $g = 2.178$  undergoes splitting at  $T_c = 147$  K. Below the phase transition temperature  $T_c$  the EPR spectrum is described by the spin hamiltonian containing Zeeman term and the fine structure term  $D(S_z^2 - \frac{2}{3})$ . This effect is related to the emergence of axial distortion for the [Ni(NH<sub>3</sub>)<sub>6</sub>]<sup>2+</sup> complex characterized by the zero-field splitting parameter  $D$  of the order of  $0.4 \text{ cm}^{-1}$ . As the temperature is further lowered to that of liquid nitrogen,  $D$  increases to  $0.8 \text{ cm}^{-1}$ .

## 1. Introduction

Hexammine complex compounds of divalent transition metal ions having the general chemical formula:  $[Me(\text{NH}_3)_6]X_2$ , where  $Me = \text{Ni, Co, Mn, Zn, Cd, Ca}$  and  $X = \text{Cl, Br, I, BF}_4, \text{ClO}_4, \text{NO}_3, \text{PF}_6$  form a regular structure similar to that of  $\text{CaF}_2$  [1]. Their high symmetry  $Fm3m (O_h^5)$  has made them the object of numerous spectroscopic investigations, especially for their Raman scattering and far infrared spectra [2, 3]. A number of the physical parameters, such as specific heat [4-6], thermal conductivity [7] and dielectric permittivity [8] are observed to undergo a sudden change at the phase transition; but most of all their crystallographic structure varies drastically. For example, [Ni(NH<sub>3</sub>)<sub>6</sub>](BF<sub>4</sub>)<sub>2</sub> has regular symmetry above the phase transition; but the temperature dependence of the X-ray pattern gives evidence that the crystal is less symmetric below  $T_c$  [9].

Palma-Vittorelli and co-workers applied the EPR method to study the local symmetry of the paramagnetic complex [10]. The method was found to be very effective due to a pronounced increase of the line width at the transition temperature [11, 12]. This was extended by Trapp and Shyr [13] and Ochi et al. [14] to the study of diluted paramagnetic

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hexammines in order to determine the zero-field splitting of the EPR spectrum. Line width transition at  $T_c = 145$  K was also detected in the EPR of  $[\text{Ni}(\text{NH}_3)_6](\text{BF}_4)_2$  [15]; while for cadmium hexammine, relaxation times for both protons and fluorines presented a discontinuity yielding  $T_c = 147$  K as measured by NMR relaxation [16]. The Mössbauer spectrum of ferrous iron hexammines, providing information on quadrupole splitting, corroborates the earlier hypothesis of trigonal distortion of the octahedron below  $T_c$  [17]. Thermal hysteresis is another typical effect accompanying phase transition in these compounds [7]. This points to the collective nature of the processes responsible for the transition. The transition temperature  $T_c$  for the deuterized compounds  $[\text{Fe}(\text{ND}_3)_6]\text{Cl}_2$  [17] and  $[\text{Ni}(\text{ND}_3)_6]\text{I}_2$  [12] yield values respectively 5 K and 6 K higher than those of non-deuterized compounds.

