Magnetic properties of the dilute antiferromagnets $M_{1-x}Zn_xF_2$ ($M = Mn^{+2}, Co^{+2}$)

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The magnetic properties of single crystals of the dilute antiferromagnets $M_{1-x}Zn_xF_2$ ($M = Mn^{+2}, Co^{+2}$) with Zn^{+2} ion concentrations $x \approx x_c \approx 0.7$–$0.8$ have been studied. The behavior found for the magnetic moment and the magnetic susceptibility as functions of the magnetic field, the temperature, and the frequency show that as the temperature is lowered to $T < T_f$ (T_f is the freezing point) at these Zn^{+2} concentrations, in the absence of a magnetic field, the $M_{1-x}Zn_xF_2$ converts into a state of a time-varying spin glass. As the temperature is lowered to $T < T_f$, the magnetic susceptibility (χ^*) measured in weak magnetic fields and at low frequencies ($\nu < 20$ Hz) is observed to increase in accordance with $\chi^* \sim 1/T$. The susceptibility χ exhibits the typical dependence on the frequency of a modulating field. As the magnetic field is increased, a stable state arises in which the magnetic moments $\mathbf{M}_i$ of the ions are oriented randomly with respect to the applied magnetic field $\mathbf{H}$. As the temperature is lowered to $T < T_f$ in this state, the magnetic susceptibility χ is slightly sensitive to the applied magnetic field and to the temperature, and the H dependence of the magnetic moment can be described by $M(H,T) = M^*(T) + \chi(H,T)H$.

Jaccarino *et al.*[4–6] and the present authors[1–3] have shown that with increasing concentration of Zn^{+2} ions replacing magnetic Mn^{+2} ions in the $Mn_{1-x}Zn_xF_2$ crystal lattice the Néel temperature of the transition to the antiferromagnetic state decreases, as do the effective fields of the exchange (H_E) and anisotropic (H_A) interactions. The lowering of the effective anisotropy fields makes it possible to observe magnetic phase transitions[1–3] in $M_{1-x}Zn_xF_2$ at magnetic fields weaker than those at which the corresponding phase transitions can be seen in MF_2. It was also shown in Refs. 1–3 that the compounds $M_{1-x}Zn_xF_2$ have magnetic properties which distinguish them from pure antiferromagnets. These properties are characteristic of systems in which interacting magnetic ions are distributed randomly in the crystal lattice. As the concentration of Zn^{+2} ions in $M_{1-x}Zn_xF_2$ is increased, the magnetic moment of a sample measured in weak magnetic fields starts to depend in a nonlinear way on a magnetic field directed perpendicular to the tetragonal axis. With decreasing temperature, $T \to 0$, the perpendicular magnetic susceptibility $\chi_\perp^*$ measured in weak magnetic fields is observed to increase. The distinctive magnetic properties of $M_{1-x}Zn_xF_2$ can be seen most clearly as the concentration (x) of Zn^{+2} ions approaches the "percolation point" x_c, above which, as Harris and Kirkpatrick have shown,[7] no phase transition to an antiferromagnetic state is observed.

We have shown[3] that as the concentration (x) of Zn^{+2} ions in $Mn_{1-x}Zn_xF_2$ approaches x_c there is a certain temperature range $T_N < T < T_f$ (T_f is the freezing point) in which curves of the field dependence of the magnetic moment, $M(H)$, are nonlinear and independent of the orientation of $\mathbf{H}$ in the crystal. These $M(H)$ curves indicate that the magnetic state of the crystal is distinct from both the usual paramagnetic and antiferromagnetic states.

In the present paper we report a study of the behavior of the magnetization and magnetic susceptibility of $M_{1-x}Zn_xF_2$ ($M = Mn^{+2}, Co^{+2}$) systems as functions of the temperature, an applied magnetic field, and the frequency of the modulating field H. We have also determined the distinctive features in the magnetic properties of these systems at concentrations $x \approx x_c$. We compare the experimental results on the behavior of the susceptibility as a function of the temperature and the applied magnetic field with the theoretical analysis of Refs. 8–13. That analysis was carried out for spin-glass systems with randomly distributed interacting magnetic ions. The reason why the magnetic properties of the $M_{1-x}Zn_xF_2$ system can have distinctive features similar to those in the magnetic properties of spin glasses is that when the M^{+2} magnetic ions are replaced by nonmagnetic ions[8] a random distribution of the interacting M^{+2} magnetic ions appears, as does a random distribution of $\pm$ exchange interactions. A random distribution of $\pm$ exchange interactions in $M_{1-x}Zn_xF_2$ systems can be found by taking into account the three nearest exchange interactions of M^{+2} ions belonging to different sublattices and to a common sublattice of the original compound MF_2. A determination of these interactions from the Néel temperature and the Curie-Weiss constant of the initial MF_2 compounds yields a negative value for the average exchange interaction not only between ions of different sublattices but also between ions in a common sublattice.[14] A negative exchange interaction of ions within a sublattice leads to an effective competition between their interactions when magnetic ions are replaced by nonmagnetic ions. Experiments[15] carried out to determine the magnitudes and signs of the exchange interactions within a sublattice in MnF_2 indicate that the exchange interaction between the M^{+2} ions is positive along the direction of the [001] tetragonal axis and negative along the [100] binary axis. This difference between the signs of the exchange interactions of M^{+2} ions within a single sublattice, combined with the basic negative exchange interaction and dipole interaction of the M^{+2} ions of different sublattices, gives rise to a random distribution of the signs of the exchange interaction and to a random distribution of the anisotropy axes of the interacting

