

which will give rise to long range order. The magnitude of  $J_d$  cannot be estimated with certainty but is probably of the order  $0.01 \text{ cm}^{-1}$ . The sharp rise in  $\chi_a$  may be interpreted as due to the existence of a small uncompensated magnetic moment along the  $a$ -axis in the ordered state. Definite conclusions cannot be made at present but it is probably related to the existence of the monoclinic cell.

## References

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- 3 For more details refer T. Ohtsuka: J. Phys. Soc. Japan **16** (1961) 1549. The presence of a monoclinic cell was not clear in the earlier results and its presence was not taken into consideration.

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## Electron Spin Resonance Linewidths of Face Centred Cubic $\text{Ni}^{2+}$ Crystals

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Recent experimental results are reported, which provide a basis for a consistent interpretation of the available data on the electron spin resonance, static susceptibility and specific heat of hexammine nickel halides. These results, although preliminary, show that a well-known motional effect gives rise to a magnetic behaviour of a new type in a class of simple crystals.

As it has been previously reported, face-centred cubic crystals of  $\text{NiX}_2 \cdot 6\text{NH}_3$  (where X stays for Cl, Br, I) exhibit a striking magnetic behaviour at low temperatures; the single isotropic electron spin resonance line, which is present at room temperature, undergoes, when the temperature is lowered through a certain critical value, an abrupt and very large broadening which might be, in principle, connected with the appreciable, though not adequately large, exchange effects exhibited by these crystals<sup>1)</sup>. On the other hand, the mentioned transition is not paralleled by an anomaly in the behaviour of the static magnetic susceptibility vs. temperature<sup>1)</sup> and this would suggest<sup>2)</sup> that motional effects rather than exchange effects could be responsible for the transition. Specific heat experiments performed by Leiden people on the iodide

salt (the specimens for all the different kinds of experiments were obtained in the same preparations) revealed anyway, at the same temperature at which the ESR transition occurs, an entropy anomaly of about  $k \ln 3$  times the number of the nickel ions<sup>3)</sup>.

In an attempt to clarify the problem, we have performed<sup>4)</sup> ESR experiments on  $\text{NiI}_2 \cdot 6\text{ND}_3$  specimens. These experiments have shown that the substitution of hydrogen by the heavier deuterium, shifts *upwards* the transition temperature (from  $19.5^\circ\text{K}$  in  $\text{NiI}_2 \cdot 6\text{NH}_3$  to about  $26.5^\circ\text{K}^*$  in  $\text{NiI}_2 \cdot 6\text{ND}_3$ ).

This result proves that the transition has

\* It has to be noted that the temperatures above  $4^\circ\text{K}$  up to about  $80^\circ\text{K}$  are here given with an accuracy of a few percents. This is due to a possible inaccuracy in the calibration of the thermometer as well as to possible temperature gradients along the microwave cavity, rather than to the temperature control itself, which works within limits by far much narrower.

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to deal with a thermally excited motion of the ammonia protons. The ratio between the two above quoted transition temperature suggests that essentially, only the motion of the protons (or deuterons) of the ammonia molecules is involved. Furthermore, since the transition temperature increases as the mass of the mobile particles increases, it is suggested that this motion occurs through potential barriers, supposedly separating different possible static configurations. Finally, the fact that the transition occurs within a small number of tenths of degree, suggests the presence of a strong correlation between the motions of the different  $H_3$  groups. (The above quoted Leiden results on the specific heat, are consistent with and further specify the presence of such correlation). Each of the different static configurations of the  $H_3$  groups does not fit the cubic symmetry of the crystals, which is preserved only when rotations take over<sup>5)</sup>. Consequently it is suggested that a well-known rotational behaviour, observable in the solid state (see, e.g. refs. 6-9)), gives here rise to a process by which the freezing down of the motional averaging of the non-cubic component of the crystal electric field, yields a presplitting of the spin levels of the  $Ni^{2+}$  ions and a distribution of quantization axes thus determining an unexpected abrupt change of the ESR linewidth.

