FERROMAGNETISM IN NiSnF6.6H2O AND NiSiF6.6H2O

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FERROMAGNETISM IN $NiSnF_6 \cdot 6H_2O$ AND $NiSiF_6 \cdot 6H_2O$ (*)

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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 ^3He - ^4He, nous étudions l'apparition du ferromagnétisme dans des monocristaux de $NiSnF_6.6H_2O$ (T_c = 0,164 ± 0,004 K) et de $NiSiF_6.6H_2O$ (T_c = 0,135 ± 0,002 K).

Abstract.- Measurements of $\chi_{//}$, $\chi_{\perp}$ and C_p down to ∿ 0.05 K in a ^3He-^4He dilution refrigerator are used to study ferromagnetic ordering in single crystal $NiSnF_6.6H_2O$ (T_c = 0.164 ± 0.004 K) and $NiSiF_6.6H_2O$ (T_c = 0.135 ± 0.002 K).

INTRODUCTION.- A number of salts with the general formula $NiMX_6.6H_2O$ crystallize in the trigonal $NiSnCl_6.6H_2O$ structure. One $[Ni(H_2O)_6]^{++}$ complex, trigonally distorted along the trigonal axis, occupies the center of the rhombohedral unit cell with $[MX_6]^{=}$ octahedra at the eight vertices. The axial distortion and spin-orbit interaction split the $^3A_2$ ground state of the Ni^{++} complex into a singlet (m_s=o) and a doublet (m_s=±1). The magnetic and thermal properties associated with these levels are described approximately by the single-ion spin Hamiltonian, $\mathcal{H} = DS_z^2 + g\mu_B \vec{H}.\vec{S}$, where z // trigonal axis, S=1, and g ≃ 2.3.

The first $NiMX_6.6H_2O$ compound to be studied was $NiSiF_6.6H_2O$. Below 20 K, it was found /1/ D/k ≃ -0.16 K. Thus the ground state is a magnetic doublet. Ferromagnetic interactions producing ordering below T_c ≃ 0.14 K were also detected /2,3/. More recently we have shown that in $NiSnCl_6.6H_2O$ itself, below 4 K, D ≃ +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 ≠ Cl, 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 evidence that, for given X^-, changing M^{4+} 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 $NiSnF_6.6H_2O$, which differs from $NiSnCl_6.6H_2O$ only in its X^- ion. We have also measured in this interval the susceptibilities and heat capacity of $NiSiF_6.6H_2O$ 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 ^3He - ^4He dilution cryostat. The heat capacity of an 8.91 g single crystal of $NiSiF_6.6H_2O$ 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 $NiSiF_6.6H_2O$. $\chi_{||} > \chi_{\perp}$ everywhere indicating that D<0. Below T_c = 0.139 ± 0.004 K, $\chi_{||}$ is constant at 0.56 cgs/cm^3. The demagnetizing factor for the specimen was $\mathcal{D} \simeq 1.86$ so that $1/\mathcal{D} \simeq 0.54 \simeq \chi_{||}$ ($T<T_c$) 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 $NiSiF_6.6H_2O$ 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 $T_c = 0.135 \pm 0.002$ K. The magnetic entropy change $S_\infty - S_o = 2.177$ cal/mole K $\simeq$ Rln 3 as expected for spin S = 1. With $H_{||} = 1200$ G, the λ-peak is rounded-off and shifted to higher temperature, as predicted by the mean field models (figure 2 inset).

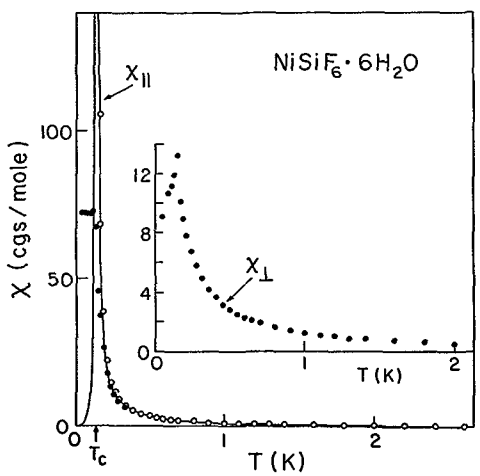

Fig. 1 : Magnetic susceptibilities of $NiSiF_6.6H_2O$. Data corrected for demagnetization are shown as open circles. Note enlarged scale for $\chi_\perp$.

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

$\chi_{//}$ and $\chi_\perp$ data for $NiSnF_6.6H_2O$, qualitatively similar to those of figure 1, reveal it also to be a uniaxial ferromagnet having $T_c = 0.164 \pm 0.004$ 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 Cl^- by F^- in $NiSnX_6.6H_2O$ 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^{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.

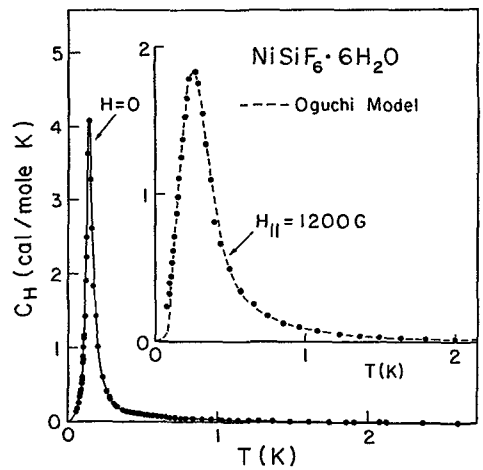

Fig. 2 : Magnetic contributions to the heat capacity of $NiSiF_6.6H_2O$ for $H_{||} = 0$ and 1200 G.

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 $NiMF_6 6H_2O$ salts.

References

/1/ Penrose, R.P. and Stevens, K.W.H., Proc. Phys. Soc. A63 (1950) 29.

/2/ Ishiguro, E., Kambe, K. and Usui, T., Physica 17 (1951) 310.

/3/ Ohtsubo, A., J. Phys. Soc. Japan 20 (1965) 76.

/4/ Friedberg, S.A., Karnezos, M. and Meier, D.L., Proc. LT14, Otaniemi, Finland (1975) 224.

/5/ Karnezos, M., Meier, D.L. and Friedberg, S.A., Phys. Rev. (1978) to appear.

/6/ Karnezos, M. and Friedberg, S.A., J. Appl. Phys. (1978) to appear.

/7/ Svare, I. and Seidel, G., Phys. Rev. 134 (1964) A172

/8/ Giauque, W.F., Hornung, E.W., Fisher, R.A. and Brodale, G.E., J. Chem. Phys. 47 (1967) 2685, and earlier papers cited therein.

/9/ How, T. and Svare, I., Physica Scripta 9 (1974) 40.