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FERROMAGNETISM IN  $\text{NiSnF}_6 \cdot 6\text{H}_2\text{O}$  AND  $\text{NiSiF}_6 \cdot 6\text{H}_2\text{O}$  (\*)

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Résumé.- Par des mesures de  $\chi_{||}$ ,  $\chi_{\perp}$ , et  $C_p$  à  $T \gtrsim 0,05$  K dans un réfrigérateur à dilution  $^3\text{He} - ^4\text{He}$ , nous étudions l'apparition du ferromagnétisme dans des monocristaux de  $\text{NiSnF}_6 \cdot 6\text{H}_2\text{O}$  ( $T_c = 0,164 \pm 0,004$  K) et de  $\text{NiSiF}_6 \cdot 6\text{H}_2\text{O}$  ( $T_c = 0,135 \pm 0,002$  K).

Abstract.- Measurements of  $\chi_{||}$ ,  $\chi_{\perp}$  and  $C_p$  down to  $\sim 0.05$  K in a  $^3\text{He}-^4\text{He}$  dilution refrigerator are used to study ferromagnetic ordering in single crystal  $\text{NiSnF}_6 \cdot 6\text{H}_2\text{O}$  ( $T_c = 0.164 \pm 0.004$  K) and  $\text{NiSiF}_6 \cdot 6\text{H}_2\text{O}$  ( $T_c = 0.135 \pm 0.002$  K).

INTRODUCTION.- A number of salts with the general formula  $\text{NiMX}_6 \cdot 6\text{H}_2\text{O}$  crystallize in the trigonal  $\text{NiSnCl}_6 \cdot 6\text{H}_2\text{O}$  structure. One  $[\text{Ni}(\text{H}_2\text{O})_6]^{++}$  complex, trigonally distorted along the trigonal axis, occupies the center of the rhombohedral unit cell with  $[\text{MX}_6]^-$  octahedra at the eight vertices. The axial distortion and spin-orbit interaction split the  $^3A_2$  ground state of the  $\text{Ni}^{++}$  complex into a singlet ( $m_s=0$ ) and a doublet ( $m_s=\pm 1$ ). The magnetic and thermal properties associated with these levels are described approximately by the single-ion spin Hamiltonian,  $\mathcal{H} = DS_z^2 + g\mu_B \vec{H} \cdot \vec{S}$ , where  $z$  // trigonal axis,  $S=1$ , and  $g \approx 2.3$ .

The first  $\text{NiMX}_6 \cdot 6\text{H}_2\text{O}$  compound to be studied was  $\text{NiSiF}_6 \cdot 6\text{H}_2\text{O}$ . Below 20 K, it was found /1/  $D/k \approx -0.16$  K. Thus the ground state is a magnetic doublet. Ferromagnetic interactions producing ordering below  $T_c \approx 0.14$  K were also detected /2,3/. More recently we have shown that in  $\text{NiSnCl}_6 \cdot 6\text{H}_2\text{O}$  itself, below 4 K,  $D \approx +0.6$  K so that the ground state is a singlet. In this case interactions of antiferromagnetic sign occur. However, they are too weak relative to  $|D|$  to cause magnetic ordering above 0 K in zero field /4/. We have also found /4/ that several compounds with  $M = \text{Pd}$  or  $\text{Pt}$  and  $X = \text{Cl}$ ,  $\text{Br}$  or  $\text{I}$  have  $D > 0$  and antiferromagnetic interactions while those with  $M = \text{Ti}$  or  $\text{Zr}$  and  $X = \text{F}$  have  $D < 0$  and become ferromagnetic /5,6/.

The sign of  $D$ , and with it the sign of the net spin interaction in these salts, appears to depend on the nature of the halogen atom  $X$ ,  $D < 0$  being associated with the presence of  $\text{F}$ , the smallest and most electronegative of the series. There is also

evidence that, for given  $X^-$ , changing  $M^{++}$  changes the magnitude of  $D$  but not its sign. To test these ideas, we have measured, between 4 and 0.05 K, the susceptibilities of  $\text{NiSnF}_6 \cdot 6\text{H}_2\text{O}$ , which differs from  $\text{NiSnCl}_6 \cdot 6\text{H}_2\text{O}$  only in its  $X^-$  ion. We have also measured in this interval the susceptibilities and heat capacity of  $\text{NiSiF}_6 \cdot 6\text{H}_2\text{O}$  for which most of the published information near  $T_c$  /3,8/ has been determined by indirect methods.

THE EXPERIMENTS.-  $\chi_{||}$  and  $\chi_{\perp}$  were determined by a mutual inductance method at 70 Hz down to 0.05 K in a  $^3\text{He} - ^4\text{He}$  dilution cryostat. The heat capacity of an 8.91 g single crystal of  $\text{NiSiF}_6 \cdot 6\text{H}_2\text{O}$  was measured by adiabatic calorimetry in the dilution cryostat for several values of  $H_{||}$  produced by a superconducting solenoid.

