Spin-spin interactions and magnetic ordering in ferromagnets with single-ion anisotropy

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A study was carried out of the effect of high hydrostatic pressure and magnetic dilution on the parameters of the spin Hamiltonian and the magnetic ordering temperature of the system $Ni_xZn_{1-x}SiF_6{\cdot}6H_2O$. The study was based on measurements and analysis of the temperature dependence of magnetic susceptibility in the temperature range 4.2–0.05 K at constant pressure and concentration. The experimental data were analyzed in the molecular-field approximation. It is shown that this approximation is valid for the description of the temperature-pressure phase diagram of nickel fluorosilicate. A microscopic examination of the effective spin-spin interaction parameter is presented.

The role of spin-spin interactions and of magnetic anisotropy in phase transitions is an important question in solid-state physics.

In magnetic systems characterized by single-ion anisotropy, the magnetic ordering temperature is determined by the relationship between the magnitudes and signs of single-ion anisotropy and spin-spin interactions, so that the magnetic properties of a crystal can be varied by varying this relationship. This can be done by using high hydrostatic pressure and magnetic dilution (substitution of diamagnetic ions for magnetic ions).

All this gives rise to considerable interest in crystals in which the effects of spin-spin interaction and magnetic anisotropy, which control the magnetic state of the magnet, are of the same order and vary within wide limits under the influence of external factors. Nickel fluorosilicate (a magnetodielectric material that is representative of the group of nickel hexahydrates) is a crystal of this kind. It is not only characterized by comparable spin-spin interaction and magnetic anisotropy effects, but also exhibits high compressibility and good solubility in the magnetic zinc fluorosilicate host, which makes it exceedingly interesting and even unique material from the point of view of studies under extreme conditions.

Nickel fluorosilicate and its solid solutions are described by the space symmetry group $R\overline{3}$. The rhombohedral unit cell which is characterized by the parameters $a = 6.26$ Å and $\alpha = 96°6'$ contains one molecule. The ground state of the nickel ion is the spin triplet which is split by the simultaneous effect of the trigonal component of the crystal ion and of the spin-orbit coupling into a singlet and doublet, where the doublet lies below the singlet. At normal pressures and temperatures $T < 20$ K, the initial splitting of the ground state of the nickel ion is $D = -0.16$ K. Using a method based on the analysis of the ESR spectrum of exchange-coupled pairs of Ni^{2+} ions in the system $Ni_xZn_{1-x}SiF_6{\cdot}H_2O$ with $x = 0.01$, Galkin *et al.*[1] have found that the exchange integrals in the three nearest coordinate spheres were $J_1 = -4.34\times10^{-2}$, $J_2 = 1.83\times10^{-2}$, $J_3 = -1.75\times10^{-2}$ K. The negative sign corresponds to the ferromagnetic nature of the exchange process. Exchange interactions ensure ferromagnetic order in this crystal below $T_c = 0.15$ K, and the magnetic moment lies along the trigonal axis. The easy-axis magnetic structure is dictated by the sign of the initial splitting parameter D, whose change under a pressure of $P = 1.3$ kbar is due to the inversion of the ground-state levels of the ion Ni^{2+} (Ref. 2). It has been shown by Bar'yakhtar *et al.*[3] that the specific behavior of the splitting D (which characterizes the single-ion anisotropy) completely determines the topology of the P-T phase diagram of nickel fluorosilicate and the anomalous behavior of the pressure dependence of the Curie temperature (the derivative dT_c/dP changes sign twice in the pressure range up to 10 kbar). The pressure dependence of the spin-spin interaction must be known for the quantitative description of the experimental P-T phase diagram. The ESR method can be used to determine the exchange integrals, but only at low concentrations of the magnetic ions. On the other hand, it is not always possible to use the parameters of the spin Hamiltonian, determined for magnetically dilute compounds, in the description of the magnetic properties of concentrated crystals. Measurements of the paramagnetic Curie temperature provide us with a reliable alternative method of determining the strength of the spin-spin interaction and its variation under the influence of external factors (pressure and magnetic-ion concentration).