Bates and Stevens [18] interpret the effects taking place in the phase transition of nickel hexammine halides by considering the electrostatic energy corresponding to all possible configurations of the  $\text{NH}_3$  group within the individual complex as well as the energies of interaction between neighbouring complexes in the crystal lattice. The proposed model accounts for the reduction of the ligand field symmetry observed in the EPR spectrum and is consistent with the structural changes taking place at this temperature. At low temperatures, the energy of the system is defined by interactions between neighbouring complexes. Such interactions favour an ordering of the octahedron distortions of trigonal symmetry of the complexes, causing the electric field acting on a nickel ion to assume axial symmetry. Above  $T_c$ , the energy of random thermal motion predominates that of electrostatic interaction between neighbouring complexes, and the  $\text{NH}_3$  groups in the individual complex rotate in a manner uncorrelated with the rotations of the neighbouring complexes. As a result of this, six rotating  $\text{NH}_3$  ligands yield a cubic field. Hence, the EPR spectrum of  $[\text{Ni}(\text{NH}_3)_6]^{2+}$  complexes at temperatures above  $T_c$  presents a single, relatively narrow line. As the neighbourhood of the paramagnetic ion undergoes axial distortion, the EPR spectrum of the  $\text{Ni}^{2+}$  ion comes to consist of lines, corresponding to the two allowed transitions within the multiplet with spin  $S = 1$ . Since this investigation deals with powders, there is a continuous distribution of lines, corresponding to variously oriented crystallites. Owing to exchange interactions between paramagnetic ions in undiluted compounds, one observes a single, broad and symmetric line at  $g = 2.17$  instead of multicomponent, asymmetric EPR spectrum fine structure.

Anisotropic studies of the EPR spectrum were performed for single crystals of hexammine nickel halides [10], however no angular dependence of the spectrum was found throughout the 4.2 K to 300 K range although this temperature range comprised the non-cubic phases of all the compounds investigated. This is due to exchange interaction, which leads to an averaging of the fine structure spectra and makes it impossible to perform a direct measurement of the zero-field splitting. With the intention of determining the value of zero-field splitting in the non-cubic phase  $T < T_c$ , we proceeded to an EPR study of the  $[\text{Ni}(\text{NH}_3)_6]^{2+}$  present in small amounts in the diamagnetic compound  $[\text{Cd}(\text{NH}_3)_6](\text{BF}_4)_2$ . Owing to the high dilution of the paramagnetic ions in the lattice of cadmium hexammine, exchange obliterating the fine structure of the spectrum can be disregarded.

## 2. Experimental

$[\text{Cd}(\text{NH}_3)_6](\text{BF}_4)_2$  samples containing 0.1%, 0.3%, and 3% of  $\text{Ni}^{2+}$  ions were prepared by Dr G. Pytasz from the Institute of Chemistry, Jagellonian University, Cracow. Samples containing 5% of  $\text{Ni}^{2+}$  were prepared by one of us (P.B.S.) by crystallizing a mixture of cadmium and nickel hexammine compounds from a liquid  $\text{NH}_3$  solution at low temperature. In order to prevent chemical decomposition, the samples were maintained in the atmosphere of gaseous ammonia at about  $4^\circ\text{C}$  (277 K). For measurement, the sample was kept in a gas tight quartz ampoule, which contained about 10 mg of the compound. Temperature was measured by means of a copper-constantan thermocouple, placed in the immediate vicinity of the sample. The system as whole was placed in the cylindrical  $\text{TE}_{011}$  microwave resonator of a Jeol — JES-3BX spectrometer.

The EPR spectrum was recorded in the form of an absorption signal derivative by modulation of the magnetic field at a frequency of 100 kHz and phase detection. Temperature-dependent measurements were performed at 9.23 GHz frequency locked to the sample cavity. A digital meter was used for reading the frequency of the resonator with 1 kHz precision.

At room temperature, all the samples of cadmium hexammine fluoroborate with various amounts of nickel exhibited single lines at  $g = 2.178$ . The line-width decreased slightly with decreasing temperature, down to a value  $2\Delta B_{1s} = 385$  Gs (38.5 mT) at 190 K for the sample containing 0.1%  $\text{Ni}^{2+}$ . Irrespective of the  $\text{Ni}^{2+}$  content, the line-width was approximately the same and did not correlate with the value predicted by the second moment calculation of diluted paramagnetic samples [19].



Fig. 1. EPR spectrum of  $\text{Ni}^{2+}$  ions in cadmium hexammine at 144 K; the central line at  $g = 2.178$  corresponds to the cubic symmetry of the crystal field

At a temperature of  $T_c = 147$  K, a steep change is observed in the EPR spectrum: the amplitude of the main line at  $g = 2.178$  decreases and satellite lines of a weaker intensity make their appearance. In the 140–150 K region, the two groups of lines apparently co-exist (Fig. 1).

