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# **Further experiments concerning an unusual low-temperature behaviour of some magnetic ammoniate crystals \***

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## *Summary*

In order to clarify the unusual magnetic behaviour of hexammine Nickel halides, further experiments have been performed on the same crystals and on single crystals of tetrammine copper sulphate. In the last crystals, a peculiar temperature-dependence of the *g*-values, of line-width and of line-shape has been evidenced, in the helium temperature range. In hexammine Nickel iodide a temperature-dependent absorption line in low fields, together with a corresponding shift of the main absorption line has been detected, in the range from 8° K to 1.3° K, which supports the hypothesis of an antiferromagnetic transition. Further work is in progress on this and on the similar Nickel halides.

## **1. INTRODUCTION.**

Electron Spin Resonance (E.S.R.) and static susceptibility measurements on single crystals of hexammine Nickel halides have yielded unexpected results [1], which may be summarized as follows:

- a)* At temperature higher than a critical value  $T_c$ , one single, strictly isotropic E.S.R. line is present. The line-width is about one hundred gauss;
- b)* A large broadening of that line from about one hundred to thousands of gauss occurs sharply at a critical temperature (characteristic of each salt), which is of the order of 20° K or higher;
- c)* The static susceptibility measured in fields of a number of thousands of gauss shows approximately a Curie-Weiss behaviour, with no detectable transition at the mentioned critical temperature. The  $\Delta$ -value so obtained is smaller for about a factor 1/6 than the transition temperature. A continuous slight curvature of the  $(1/\chi, T)$  curve might be present, but it is not evidenced within the experimental accuracy.

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Remarkable exchange phenomena may be present in these crystals due to the charge-transfer which occurs between the  $\text{Ni}^{++}$  ions and the ammonia molecules. This is evidenced by a sizable reduction of the  $\lambda$  spin-orbit coupling constant, compared with the free-ion  $\lambda_0$  value [2, 3]. The crystals are f.c.c. and the Nickel ions are at the corners and at the face centres, surrounded each by an octahedron of ammonia molecules. In a f.c.c. lattice an antiferromagnetic ordering cannot be built in a simple way [4, 5]: this fact is rather peculiar and as pointed out by Stevens [6] it may give rise to unusual behaviours.

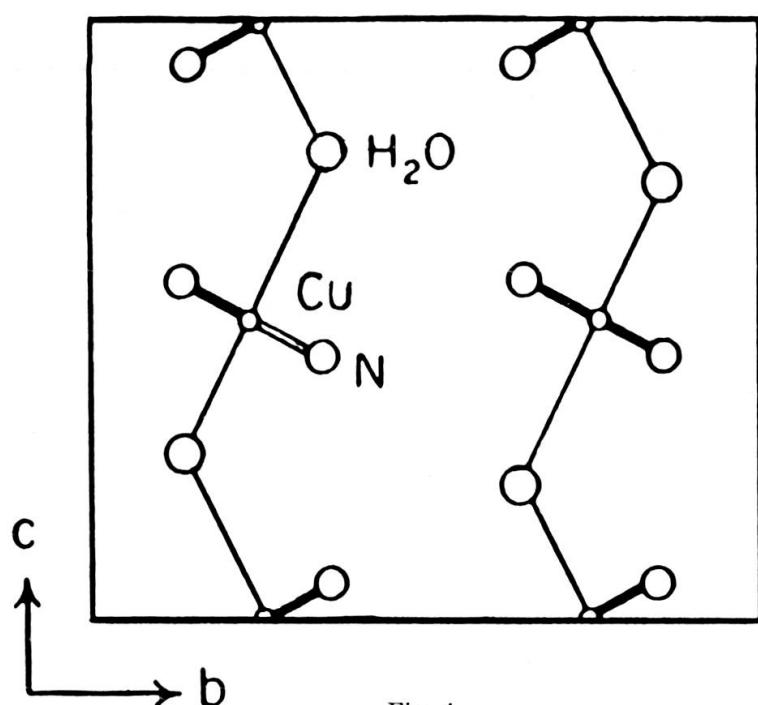


Fig. 1.

Crystal structure of  $\text{Cu}(\text{NH}_3)_4\text{SO}_4 \cdot \text{H}_2\text{O}$ .  
Projection of the unit cell on the (100) plane (after Mazzi).

To check the role of ammonia in a non-cubic crystal and find if it would be responsible also in that case for an unusual behaviour, we have performed E.S.R. experiments on  $\text{Cu}(\text{NH}_3)_4\text{SO}_4 \cdot \text{H}_2\text{O}$  single crystals.