We have investigated the pressure dependence of the magnetic susceptibility of nickel fluorosilicate and its solid solutions in the paramagnetic and magnetically ordered phases in a wide range of nickel-ion concentrations $(0.05 \leqslant x \leqslant 1)$.

EXPERIMENTAL METHOD

The original design of the apparatus enabled us to measure the absolute value of the magnetic susceptibility of the crystals under investigation in the temperature range 10–0.4 K under hydrostatic pressures up to 10 kbar, and to replace the specimens without raising the temperature in the cryostat.[4] The susceptibility was measured inductively at 32 Hz, using a modulating-field amplitude of 0.3–25 Oe. The high-

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frequency field was polarized along the axis of the cylindrical specimen. A coaxial measuring coil was used (number of turns $N_1 = 4000$ and $N_2 = 1270$). At low temperatures, electronic compensation of self-induced emf in the measuring system ensured that its sensitivity in susceptibility was 10^{-6} deg^{-1}.

The pressure was produced by the traditional piston-in-cylinder method. The system was sealed using a friction-fit piston and a rubber seal instead of copper-lead rings. The beryllium-bronze high-pressure vessel had an external diameter of 4 mm and channel diameter of 1.3 mm. The superconducting transition in tin was used to determine the pressure to within ± 0.3 kbar.

We have investigated cylindrical single-crystal specimens (length to diameter ratio 5) in which the cylinder axis was parallel and perpendicular to the trigonal axis. The $\mathrm{Ni}_x\mathrm{Zn}_{1-x}\mathrm{SiF}_6$ single crystals were grown by the temperature-reducing method from a water solution of the original salts in a thermostat with electronically controlled temperature. In measurements of the effect of magnetic dilution, the diamagnetic "partner" for $\mathrm{NiSiF_6{\cdot}6H_2O}$ was taken to be zinc fluorosilicate, since it is the closest diamagnetic host insofar as the lattice parameters and radius of the divalent metal ion are concerned. The lattice parameter increases by 0.6% as the nickel concentration is varied from $x = 1$ to $x = 0$. Since the solubilities of $\mathrm{NiSiF_6{\cdot}6H_2O}$ and $\mathrm{ZnSiF_6{\cdot}6H_2O}$ in water are not very different, the concentration of the nickel ions in $\mathrm{Ni}_x\mathrm{Zn}_{1-x}\mathrm{SiF_6{\cdot}6H_2O}$ turns out to be higher than in the parent solution (see Table I).

The specimens were aligned by optical and x-ray methods. Some of the measurements were performed on powdered specimens (mean grain diameter 50 μm) compacted into a cylinder. The paramagnetic Curie point Θ was determined by extrapolating the $\chi^{-1}(T,x)$ curve to the temperature axis. The uncertainty in the Curie point determined in this way was ± 0.01 K.

The $\mathrm{He^3}$–$\mathrm{He^4}$ dilution refrigerator producing $T = 50$ mK was used in magnetic measurements on the magnetically ordered phase. The experimental results were subsequently processed on a computer by the method of least squares.

RESULTS AND DISCUSSION

A. Pressure dependence of the parameters of the spin Hamiltonian of the system NiSiF$_6$·6H$_2$O

The magnetic properties of nickel fluorosilicate at high pressures are described by the axially symmetric spin Hamiltonian

$$\mathscr{H}=D\hat{S}_z^2+g\mu_B\mathbf{H}'\mathbf{S}, \qquad (1)$$

which takes into account the spin-spin interaction in the molecular-ion approximation,[3] where $\hat{S}$ is the effective spin operator, $S = 1$, $g = 2.24$, H' is the effective field equal to the sum of the external magnetic field and the exchange interaction field H^e given by

$$H^e=\lambda M=\lambda ng\mu_B\langle\hat{S}\rangle, \qquad (2)$$

λ is the molecular-field constant characterizing the isotropic exchange interaction, n is the number of magnetic ions per unit volume, and M is the magnetization.