As the temperature is further lowered, the main line vanishes. The dashed curve on Fig. 2 represents the intensity  $I$  of the vanishing line in arbitrary units. Two asymmetric

signals of  $\text{Ni}^{2+}$  EPR fine structure are recorded below 147 K, their resonance fields varying between 0.1 and 0.6 T dependent on temperature (Fig. 2).

EPR spectrum anomaly at  $T_c = 147$  K is accompanied by a sudden 5 MHz increase in the resonance frequency of the sample cavity that could result either from a dielectric anomaly or the sample dilatation occurring at this temperature.

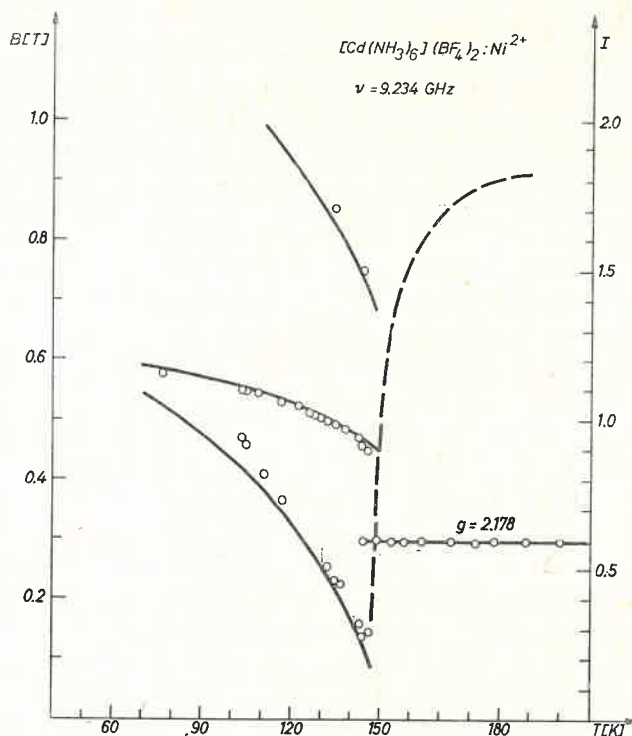


Fig. 2. Values of resonance fields  $B_{||}^{(1)}$ ,  $B_{||}^{(2)}$  and  $B_{||}^{(3)}$  versus temperature. Dashed curve represents the intensity of the cubic-phase signal in arbitrary units

In this narrow temperature range a small signal is also observed at 0.75 T. Its resonance field shifts upwards when the temperature is lowered (Fig. 2). All the EPR signals, their position marked with circles, will be shown to confirm the assumption of a non-zero zero-field splitting term in spin hamiltonian increasing when the temperature is lowered.

### 3. Interpretation of the results

The ground state of a nickel ion  $\text{Ni}^{2+}$  in a crystal field of regular symmetry is defined by the orbital singlet  $A_2$  [20]. The three-fold degeneracy of this state related to the spin  $S = 1$  is removed by the magnetic field  $\mathbf{B}$ , and the energy of the Zeeman levels is given by the simple hamiltonian:

$$\mathcal{H} = g\mu_B \mathbf{B} \cdot \mathbf{S}, \quad (1)$$

where  $\mu_B$  is the Bohr magneton. As a result of transitions stimulated by the magnetic vector of the microwave field of frequency  $\nu$  between the states of the spin multiplet, a single resonance line is observed in the field  $B_0 = h\nu/g\mu_B$ . The spin hamiltonian describing the energy levels of  $\text{Ni}^{2+}$  in a crystal field having a lower, axial symmetry contains moreover a term accounting for the splitting of spin levels at zero magnetic field; this term is of the form:

$$\mathcal{H} = g\mu_B \mathbf{B} \cdot \mathbf{S} + D(S_z^2 - \frac{2}{3}), \quad (2)$$

where  $D$  denotes the energy difference between the spin doublet  $|\pm 1\rangle$  and singlet  $|0\rangle$  in the absence of the magnetic field.