The temperature-dependence of the ESR linewidth has been more closely investigated in the chloride, bromide and iodide crystals. The results are shown in Fig. 1. As one may note, for the three crystals, the linewidth decreases with the temperature, down to

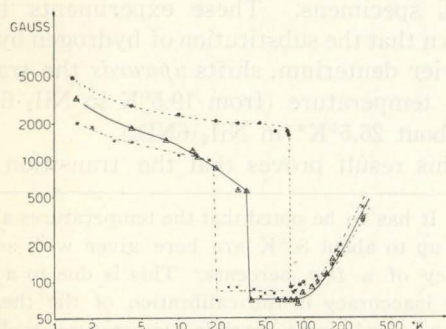


Fig. 1. ESR full linewidths vs. temperature (Max. slope; 9300 Mc); × Iodide, Δ Bromide, ● Chloride.

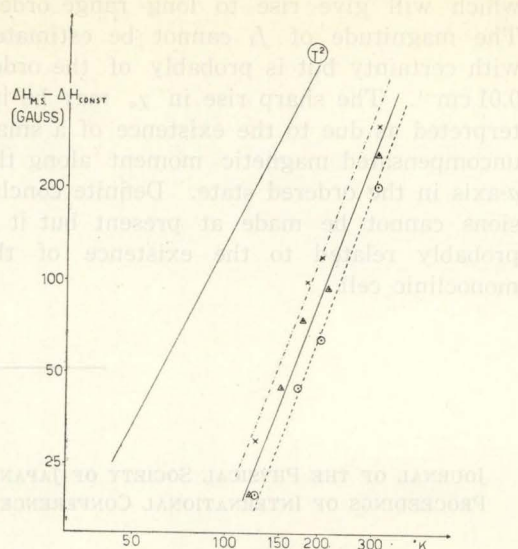


Fig. 2. Higher temperature contribution to the linewidth, obtained as the difference between the actual width and the value just above the transition. (see Fig. 1); × Iodide, Δ Bromide, ● Chloride.

about 100°K. This contribution, which follows approximately a  $T^{(2.5 \pm 0.5)}$  law (see Fig. 2), may be due to the temperature-dependence of the spin-lattice relaxation time. In fact, a  $T^{-2}$  law is expected for this contribution, at least at temperatures larger than the Debye temperature<sup>10)</sup> or when in the phonon spectrum, frequencies for which  $h\nu \ll kT$  predominate in the relaxation mechanism. Alternatively, the mentioned contribution to the linewidth, may be due to a dynamical splitting of the spin levels, due to the vibrational distortions of the  $Ni-6NH_3$  octahedra, occurring at these temperatures<sup>11)</sup>.

In the range between about 100°K and the transition temperature, the linewidths are temperature-independent and have values sensibly smaller than the calculated<sup>1)</sup> dipole-dipole broadening (which is of the order of 450 gauss).

From immediately below the transition temperature, down to about 1.4°K the linewidths, for all the crystals investigated, keep increasing, up to values of a few thousand gauss. A small "resonance" line found recently<sup>12)</sup> at low temperatures and low fields, has proved to be of instrumental origin.

The further increase of the line width at the lowest temperatures is hardly explained

in terms of motional effects. This broadening is perhaps due to the presence of exchange effects, and might be an indication for the onset at very low temperatures (of the order of  $1^\circ\text{K}$  or less) of an antiferromagnetic ordering. This is consistent with the results of NMR experiments performed recently at Leiden<sup>13)</sup> on the chloride crystals.

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### DISCUSSION

K. TOMITA: Is there any nuclear resonance (proton resonance) experiment? How does it behave around  $20^\circ\text{K}$  where you found the anomaly in the width of paramagnetic resonance?

M.U. PALMA: We have not been directly concerned with the proton resonance experiments. These experiments have been performed at Leiden (for the chloride, mainly) and, as far as I know, the results are in complete agreement with our results and interpretation. Dr. Poulis might perhaps give you more details.

N.J. POULIS: We observed no anomaly in the proton resonance data at that temperature range. In the case of  $\text{Ni}(\text{NH}_3)_6\text{Cl}_2$ , we were able to detect the proton resonance lines at  $1.1^\circ\text{K}$  which correspond to the antiferromagnetic state. We could measure the strength of the internal field there.

T. SUGAWARA: Dr. Kim and myself measured the proton resonance in powdered sample of  $\text{Ni}(\text{NH}_3)_6\text{Cl}_2$  between the room temperature and  $1.3^\circ\text{K}$ . We could not find any change in the line width nor shift at the transition temperature found by Palma et al. Is there any change in the area under the absorption curve of ESR at the transition temperature?