Analysis of the Hamiltonian (1) has led to the following expressions for the susceptibility along $C_3(\chi_\parallel)$ and in the basal plane $(\chi_\perp)$ in the paramagnetic temperature range in the absence of the magnetic field:

$$\chi_\parallel=ng^2\mu_B^2[{}^1/_2(e^{D/T}+2)-\lambda ng^2\mu_B^2]^{-1}, \qquad (3)$$

$$\chi_\perp=ng^2\mu_B^2[{}^1/_2D(e^{D/T}+2)\,(e^{D/T}-1)-\lambda ng^2\mu \qquad (4)$$

It will be convenient to denote $T_0 = 2/3\lambda ng^2\mu_B{}^2$. The exchange interaction parameter T_0 is numerically equal to the sum $-2/3\Sigma_i Z_i J_i$, where Z_i and J_i are the number of magnetic ions and the exchange integral in the ith coordination sphere, respectively.

The expressions for $\chi_\parallel$ and $\chi_\perp$ then assume the form

$$\chi_\parallel=C[{}^1/_3(e^{D/T}+2)\,T-T_0]^{-1}, \qquad (5)$$

$$\chi_\perp=C[{}^1/_3D(e^{D/T}+2)/(e^{D/T}-1)-T_0]^{-1}, \qquad (6)$$

where $C = 2/3g^2\mu_B{}^2n$.

At high temperatures ($T \gg |D|$, T_0) we have

$$\chi_\parallel=\frac{C}{T-(T_0-D/3)}, \quad \chi_\perp=\frac{C}{T-(T_0+D/6)}, \qquad (7)$$

and hence

$$\Theta_\parallel=T_0-D/3, \quad \Theta_\perp=T_0+D/6. \qquad (8)$$

Since fluctuation effects restricting the precision of the molecular-ion approximation are unimportant for $T \gg T_{c'}$, the expressions given by (7) and (8) are sufficiently precise. The use of powdered specimens enables us to exclude the effect of single-ion anisotropy on the susceptibility. Using the relation $\chi_p = (\chi_\parallel + 2\chi_\perp)/3$ for the powdered specimen, we obtain

$$\chi_p=C/(T-T_0). \qquad (9)$$

Our analysis of the temperature dependence of paramagnetic susceptibility has shown that it follows the Curie-Weiss law in the temperature range 0.5–4.2 K at all the pressures that we have used. We have determined the Curie constants ($C_\parallel = 4.095\cdot10^{-3}$ cm^3 deg/g, $C_\perp = 3.915\cdot10^{-3}$ cm^3 deg/g) and g factors ($g_\parallel = 2.24 \pm 0.01$, $g_\perp = 2.22 \pm 0.01$), which are independent of pressure, and the para-

TABLE I.

	concentration of Ni, %								
Parent solution	3	10	13	35	40	55	65	80	100
$\mathrm{Ni}_x\mathrm{Zn}_{1-x}\mathrm{SiF_6{\cdot}6H_2O}$	5,5	15	18	41	50	61	72	95	100

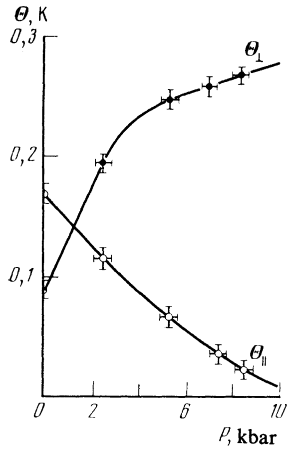

FIG. 1. Effect of pressure on the paramagnetic Curie point of nickel fluorosilicate.