The EPR spectrum of one type of complexes in the crystal exhibits anisotropy, and the number of lines observed depends on the numerical relation between the energy of the microwave quantum  $h\nu$  and the magnitude of  $D$ . The direct measurement of  $D$  is feasible from the electron paramagnetic resonance spectrum of the monocrystal at a well defined orientation of the magnetic field  $\mathbf{B}$ .

In powders, we deal with a situation in which the anisotropic properties of the spectrum undergo an averaging. The shape of the envelope of the paramagnetic absorption signals from the randomly oriented magnetic complexes can be reconstructed by computer simulation of the spectrum. This requires calculating the eigenvalues of the hamiltonian (2) for all possible orientations of the complex in the field  $\mathbf{B}$  and the summation of their contributions to the total paramagnetic absorption of the powder with single line shape and transition probability taken into account.

Computations by Wasserman and Snyder [21] show that in the case of the EPR spectra of triplet states of organic molecules, the maxima of the absorption signal envelope

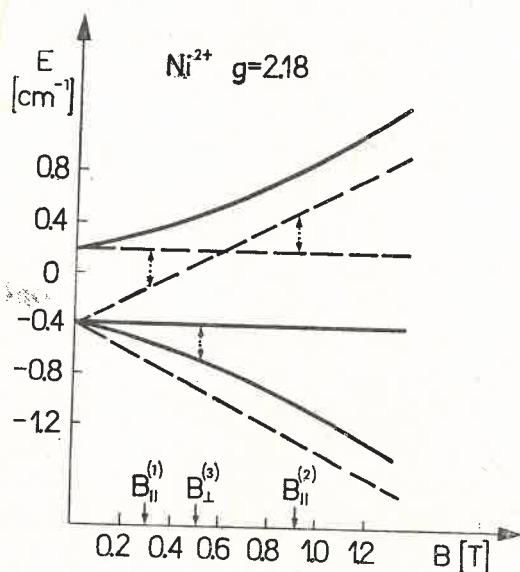


Fig. 3. Energy levels and allowed transitions for spin  $S = 1$  in the crystal field of axial symmetry.  $D = -0.6 \text{ cm}^{-1}$



lie close to the resonance field values  $B_r$  for the transitions between the Zeeman levels as calculated for parallel and perpendicular orientation. Their results, applied to nickel hexammine complexes which too are characterized by a triplet state, lead us to predict that the maxima of the absorption signal envelope will occur near the resonance field values for transitions with  $\Delta m = \pm 1$  within the set of Zeeman levels corresponding to a perpendicular orientation of the trigonal axis  $\mathcal{C}_3$  of the complex with respect to the external magnetic field  $\mathbf{B}$  as well as in the set of levels for parallel orientation of  $\mathcal{C}_3$  and  $\mathbf{B}$  (Fig. 3). The graph of Fig. 3 is plotted for a zero-field splitting  $D$  equal  $-0.6 \text{ cm}^{-1}$  and a quantum energy of  $h\nu = 0.3 \text{ cm}^{-1}$ . The solid line shows the energy levels of the  $\text{Ni}^{2+}$  ion in a complex, the principal direction of which subtends an angle of  $90^\circ$  with the magnetic field. The dashed line is for  $\mathcal{C}_3$  and  $\mathbf{B}$  parallel i. e. the angle  $\Theta = 0^\circ$ .