In the present note, account will be given of such results, together with further results on hexammine Nickel halides. A possible line of interpretation will be given. That interpretation leads to difficulties, and is mainly intended to give a basis for a discussion rather than a definitive opinion of the authors.

2. RESULTS ON  $\text{Cu}(\text{NH}_3)_4\text{SO}_4 \cdot \text{H}_2\text{O}$  AND DISCUSSION.

The crystal structure is schematically shown in Fig. 1 [7]. The elementary cell contains four  $\text{Cu}^{++}$  ions, arranged in chains, each surrounded by an octahedron of 4 ammonia and 2 water molecules, considerably distorted along the fourfold axis on which the water molecules are lying. The distortion axes of the octahedra are parallel in couples. Each  $\text{Cu}^{++}$  ion has eight  $\text{Cu}^{++}$  neighbours, at comparable distances, six of which equivalent to it, and two non-equivalent, lying along the  $c$ -axis. On this basis the very remarkable exchange-narrowing effects exhibited at room temperature may be accounted for.

The susceptibility of this salt has been theoretically investigated by Eisenstein [8]. It exhibits a maximum at  $3.15^\circ\text{ K}$  for any direction of the magnetic field with respect to the crystal axes [9]. Preliminary E.S.R. data have been given by Gerritsen [10] and by Date [11], showing that the line-width increases when the temperature is lowered, in the liquid helium temperature range.

The main features of the present results, summarized in Fig. 2 are the following:

- 1) The anisotropy in the  $g$ -values decreases when the temperature is lowered from  $4^\circ$  to about  $2^\circ\text{ K}$ ;
- 2) For the same change of temperature, the full line-widths at the half-maximum points and at the maximum-slope points, and the second-moment square root strongly increase, while the ratio  $\frac{\sqrt{M_2}}{\Delta H_{\frac{1}{2}}}$  decreases (the line broadening is in this case much less sharp and material than in the hexammine Nickel halides [1]);
- 3) The inverse changes occur when the temperature is lowered from about  $2^\circ\text{ K}$  to  $1.3^\circ\text{ K}$ .

These results are not in full agreement with the ones of Gerritsen and of Date, who find that the line-width still increases at  $1.4^\circ\text{ K}$  reaching values significantly larger than ours. We believe that the internal consistency of our results (see Fig. 2) evidences that the mentioned reversal of the sign of the changes, which we have measured, is a real one, while it is possible that it occurs at a temperature between  $2^\circ\text{ K}$  and  $1.3^\circ\text{ K}$  rather than just at  $2^\circ\text{ K}$ . This, together with some slight error in the temperature

measurements, might explain the discrepancy, but we are convinced that the reversal in the sign of the changes is real. The temperature range between  $2^{\circ}$  K and  $1.3^{\circ}$  K (labeled by *a* in Fig. 2) is now being investigated (to better locate the temperature at which the mentioned reversal occurs) together with the range labeled by *b*.

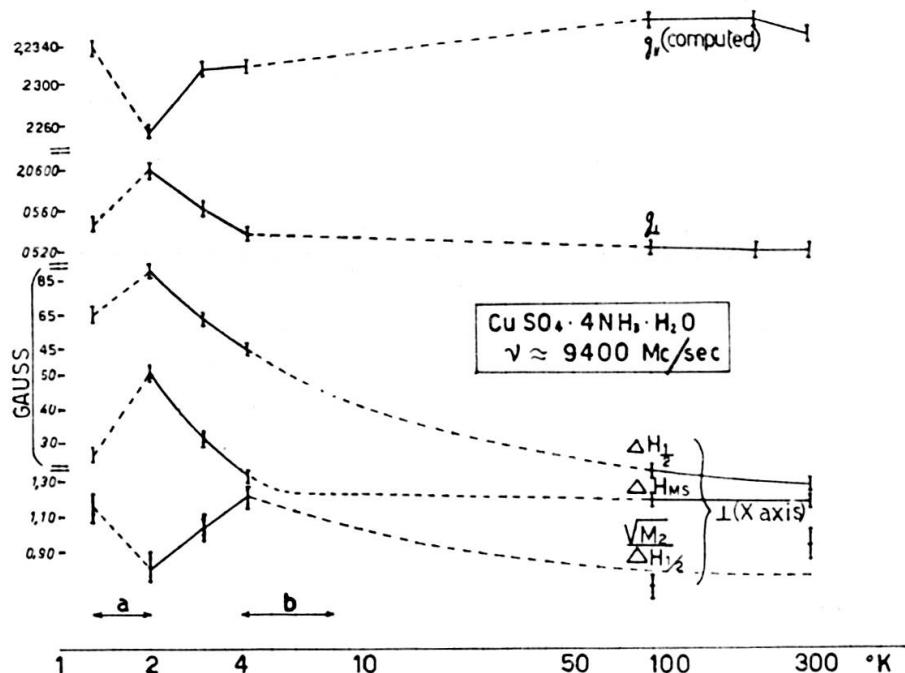


Fig. 2.