magnetic Curie points. The measured $\Theta_\parallel$ and $\Theta_\perp$ are shown in Fig. 1 as functions of pressure. The monotonic reduction in $\Theta_\parallel$ and increase in $\Theta_\perp$ with increasing pressure are due to the pressure dependence of the parameter D. Using the functions $\Theta_\parallel(P)$, $\Theta_\perp(P)$ and the expressions

$$T_0(P)={}^1/_3[\Theta_\parallel(P)+2\Theta_\perp(P)], \tag{10}$$

$$D(P)=2[\Theta_\perp(P)-\Theta_\parallel(P)], \tag{11}$$

we can determine the pressure dependence of the parameters of the spin Hamiltonian (Fig. 2). The function $D(P)$ is linear. It crosses the horizontal axis at $P=1.4$ kbar and its slope changes at $P=4$ kbar. There is complete agreement with ESR data,[2] which shows unambiguously that the anisotropy of nickel fluorosilicate in the pressure range $0 \leqslant P < 10$ kbar is largely due to the initial splitting D of the ground state of the nickel ions, and is of the single-ion type.

The effective spin-spin interaction parameter increases monotonically with increasing pressure and is such that, for pressures in the range 0–4 kbar, the pressure coefficient is $\Delta T_0/\Delta P \approx 0.02$ deg/kbar, whereas for $P>4$ kbar it is $\Delta T_0/\Delta P \approx 0.001$ deg/kbar.

The change in the slope of the $T_0(P)$ curve at $P \approx 4$ kbar correlates with the change in the slope of the $D(P)$ curve, which is clearly due to a change in the ligand environment of the ion Ni^{2+}.

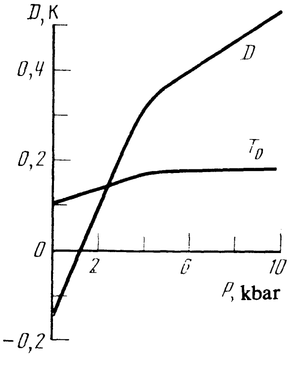

FIG. 2. Pressure dependence of D and T_0 for $NiSiF_6 \cdot 6H_2O$.

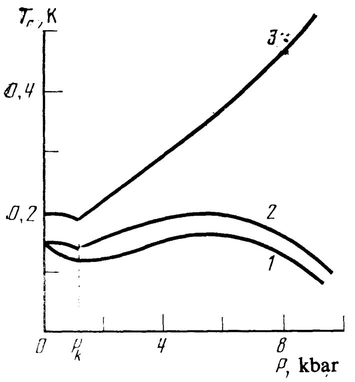

FIG. 3. Pressure dependence of the Curie point of nickel fluorosilicate: curve 1—experiment,[3] 2—calculated from paramagnetic susceptibility data, 3—calculated from ESR spectroscopy data.

Comparison of the function $T_0(P)$ with the pressure dependence of the effective exchange interaction parameter of nickel fluorosilicate, obtained by analyzing the ESR spectrum of exchange-coupled pairs of Ni ions in the system $Ni_{0.01}Zn_{0.99}SiF_6 \cdot 6H_2O$, shows that there is a qualitative difference between the pressure dependence of the parameter T_0 determined by the two independent methods.

We have used our values of $D(P)$ and $T_0(P)$ to calculate the T–P phase diagram for nickel fluorosilicate (Fig. 3). The Curie point T_c was determined from the following formulas:[3]

$$T_c\left[2+\exp\frac{D}{T_c}\right]=3T_0, \quad D\leqslant 0, \tag{12}$$

$$T_c=D\left[\ln\frac{3T_0+2D}{3T_0-D}\right]^{-1}, \quad D\geqslant 0. \tag{13}$$

Figure 3 also shows the experimental function $T_c(P)$ (Ref. 3) and the function calculated from the measured exchange integrals of exchange-coupled pairs of nickel ions in