The numerical computation of resonant fields  $B_r$  for  $\Theta = 0^\circ$  and  $\Theta = 90^\circ$  requires one to assume values for  $D$  and  $h\nu$ . When zero-field splitting is very small compared with  $h\nu$ , the paramagnetic absorption signal from the powders will present four maxima, separated by  $\pm D$  and  $\pm D/2$  from the main line positioned at  $B_0$ . EPR spectra simulated for this case fail to coincide with those observed for  $\text{Ni}^{2+}$  doped cadmium hexammine powders. We hence assume that, in this compound, zero-field splitting is larger than the energy of the microwave quantum  $h\nu$ . The resonance fields  $B_r$  are now:

$$\begin{aligned} B_{\parallel}^{(1)} &= D - B_0 \quad \text{for} \quad \Theta = 0^\circ \\ B_{\parallel}^{(2)} &= D + B_0 \\ B_{\perp}^{(3)} &= \sqrt{B_0(D + B_0)} \quad \text{for} \quad \Theta = 90^\circ, \end{aligned} \quad (3)$$

where  $B_0 = h\nu/g\mu_B$ . From the EPR spectra simulated for triplet states it is known that signals corresponding to the perpendicular orientation of complexes observed at  $B_{\perp}^{(3)}$  has a higher intensity relative to the remaining lines [21]. Numerous experimental points

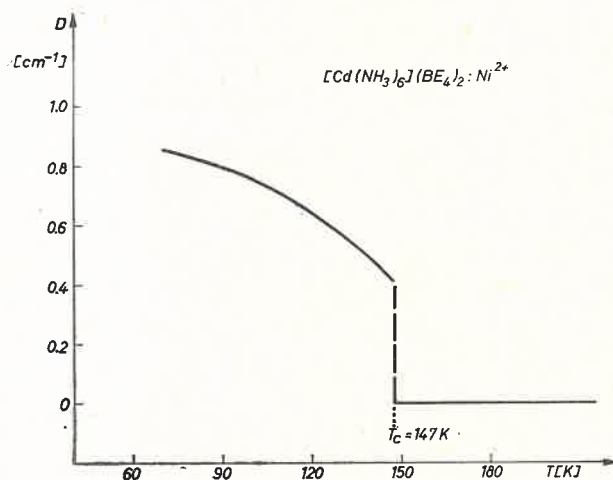


Fig. 4. Zero-field splitting  $D$  vs. temperature for  $\text{Ni}^{2+}$  in cadmium hexammine fluoroborate

refer to the  $B_{\perp}^{(3)}$  resonance field value of the graph (Fig. 2). From Eq. (3) the  $D$  parameters can be calculated, and an average found for each temperature point. The graph showing the temperature dependence of  $D$  (Fig. 4) gives a best fit with the experimental results. Recalculated positions of resonance fields  $B_{\parallel}^{(1)}$ ,  $B_{\parallel}^{(2)}$  and  $B_{\perp}^{(3)}$  is then shown by solid lines on Fig. 2.

A computer simulation applied to the case of randomly oriented nickel hexamine complexes would lower the discrepancies between experimental points and the calculated curves but the character of  $D$  vs. temperature dependence would remained unaltered (Fig. 4).

#### 4. Discussion and conclusions

It results from the investigation of the EPR of the nickel hexammine complex in cadmium hexammine fluoroborate that the distortion of the crystal field is associated with a change of the crystal structure. Both, the sharp increase in  $D$ , representing a paramagnetic complex and the discontinuity of NMR relaxing time, coincide at the same value of transition temperature specified for the pure cadmium hexammine fluoroborate. It points to the inter-ionic interactions dominating the possible intra-ionic  $[Me(NH_3)_6]^{2+}$  forces during the process of growing the low symmetry phase. The assumption is further confirmed by the strong  $D$  dependence on temperature: it varies from  $0.4 \text{ cm}^{-1}$  at 140 K to  $0.8 \text{ cm}^{-1}$  at that of liquid nitrogen. It indicates a strong vibronic coupling of the paramagnetic complex to the lattice. The effect is due to a rapid reorientation of the  $(BF_4)^-$  anion demonstrated by the NMR relaxation of fluorine nuclei even down to the temperature of liquid nitrogen. However, the analysis of EPR spectra of powdered samples does not reveal any non-axial distortion, thus, the neighbourhood of the  $Ni^{2+}$  ion has to be assumed of axial symmetry.