RESULTS AND DISCUSSION.- Figure 1 shows the temperature variation of  $\chi_{||}$  and  $\chi_{\perp}$  for  $\text{NiSiF}_6 \cdot 6\text{H}_2\text{O}$ .  $\chi_{||} > \chi_{\perp}$  everywhere indicating that  $D < 0$ . Below  $T_c = 0.139 \pm 0.004$  K,  $\chi_{||}$  is constant at  $0.56$  cgs/cm<sup>3</sup>. The demagnetizing factor for the specimen was  $\mathcal{D} \approx 1.86$  so that  $1/\mathcal{D} \approx 0.54 \approx \chi_{||} (T < T_c)$  as expected for  $H_{||}$  the easy axis of a ferromagnet without remanence. The  $\chi_{||} (T > T_c)$  data were corrected to infinite needle geometry and fitted with two models of a uniaxial ferromagnet; a simple mean field model, and an Oguchi model /5/ in which pairs of exchange-coupled spins are treated exactly and interpair interactions are represented by a mean field. The fitted parameters are essentially the same for both models, namely,  $D/k = -0.166$  K,  $g = 2.24$  and an effective exchange constant  $qJ/k = +0.084$  K. The solid curve in figure 1 is calculated for the Oguchi model which fails below  $T_c$  where it consists of only a

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single domain. There is good agreement between our values of  $D$ ,  $g$  and  $qJ$  and those determined by other methods /1,7,8/.

The measured  $C_p(H=0)$  values for  $\text{NiSiF}_6 \cdot 6\text{H}_2\text{O}$  are in reasonable agreement with earlier data /3,8/. A lattice correction,  $C(\text{latt.}) \approx 3.24 \times 10^{-4} T^3 \text{ cal/mole K}$ , has been applied to the data shown in figure 2. The cooperative peak in  $C_p(H=0)$  occurs at  $T_c = 0.135 \pm 0.002 \text{ K}$ . The magnetic entropy change  $S_\infty - S_0 = 2.177 \text{ cal/mole K} \approx R \ln 3$  as expected for spin  $S = 1$ . With  $H_{\parallel} = 1200 \text{ G}$ , the  $\lambda$ -peak is rounded-off and shifted to higher temperature, as predicted by the mean field models (figure 2 inset).

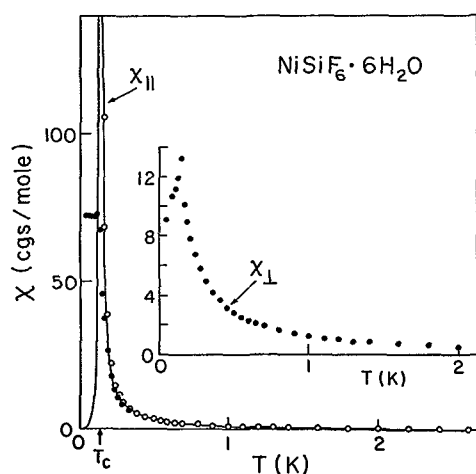


Fig. 1 : Magnetic susceptibilities of  $\text{NiSiF}_6 \cdot 6\text{H}_2\text{O}$ . Data corrected for demagnetization are shown as open circles. Note enlarged scale for  $\chi_{\perp}$ .

The Oguchi model with  $D/k = -0.166 \text{ K}$ ,  $g = 2.24$  and  $qJ/k = +0.120 \text{ K}$  gives the dashed curve of figure 2 which fits the data well.

$\chi_{\parallel}$  and  $\chi_{\perp}$  data for  $\text{NiSnF}_6 \cdot 6\text{H}_2\text{O}$ , qualitatively similar to those of figure 1, reveal it also to be a uniaxial ferromagnet having  $T_c = 0.164 \pm 0.004 \text{ K}$ . The Oguchi model, with  $D/k = -2.55 \text{ K}$ ,  $g = 2.26$  and  $qJ/k = +0.084 \text{ K}$ , provides an excellent fit,  $|D|$  and  $g$  agreeing with EPR results /9/. Replacement of  $\text{Cl}^-$  by  $\text{F}^-$  in  $\text{NiSnX}_6 \cdot 6\text{H}_2\text{O}$  changes the signs of  $D$  and  $J$  as previously conjectured. With  $X = \text{F}$  and  $M = \text{Si, Ti, Sn, and Zr}$ , we now find that  $|D|$  varies linearly with the  $M^{4+}$  ion radius and the unit cell edge length. In the presence of Ising-like single-ion anisotropy ( $D < 0$ ) the dipolar interaction in these crystals favors ferromagnetic ordering accounting in part for the connection between the signs

of  $D$  and the effective coupling constant  $J$ .

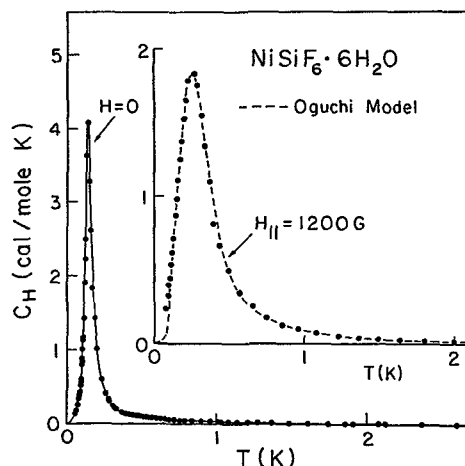


Fig. 2 : Magnetic contributions to the heat capacity of  $\text{NiSiF}_6 \cdot 6\text{H}_2\text{O}$  for  $H_{\parallel} = 0$  and  $1200 \text{ G}$ .

About 25 % of the coupling energy is dipolar while  $|D/qJ| > 1$  and the Ising character is pronounced. This may explain the success of mean field models in describing the properties of the  $\text{NiMF}_6 \cdot 6\text{H}_2\text{O}$  salts.

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