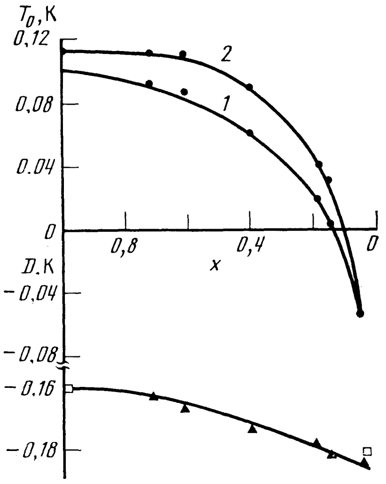

FIG. 4. Effect of magnetic dilution on the parameters of spin-spin interactions and single-ion anisotropy in $Ni_xZn_{1-x}SiF_6 \cdot 6H_2O$: curve 2—determined from measurements on single-crystal specimens, 1—powdered specimen; □—ESR spectroscopy data.

the system $Ni_{0.01}Zn_{0.99}SiF_6 \cdot 6H_2O$. The considerable discrepancy between the experimental function $T_c(P)$ and that calculated from the ESR data can hardly be ascribed to the use of the molecular field approximation. Acutally, the agreement between curves 1 and 2 can be regarded as satisfactory in the entire range of pressure, indicating that the molecular field approximation is valid in the description of the pressure dependence of the Curie temperature of nickel fluorosilicate under hydrostatic pressure. The different form of curves 2 and 3 must therefore be due to a difference between exchange coupling between the Ni^{2+} ions in nickel fluorosilicate and the system $Ni_{0.01}Zn_{0.99}SiF_6 \cdot 6H_2O$ and to a manifestation of the collective character of the interaction of not only the pairs but also a large number of ions.

B. Effect of magnetic dilution on spin-spin interaction in the system $Ni_xZn_{1-x}SiF_6 \cdot 6H_2O$

Investigation of the temperature dependence of the absolute magnetic susceptibility for different nickel concentrations shows that the Curie-Weiss law is satisfied for all $0.05 \leqslant x \leqslant 1$ in the temperature range 4.2–0.5 K. Measurements of susceptibility reveal a clearly nonlinear variation of the paramagnetic Curie temperature with the concentration of magnetic nickel ions where, if $\Theta_{\parallel} > 0$ in the particular range of concentrations under investigation, then $\Theta_{\perp} > 0$ only for $x > 0.15$. Using the functions $\Theta_{\parallel}(x)$, $\Theta_{\perp}(x)$ and the relationships between the paramagnetic Curie point and the parameters of the spin Hamiltonian, we can determine the concentration dependence of the spin-spin interaction and the magnetic anisotropy (Fig. 4). A reduction in nickel concentration leads to a substantial nonlinear change in the spin-spin interaction parameter T_0 and also to a change in sign at $x = 0.15$. It is important to note that the variation in T_0 with concentration is a source of information about the variation in the effective spin-spin interaction that consists of dipole and exchange contributions. The dipole contribution in concentrated nickel fluorosilicate is about 25% of the effective spin-spin interaction and is largely determined by the Lorentz term which decreases linearly with decreasing magnetic-ion concentration. The inclusion of this contribution has no effect on $T_0(x)$. We may therefore conclude that the variation in the spin-spin interaction with Ni ion concentration characterizes the variation in the exchange interaction in the magnetically diluted system $Ni_xZn_{1-x}SiF_6 \cdot 6H_2O$. An analogous function $T_0(x)$ has been obtained for the powdered specimen. The exchange contribution to T_0 is determined by the values and signs of exchange integrals of the interacting magnetic ions, i.e., it is an integrated characteristic of the crystal:

$$T_0(x) = -{}^2/_3 \sum_{i=1}^{k} Z_i(x) J_i(x), \tag{14}$$

where k is the number of interacting coordination spheres.

The nonlinear behavior of $T_0(x)$ may be due to both a variation in exchange coupling with varying concentration and a nonequally probable distribution of magnetic ions within the coordination spheres. The former effect has been established by measurements of the pressure dependence of the effective spin-spin interaction parameter of nickel fluorosilicate.