We are grateful to Professor J. A. Janik and Dr hab. J. M. Janik for valuable discussions and for communicating their results on specific heat anomalies and the Raman spectra of the hexammines group to us. Thanks are due to Dr G. Pytasz for his aid in preparation of the samples.

#### REFERENCES

- [1] R. W. G. Wyckoff, *Crystal Structure*, Interscience, New York 1965, p. 783.
- [2] J. A. Janik, W. Jakób, J. M. Janik, *Acta Phys. Pol.* **A38**, 467 (1970).
- [3] T. Grzybek, J. A. Janik, J. M. Janik, A. Kulczycki, G. Pytasz, E. Ścieszńska, J. Ścieszński, *J. Raman Spectroscopy* **1**, 185 (1973).
- [4] F. W. Klaajisen, H. Suga, Z. Dokoupil, *Physica* **51**, 630 (1971)..
- [5] T. Matsui, S. Hiroshi, S. Synco, *Bull. Chem. Soc. Jap.* **44**, 1171 (1971).
- [6] T. Grzybek, J. A. Janik, J. Mayer, G. Pytasz, M. Rachwalska, T. Waluga, *Phys. Status Solidi a* **16**, K165 (1973).
- [7] A. Elgsaeter, I. Svare, *J. Phys. Chem. Solids* **31**, 1405 (1970); D. G. Thomas, L. A. K. Staveley, A. F. Cullis, *J. Chem. Soc.* 1727 (1952).
- [8] G. Aiello, M. B. Palma-Vittorelli, *Phys. Rev. Lett.* **21**, 137 (1968).
- [9] E. Dynowska, *Phys. Status Solidi a* **31**, K23 (1975).

- [10] M. B. Palma-Vittorelli, M. U. Palma, G. W. J. Drewes, W. Koerts, *Physica* **26**, 922 (1960).
- [11] M. B. Palma-Vittorelli, M. U. Palma, F. Persico, *J. Phys. Soc. Jap.* **17**, 475 (1962), Supplement B1.
- [12] T. Garofano, M. B. Palma-Vittorelli, M. U. Palma, F. Persico, *Paramagnetic Resonance*, Proceedings of the International Conference, Jerusalem 1962, vol. II, p. 582; M. Date, *J. Phys. Soc Jap.* **15**, 2115 (1960).
- [13] Ch. Trapp, Chin-I-Shyr, *J. Chem. Phys.* **54**, 196 (1971).
- [14] J. A. Ochi, W. Sano, S. Isotani, C. F. Hennies, *J. Chem. Phys.* **62**, 2115 (1975).
- [15] J. Stankowski, J. M. Janik, A. Dezor, B. Sczaniecki, *Phys. Status Solidi a* **16**, K167 (1973).
- [16] N. Piślewski, J. Stankowski, L. Laryś, *Phys. Status Solidi a* **31**, 415 (1975).
- [17] L. Asch, G. K. Shenoy, J. M. Friedt, J. P. Adloff, R. Kleinberger, *J. Chem. Phys.* **62**, 2335 (1975).
- [18] A. R. Bates, K. W. H. Stevens, *J. Phys.* **C2**, 1573 (1969); A. R. Bates, *J. Phys.* **C3**, 1825 (1970).
- [19] C. Kittel, E. Abrahams, *Phys. Rev.* **90**, 238 (1953).
- [20] J. W. Tucker, V. W. Rampton, *Microwave Ultrasonics*, North-Holland, Amsterdam 1972, chapt. VI.
- [21] E. Wasserman, L. C. Snyder, W. A. Yager, *J. Chem. Phys.* **41**, 1763 (1964).