M.U. PALMA: Since both the line width and shape change so much, we have not tried an exhaustive set of measurements.

E. KANDA: Mr. Ukei and myself have measured the specific heat of  $\text{Ni}(\text{NH}_3)_6\text{Cl}_2$  and  $\text{Ni}(\text{NH}_3)_6\text{Br}_2$ . In chloride salt the specific heat shows a Schottky anomaly at about  $3^\circ\text{K}$  and a  $\lambda$ -type peak showing magnetic ordering at  $1.5^\circ\text{K}$ . In bromide, we didn't observe such an anomaly down to  $1.4^\circ\text{K}$ . The magnetic susceptibility measurement by Dr. Watanabe on  $\text{Ni}(\text{NH}_3)_6\text{Cl}_2$  and  $\text{Ni}(\text{NH}_3)_6\text{Br}_2$  does not show any anomalous temperature dependence between  $20^\circ\text{K}$  and  $100^\circ\text{K}$ .

M. DATE: I performed the ESR experiment on  $\text{Ni}(\text{NH}_3)_6\text{Cl}_2$  and found that the absorption intensity decreases suddenly between  $76\sim 74^\circ\text{K}$ .

M.U. PALMA: I thank Dr. Poulis and Professors Sugawara and Kanda for the kind communication of their results, which are in full agreement with the present interpretation.

B. BLEANEY: Is the line width below the transition equal to or greater than that calculated from dipole-dipole interaction?

M.U. PALMA: It is remarkably larger, consistent with our present interpretation. In fact, it is suggested that below the transition temperature (i.e., when the rotations are frozen), the cubic symmetry is no longer preserved and there is a distribution

of distortion axes within the crystal. This originates a broad ESR curve.

T. MITSUMA: What is the origin of reduction of line width below the value of calculated dipole-dipole interaction at the temperature range between 200°K and the transition temperature?

M.U. PALMA: There is little doubt that this is exchange narrowing. The magnitude of this exchange, as estimated from the Curie-Weiss constant, is consistent with the narrowing.

R.D. SPENCE: Is there a color change at the transition?

M.U. PALMA: Yes. We suspected the presence of this effect. Experiments are being made just now by one of our associates at Palermo.

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## The Néel Temperature of Mixed Crystals of Zinc and Iron Group Fluorides

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An attempt has been made to measure the Néel temperature,  $T_N$ , of mixed crystals of  $\text{Mn/ZnF}_2$  and  $\text{Co/ZnF}_2$  of various composition by finding the temperature  $T_c$  at which the nuclear magnetic resonance of the fluorine nuclei disappears on cooling from room temperature. The dependence of  $T_c$  upon concentration of paramagnetic ion is compared with theoretical predictions of the concentration dependence of  $T_N$ . Measurements of the variation of linewidth with temperature above  $T_c$  are also discussed.

The Néel temperature,  $T_N$ , of several materials has been measured by observation of the disappearance of the magnetic resonance of nuclei in the material when antiferromagnetism sets in. We have attempted to measure the Néel temperature of mixed crystals of  $\text{Mn/ZnF}_2$  by observing the temperature,  $T_c$ , at which the fluorine nuclear resonance disappears. Current theories of dilute systems suggest that there is a critical concentration below which antiferromagnetism does not occur, and our measurements were made to test these theories.

The samples were prepared by the Stockbarger technique. The speed of growth used ( $\sim 10 \text{ mm hr.}^{-1}$ ) was considerably higher than normal in order to avoid segregation. Some

of the crystals were of good optical quality, others were polycrystalline and of more doubtful uniformity. In many of the samples pieces from two different places in the sample were analysed to see if the concentration varied.

The fluorine NMR line does not remain unchanged down to  $T_c$  and then disappear, but broadens as the temperature is lowered towards  $T_c$ . The width of the line,  $\Delta H$ , is mainly due to interaction with the electronic magnetic moments. At high temperatures the line is narrowed by rapid flipping of these magnetic moments due to exchange interactions between them. As the temperature approaches  $T_N$  short range order increases and tends to inhibit the exchange