Exchange coupling between the Ni^{2+} ions in solid solutions of nickel fluorosilicate in zinc fluorosilicate varies with decreasing magnetic-ion concentration both because of the increase in separation between the magnetic ions and because of the change in the superexchange angles. The latter is also confirmed by the observed dependence of the single-ion anisotropy parameter $D(z)$, which is a source of information about distortions of the octahedra surrounding the magnetic ion, i.e., changes in the position of ions through which indirect exchange takes place.

At low concentrations of mgnetic ions ($x < 0.15$), the parameter T_0 is negative ($T_0 = -0.06$ K for $x = 0.05$). The exchange integrals for the exchange-coupled pairs of nickel ions at these concentrations, determined previously by the ESR method, can give rise to only positive T_0 for a random distribution of magnetic ions over the coordination spheres. Since the exchange integral in the second coordination sphere is antiferromagnetic in character, and its value is lower by a factor of only two as compared with the exchange integral in the first coordination sphere, we may suppose that the negative value of T_0 is due to a nonuniform distribution of magnetic ions over the coordination spheres and to competing interactions of different sign between the nearest and next-nearest nickel ions. The net result of all these factors is that the dominating effects for $x = 1$–0.15 and $x < 0.15$ are the ferromagnetic and antiferromagnetic interaction, respectively.

C. Concentration dependence of the phase transition temperature of nickel fluorosilicate

To elucidate the nature of the magnetic order in solid solutions of the form $Ni_xZn_{1-x}SiF_6 \cdot 6H_2O$, we measured the susceptibility in the millidegree temperature range.

The temperature dependence of the susceptibility along the C_3 axis is shown in Fig. 5 for different nickel-ion concentrations. All curves with the exception of $x = 0.18$ have a characteristic maximum corresponding to susceptibility equal to $1/4\pi N$ (N is the demagnetizing factor of the specimen). Measurements of the amplitude and frequency dependence of the susceptibility at temperatures corresponding to the magnetically ordered state lead to the conclusion that the solid solutions $Ni_xZn_{1-x}SiF_6 \cdot 6H_2O$ with $x \geqslant 0.4$ have purely ferromagnetic order.

Figure 6 shows the measured concentration dependence of the reduced Curie temperature and the calculated ratio $T_c(x)/T_c(1)$ obtained from (12) using the above values of $T_0(x)$ and $D(x)$. It is clear that there is good qualitative agreement between the experimental and theoretical curves. The behavior of $T_c(x)$ is anomalous. The parameter

$$\alpha = \left[\frac{1}{T_c(x)} \frac{dT_c(x)}{dx} \right]_{x \to 1}$$

is less than unity, whereas $\alpha > 1$ and $\alpha = 1$ for the Heisenberg and Ising models. The nonlinear reduction in $T_c(x)$ and the way it is "pulled" toward lower concentrations are determined by the character of the variation in the spin-spin inter-

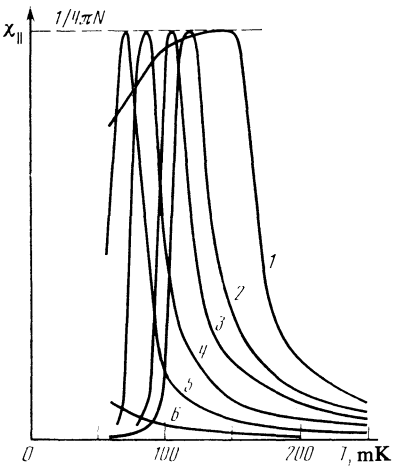

FIG. 5. Temperature dependence of the magnetic susceptibility of the solid solution $Ni_xZn_{1-x}SiF_6\cdot 6H_2O$ near the ordering temperature for different concentrations of the Ni^{2+} ions: 1—$x = 1$; 2—0.72; 3—0.6; 4—0.5; 5—0.4; 6—0.18.

action with varying nickel concentration. The observed quantitative difference between experimental and theoretical curves is probably due to the fact that the molecular-field approximation does not take into account fluctuation phenomena which lead to lower measured values for the Curie point.

