Anomalies in the magnetic properties of nickel fluorosilicate at high pressures and ultralow temperatures

A. A. Galkin, I. M. Vitebskiĭ, V. P. D'yakonov, I. M. Fita, and G. A. Tsintsadze
Donetsk Physicotechnical Institute, Academy of Sciences of the Ukrainian SSR

(Submitted 1 April 1982)

Pis'ma Zh. Eksp. Teor. Fiz. **35**, No. 9, 384–386 (5 May 1982)

The effect of pressure on the temperature and nature of the magnetic ordering in $NiSiF_6 \cdot 6H_2O$ has been studied for the first time. A P-T phase diagram has been constructed. A region in which a paramagnetic phase is stable and regions in which two ferromagnetic phases are stable touch at a triple point on this phase diagram, and the derivative dT_c/dP changes sign at this point. The two ferromagnetic phases are an easy-axis phase and an easy-plane phase.

PACS numbers: 75.30.Kz, 75.50.Dd

Nickel fluorosilicate, $NiSiF_6 \cdot 6H_2O$ (Fedorov symmetry group $R\bar{3}$), is one of the model magnetic materials, whose magnetic and resonance properties have been studied thoroughly.[1] A ferromagnetic ordering is observed in this compound below $T_c = 0.150$ K with a magnetic moment directed along the C_3 axis.

The ground state of the Ni^{2+} ion in the crystal field, of trigonal symmetry, is a spin triplet. The initial splitting is $\mathscr{D} = -0.16$ K. Studies of the ESR spectra of Ni^{2+} ions[2] have shown that the parameter $\mathscr{D}$ increases and crosses zero as the pressure is increased. There is accordingly interest in determining how this inversion of the energy levels of the Ni^{2+} ground state affects the magnetic properties of the crystal.

In the present experiments we studied the effect of hydrostatic compression (up to 5 kbar) on the temperature and nature of the magnetic ordering of nickel fluorosilicate. The primary distinguishing feature of these experiments was that the magnetic measurements under pressure were carried out at ultralow temperatures (0.5–0.05 K) in a dissolution refrigerator. We studied single-crystal samples by an induction procedure at a frequency of 30 Hz (the amplitude of the varying magnetic field at the sample was 1–0.3 Oe). The pressure dependence of the Curie temperature was determined from the shift of the magnetic-susceptibility peak in the easy-magnetization direction.

Evidence of magnetic ordering is a sharp increase in the susceptibility, to $\sim(1/4)\pi N$, where N is the demagnetizing factor of the sample. As the temperature is lowered further, the susceptibility amplitude remains essentially constant, implying the presence of a domain structure. The fact that only $\chi_\parallel$ (the susceptibility along the trigonal axis) exhibits this behavior at $P < 1.3$ kbar, while only $\chi_\perp$ exhibits it at $P > 1.3$ kbar, unambiguously shows that in the former case the magnetic moments are ordered along the C_3 axis, while in the latter case they are ordered perpendicular to this axis. In other words, a pressure-induced spin-reorientation transition occurs.

The P-T phase diagram constructed in this manner is shown in Fig. 1a. While previ-

ous studies using hydrostatic compression have established only an increase or decrease in the critical temperature, in the present experiments we have observed an anomalous, sign-changing dependence of the Curie temperature on the pressure (the line AOB in Fig. 1a) in a magnetic insulator. At the critical point, O ($P_{cr} = 1.3$ kbar, $T_{cr} = 0.120$ K), the derivative dT_c/dP changes sign.

The $T_c(P)$ dependence found here has been analyzed theoretically in the molecular-field approximation by the spin-Hamiltonian method. The following expressions have been derived for the Curie temperature T_c:

$$T_c\,(2+\exp\{\mathcal{D}/T_c\}) = 3\,T_0 \quad \text{for } \mathcal{D} < 0, \tag{1}$$

$$T_c = \mathcal{D}\left\{\ln\frac{T_0 + 2\mathcal{D}/3}{T_0 - \mathcal{D}/3}\right\}^{-1} \quad \text{for } \mathcal{D} > 0\,. \tag{2}$$

Here T_0 is the exchange-interaction parameter

$$T_0 = \frac{2}{3}\,\lambda\mu_B^2 g^2 n, \tag{3}$$

where λ is the molecular-field constant, a measure of the isotropic exchange interaction; n is the number of magnetic ions per unit volume; and the g factor is 2.24, essentially isotropic.