E.S.R. results on  $\text{Cu}(\text{NH}_3)_4 \text{SO}_4 \cdot \text{H}_2\text{O}$ ;  $\Delta H_{\frac{1}{2}}$  (half maximum full line-width),  $\Delta H_{ms}$  (maximum-slope full line-width),  $\frac{\sqrt{M_2}}{\Delta H_{\frac{1}{2}}}$  ( $M_2$  = second moment) are taken along the *a*-axis which is perpendicular to the magnetic axes of all the Cu ions.

The decrease in the *g*-value anisotropy between about  $4^{\circ}$  and  $2^{\circ}$  K, shows that the non-cubic component of the crystal electric field decreases. This might be due to a decrease of the  $\text{Cu}^{++}\text{-H}_2\text{O}$  distance, compared with the  $\text{Cu}^{++}\text{-NH}_3$  distance, which approximately means a relative decrease of the *c* dimension of the cell. The distance between the non-equivalent neighbours would then be decreased, compared with the distance between equivalent neighbours. As a consequence, the exchange broadening would be increased, in agreement with the  $\Delta H_{\frac{1}{2}}$  and  $\Delta H_{ms}$  behaviour. The behaviour of  $\frac{\sqrt{M_2}}{\Delta H_{\frac{1}{2}}}$  illustrates the decrease of the exchange-narrowing

to exchange-broadening ratio. Between  $2^{\circ}$  K and  $1^{\circ}$  K, the inverse process seems to occur. This peculiar behaviour might perhaps be connected with a kind of magnetostriction, in connection with the observed transition in the magnetic susceptibility.

### 3. FURTHER RESULTS ON NICKEL HALIDES AND DISCUSSION.

At temperatures lower than about  $8^{\circ}$  K and at a frequency of about 9400 Mc/sec, a weak E.S.R. line has been detected in low fields, in  $\text{NiI}_2 \cdot 6\text{NH}_3$

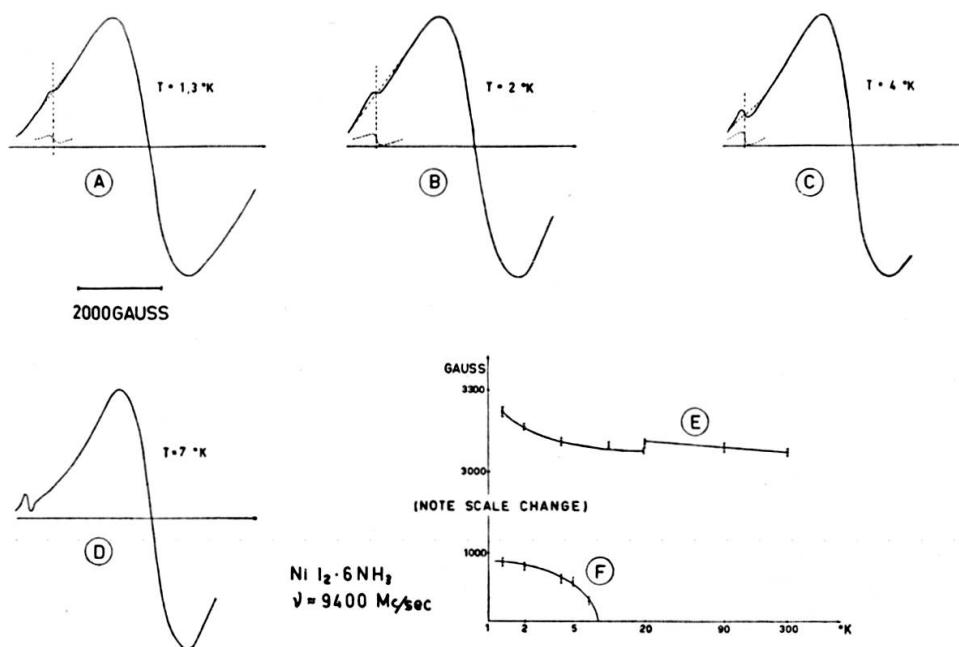


Fig. 3.

E.S.R. spectra of  $\text{NiI}_2 \cdot 6\text{NH}_3$  at different temperatures,  $\nu \approx 9400$  Mc/sec.