According to the measured function $T_c(x)$, the concentration at which long-range magnetic order cannot be established is less than $x = 0.4$. The calculated critical concentration is determined by $x_c = 0.18$. Since the calculated $T_c(x)$ is always greater than the measured, the lower bound of the critical concentration is determined by $x_c = 0.18$. Consequently, the critical concentration for the system $Ni_xZn_{1-x}SiF_6\cdot 6H_2O$ lies in the range $0.18 < x < 0.4$. It must be remembered that the calculated curves were obtained in the molecular-field approximation whereas the description of the T-X phase diagram for $x \rightarrow 0$ requires the use of more accurate theories.

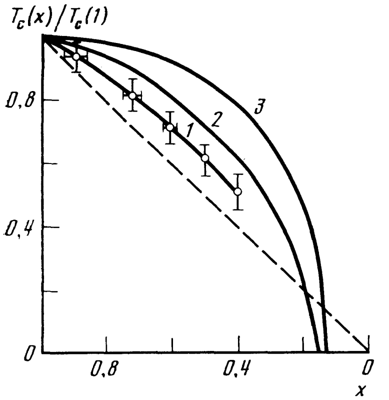

FIG. 6. Experimental and calculated reduced Curie temperatures $T_c(x)/T_c(1)$ plotted against concentration in $Ni_xZn_{1-x}SiF_6\cdot 6H_2O$: curve 1—measured; 2, 3—calculated (2—T_0 determined from data on powdered specimens and 3—single-crystal specimens). The dashed line shows the molecular-field approximation.

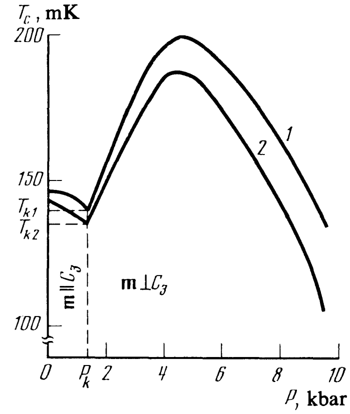

FIG. 7. Magnetic T-P phase diagrams: 1—$NiSiF_6\cdot 6H_2O$; 2—$Ni_{0.72}Zn_{0.28}SiF_6\cdot 6H_2O$.

We also note that other phases may be formed at concentrations below critical. However, since the measured and calculated curves are in qualitative agreement up to $x = 0.4$, there are no reasons to suppose that the experimental curve will cross the calculated curve, so that at least for ferromagnetic order the critical concentration will have the lower bound $x = 0.18$.

The reduction in the spin-spin interaction with decreasing concentration of magnetic ions in the solid solutions $Ni_xZn_{1-x}SiF_6\cdot 6H_2O$ at small changes in the single-ion anisotropy parameter should give rise to a substantial change on the T-P phase diagram of nickel fluorosilicate. This was investigated for $Ni_{0.72}Zn_{0.28}\cdot SiF_6\cdot 6H_2O$. In fact, an increase in the ratio D/T_0 for this system, due to a slight reduction in the effective spin-spin interaction, leads to a shift of the Curie point toward lower temperatures under all pressures (Fig. 7). Comparison with the calculated pressure dependence of the magnetic ordering temperature for $NiSiF_6\cdot 6H_2O$ shows that the character of the function $T_c(P)$ is preserved, the pressure corresponding to the spin-flip transition remains practically the same, and the region of existence of the ferromagnetic phase with magnetization vector $m \perp C_3$ $(D > 0)$ becomes narrower. This facilitates the attainment of the Moriya criterion $(D = 3T_0)$, which ensures that there is no magnetic order in ferromagnets with a singlet ground state.

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