The parameters T_0 and $\mathcal{D}$ are monotonically increasing functions of the pressure.[2] The reason for the different analytic forms of the expressions for T_c in the cases $\mathcal{D}<0$ and $\mathcal{D}>0$ is that at $\mathcal{D}<0$ the minimum of the free energy (at $T<T_c$) corresponds to a state with a magnetization $\mathbf{m} \parallel C_3$, while at $\mathcal{D}>0$ it corresponds to a state with $\mathbf{m} \perp C_3$. Near the critical point, i.e., at $|\mathcal{D}| \ll T_0$, expressions (1) and (2) can be replaced by the approximate expressions

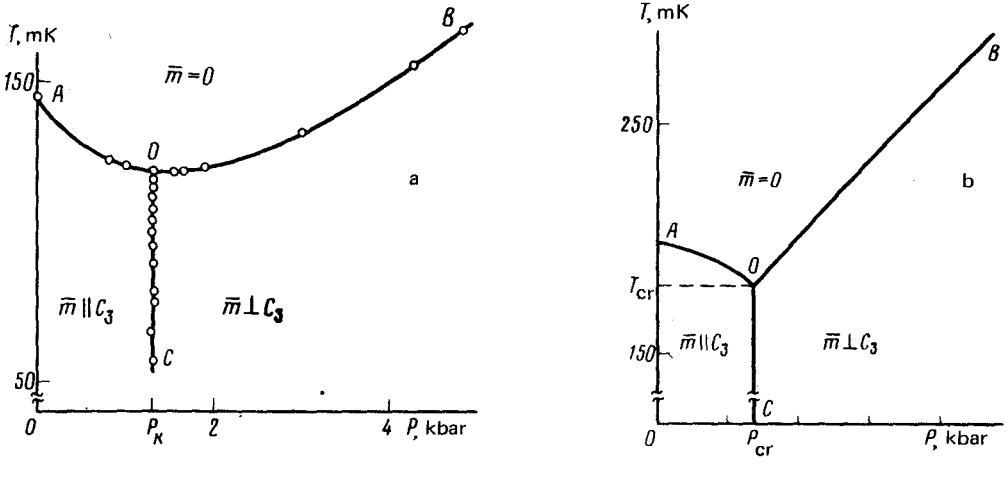

FIG. 1. Magnetic phase diagram of nickel fluorosilicate under pressure. a—Experimental; b—constructed from expressions (1) and (2).

$$T_c \approx T_0 - \mathcal{D}/3 \quad \text{for} \quad \mathcal{D} < 0, \tag{4}$$

$$T_c \approx T_0 + \mathcal{D}/6 \quad \text{for} \quad \mathcal{D} > 0. \tag{5}$$

The line AOB in Fig. 1b shows the theoretical behavior $T_c(P)$ according to expressions (1) and (2). The experimental values of T_c at the various pressures are lower than the theoretical values by a factor of about 1.5. This discrepancy is not surprising when we consider that the exchange-interaction parameter T_0 in concentrated nickel fluorosilicate would not necessarily be the same as the corresponding parameter for the dilute solution $Ni_xZn_{1-x}SiF_6 \cdot 6H_2O$ for which the $T_0(P)$ dependence was found. A governing consideration from the standpoint of the topology of the phase diagram is the solidly established fact that $\mathcal{D}(P)$ passes through 0 at $P=P_{cr}$. The point O is therefore a triple point, at which three regions meet: a region in which a paramagnetic phase is stable and regions in which two ferromagnetic phases are stable (one is an easy-axis phase, and the other is an easy-plane phase). The OC is the line of the magnetic orientational transition.

The theoretical model used above, which is based on a spin Hamiltonian of axial symmetry,[1,2] and which incorporates a single-ion anisotropy of the $\mathcal{D}\hat{S}_z^2$ type, does not tell us the nature of the phase transition which occurs between the two ferromagnetic states as the pressure is changed. Working from symmetry considerations in the phenomenological theory of phase transitions, we can show that a) a transition from a state with $\mathbf{m} \parallel C_3$ to one with $\mathbf{m}_\perp \neq 0$ would have to be a first-order transition (because there are invariants of third order in the corresponding order parameter) and b) a state with $\mathbf{m} \perp C_3$ could not, strictly speaking, occur at all, because even at $P > P_{cr}$ the vector $\mathbf{m}$ does not lie exactly in the basis plane.

Unfortunately, we were not able to detect these features experimentally in the temperature range studied, since at $P \sim P_{cr}$ both components of the magnetic susceptibility ($\chi_\parallel$ and $\chi_\perp$) are anomalously large.

We are sincerely indebted to V. G. Bar'yakhtar for interest in this work and for useful discussions.

1. R. M. Valishev, in: Paramagnitnyĭ rezonans (Paramagnetic Resonance), Kazan', 1968, p. 35.
2. A. A. Galkin, A. Yu. Kozhukhar', and G. A. Tsintsadze, Zh. Eksp. Teor. Fiz. **70**, 248 (1976) [Sov. Phys. JETP **43**, 128 (1976)].

Translated by Dave Parsons
Edited by S. J. Amoretty