A) B) C) D) temperature-dependence of the two resonance lines.

E) F) Resonance fields (main line and low-field line) vs. temperature. (Note scale change.)

single crystals (the search is now being extended to the similar chloride and bromide crystals). When the temperature is lowered in the range from  $8^{\circ}$  K to  $1.3^{\circ}$  K, both the main and the weaker line shift toward higher field values, while the main line keeps broadening. Neither one of the lines shows any detectable angular dependence. The E.S.R. absorption spectra (derivative) at different temperatures and plots of the resonance fields of

the main and of the weaker line against temperature are shown in Fig. 3. From this figure one may also get a rough estimate of the percentage of spins concerned with the weaker resonance.

The temperature-dependence of the above results, mainly of the low-field line, suggests to assume that we are dealing with antiferromagnetism. This hypothesis is also consistent with a marked anomaly which has been recently found at Leiden [12] in the specific heat of the iodide salt at about  $19,5^\circ$  K (the entropy of the anomaly being of the order of  $K \ln 3$  times the number of Nickel ions). Nevertheless, against a complete interpretation in terms of an antiferromagnetic ordering, there is the fact that the static susceptibility as measured in a field of a number of Kilogauss, does not exhibit within the experimental errors any abrupt variation [1] in correspondence with the mentioned abrupt entropy change, the more so as a large external field gives hardly any change in the mentioned specific heat anomaly, neither in place nor in magnitude [12].

In favour of the hypothesis of an antiferromagnetic ordering, it has to be anyway noted that in crystals having a f.c.c. structure, as it is our case, the magnetic susceptibility behaves in unusual ways with temperature, as it has to be expected [6, 13, 14].

If one thinks tentatively in terms of antiferromagnetism, the kind of ordering to be assumed depends of whether the next-nearest-neighbours exchange energy is large or small compared with the nearest-neighbours one. We will (again tentatively) assume that  $J_{nn} \gg J_{nnn}$ . In this case, the spins order into chains, each chain having parallel spins. No super-lattice is determined, since different groups of chains may be oriented in different ways with no change of the exchange energy. The ordering is then not complete, but it is easy to see that the residual contribution to the entropy is negligible [6]. No preferential direction for the spins is determined, and therefore in this case the threshold field will be in practice zero. This would account for the absence of a remarkable shift in the E.S.R. line in correspondence with the transition, while the large broadening of the line would be accounted for, by exchange interaction with (possibly short range-) ordered spins.

At temperatures lower than  $8^\circ$  K, the next-nearest-neighbours interaction may become important, giving an anisotropy field and a critical field  $H_c$ . The low-field line could perhaps correspond with the orientation resonance at  $H = H_c$ . This threshold field would also cause a shift of the main line, which would occur at

$$H = (H_0^2 + H_c^2)^{\frac{1}{2}}$$

The above equation is verified within the experimental errors, if for  $H_c$  is used the temperature-dependent value corresponding to the low field absorption. More points in the  $H$  vs.  $T$  diagram are anyway needed, in order to have a better test of the above relation.

In order to explain the susceptibility results, it should be assumed that the spins are partially oriented by the magnetic field, in spite of the fact that the energy in the external magnetic field is much lower than the exchange energy (which has to be strong enough to cause an ordering at 20° K). It seems worth to note that if the resonance of the weak line occurs at  $H_c$ , then its temperature-dependence depicts a temperature-dependence of the exchange energy. This could be involved with the behaviour of the static susceptibility.

More experimental data are needed: experiments are in progress, on the behaviour of the low-field absorption as a function of frequency, and on the magnetic behaviour of similar salts. It would be moreover of interest to know more points of the  $1/\chi$  vs.  $T$  diagrams, in order to evidence a possible curvature above the transition temperature [14].

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*Résumé*

Afin de clarifier le comportement magnétique inhabituel d'halogénures de nickel hexammine, de nouvelles expériences ont été entreprises sur ce même cristal ainsi que sur un monocrystal de sulfate de cuivre tétramine. Dans ces derniers cristaux, les valeurs de « *g* », les largeurs de raies et les formes de raies présentent une dépendance particulière vis-à-vis de la température, dans le domaine de température de l'hélium. Dans l'iodure de nickel hexammine, on a trouvé une ligne d'absorption dépendant de la température pour des champs faibles en même temps qu'un shift correspondant de la principale raie d'absorption, ceci pour un domaine de températures s'étendant de 8° K à 1,3° K; ces propriétés donnent un fondement à l'hypothèse de transitions antiferromagnétiques. Un travail ultérieur concernant ces produits et également des halogénures de nickel semblables est en progrès sur celui présenté ici.

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