

## FERROMAGNETISM IN NiSnF6.6H2O AND NiSiF6.6H2O

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Résumé.- Par des mesures de  $\chi_{//}$ ,  $\chi_{\perp}$ , et C<sub>2</sub> à T  $\stackrel{>}{\sim}$  0,05 K dans un réfrigérateur à dilution <sup>3</sup>He - <sup>4</sup>He, nous étudions l'apparition du ferromagnétisme dans des monocristaux de NiSnF<sub>6</sub>.6H<sub>2</sub>0 (T<sub>C</sub> = 0,164 ± 0,004 K) et de NiSiF<sub>6</sub>.6H<sub>2</sub>0 (T<sub>C</sub> = 0,135 ± 0,002 K).

Abstract.- Measurements of  $\chi//$ ,  $\chi_{\perp}$  and  $C_p$  down to  $\sim 0.05$  K in a <sup>3</sup>He-<sup>4</sup>He dilution refrigerator are used to study ferromagnetic ordering in Single crystal NiSnF<sub>6</sub>.6H<sub>2</sub>0 (T<sub>c</sub> = 0.164 ± 0.004 K) and NiSiF<sub>6</sub>.6H<sub>2</sub>0 (T<sub>c</sub> = 0.135 ± 0.002 K).

INTRODUCTION.- A number of salts with the general formula NiMX<sub>6</sub>.6H<sub>2</sub>O crystallize in the trigonal NiSnCl<sub>6</sub>.6H<sub>2</sub>O structure. One  $[Ni(H_2O)_6]^{++}$  complex, trigonally distorted along the trigonal axis, occupies the center of the rhombohedral unit cell with  $[MX_{-}]^{-}$  octahedra at the eight vertices. The axial distortion and spin-orbit interaction split the  ${}^{3}A_{2}$  ground state of the Ni<sup>++</sup> complex into a singlet  $(m_{s}=0)$  and a doublet  $(m_{s}=\pm1)$ . The magnetic and thermal properties associated with these levels are described approximately by the single-ion spin Hamiltonian,  $M_{-}^{2} = DS_{2}^{2} + g\mu_{B} H.S$ , where z // trigonal axis, S=1, and g  $\simeq 2.3$ .

The first NiMX  $_{6}$   $^{6}$   $^{2}$  0 compound to be studied was NiSiF .6H 0. Below 20 K, it was found /1/ D/k  $\simeq$  -0.16 K. Thus the ground state is a magnetic doublet. Ferromagnetic interactions producing ordering below T<sub>c</sub>  $\simeq$  0.14 K were also detected /2,3/. More recently we have shown that in NiSnC1 .6H 0 itself, below 4 K, D  $\simeq$  +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 = Pd or Pt and X  $\approx$  C1, Br or I have D>0 and antiferromagnetic interactions while those with M = Ti or Zr and X = 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 F, the smallest and most electronegative of the series. There is also

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evidence that, for given X<sup>-</sup>, 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 NiSnF .6H 0, which differs from NiSnCl .6H 0 only in its  $X^{-}$  ion. We have also measured in this interval the susceptibilities and heat capacity of NiSiF .6H 0 for which most of the published information near  $T_c$  /3,8/ has been determined by indirect methods.

THE EXPERIMENTS.-  $\chi_{\parallel}$  and  $\chi_{\perp}$  were determined by a mutual inductance method at 70 Hz down to 0.05 K in a <sup>3</sup>He - <sup>4</sup>He dilution cryostat. The heat capacity of an 8.91 g single crystal of NiSiF .6H 0 was measured by adiabatic calorimetry in the dilution cryostat for several values of H<sub>//</sub> produced by a superconducting solenoid.

RESULTS AND DISCUSSION .- Figure 1 shows the temperature variation of  $\chi_{11}$  and  $\chi_{\perp}$  for NiSiF .6H 0.  $\chi_{11}$ >  $\chi_{\perp}$  everywhere indicating that D<0. Below  $T_{c}$  = 0.139 ± 0.004 K,  $\chi_{||}$  is constant at 0.56 cgs/cm<sup>3</sup> The demagnetizing factor for the specimen was  $\mathfrak Y$   $\simeq$ 1.86 so that  $|\Delta = 0.54 \simeq \chi_{||}$  (T<T<sub>c</sub>) as expected for H<sub>||</sub> the easy axis of a ferromagnet without remanence. The  $\chi_{||}$  (T>T<sub>c</sub>)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 where it consists of only a

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 NiSiF .6H 0 are in reasonable agreement with earlier data /3,8/. A lattice correction, C(latt.)  $\simeq 3.24 \times 10^{-4} T^3 cal/$ 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 ± 0.002 K. The magnetic entropy change  $S_{\infty}-S_0 = 2.177$  cal/mole K  $\simeq$  Rln 3 as expected for spin S = 1. With H<sub>11</sub> = 1200 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 NiSiF<sub>6</sub>.6H<sub>2</sub>0. Data corrected for demagnetization are shown as open circles. Note enlarged scale for  $\chi_{\perp}$ .

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

 $\chi_{/\!/}$  and  $\chi_{\perp}$  data for NiSnF<sub>6</sub>.6H<sub>2</sub>0, qualitatively similar to those of figure 1, reveal it also to be a uniaxial ferromagnet having T<sub>c</sub> = 0.164 ± 0.004 K. The Oguchi model, with D/k =-2.55 K, g = 2.26 and qJ/k = +0.084 K, provides an excellent fit, |D| and g agreeing with EPR results /9/. Replacement of CI<sup>-</sup> by F<sup>-</sup> in NiSnX<sub>6</sub>.6H<sub>2</sub>0 changes the signs of D and J as previously conjectured. With X = F and M = Si, Ti, Sn, and Zr, we now find that |D| varies linearly with the M<sup>4+</sup> ion radius and the unit cell edge length. In the presence of Ising-like singleion 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  $NiSiF_{e}.6H_{2}0$  for  $H_{11} = 0$  and 1200 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 NiMF<sub>8</sub>6H<sub>2</sub>O salts.

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