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magnetic ions, as is characteristic of spin-glass problems.[8]

A distinctive feature of the $Co_{1-x}Zn_xF_2$ system is that CoF_2 has a Dzyaloshinskiĭ interaction strong in comparison with that in MnF_2, because of the weak ferromagnetism of CoF_2 for certain orientations of the antiferromagnetic vector.[16] A random distribution of not only the exchange interaction but also the Dzyaloshinskiĭ interaction arises in the $Co_{1-x}Zn_xF_2$ system. We felt it worthwhile to study those features in the magnetic properties of $Co_{1-x}Zn_xF_2$ which are not seen in $Mn_{1-x}Zn_xF_2$.

Experiments on the magnetization curves $M(H)$ were carried out on a magnetometer with a vibrating sample[17] in magnetic fields ranging from 300 Oe to 60 kOe at temperatures T ranging from 2 to 40 K.

Experiments on the frequency dependence of the magnetic susceptibility were carried out on a standard apparatus designed for such measurements.[18] We used two compensated measuring coils (the sample was inserted into one of these coils during the experiment) and a coil to modulate the magnetic field. As was shown in Ref. 18, the signal from the measuring coils is proportional to the magnitude and frequency (ν) of the modulating field and to the magnetic susceptibility of the sample. Experiments were carried out in magnetic fields up to 100 Oe. The sensitivity of the apparatus in terms of the susceptibility was $\sim 10^{-4}$ cgs emu (at a filling factor on the order of 1).

The single crystals of $Mn_{1-x}Zn_xF_2$ ($x = 0.67$, 0.75, and 0.8) and $Co_{1-x}Zn_xF_2$ ($x = 0.72$ and 0.83) were oriented beforehand in an x-ray apparatus. The error in the determination of the crystal axes was no greater than 1–2°. The error in the determination of the concentration of the M^{+2} ions in $M_{1-x}Zn_xF_2$ from the magnetic susceptibility at room temperature[2] was no worse than 10%. For several of the $Mn_{1-x}Zn_xF_2$ samples, an x-ray microspectral analysis of the concentrations of Mn^{+2} and Zn^{+2} ions in the samples and the uniformity of their distribution was carried out on the SAMESA apparatus at the L. Ya. Karpov Physicochemical Institute. The results of this analysis[1)] showed that the distributions of the Mn^{+2} ions in the samples are uniform within 10%. At the sensitivity of the SAMESA apparatus it is possible to record x-ray photographs of regions of the crystal with linear dimensions on the order of 300Å. The x-ray micrographs were recorded in various parts of the single crystal with linear dimensions on the order of 1 mm. The error in the determination of the concentrations in this region was no more than 10% of the concentrations reported for the magnetic ions.

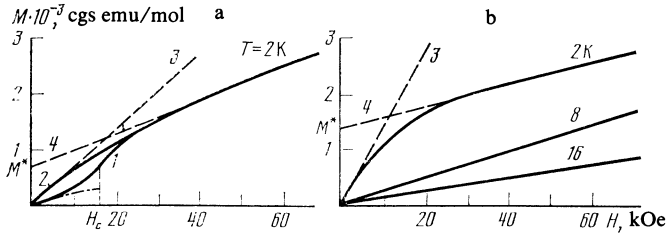

FIG. 1. Magnetic moment versus the applied magnetic field in $Mn_{1-x}Zn_xF_2$ single crystals. *a*: $x = 0.67$. 1–**H** ∥ [001]; 2–**H** ∥ [100]. *b*: $x = 0.8$. Line 3–$M = \chi^* H$; line 4–$M = M^* + \chi H$.

EXPERIMENTAL RESULTS

Figure 1 shows the magnetic moment versus the applied magnetic field for $Mn_{1-x}Zn_xF_2$ single crystals with $x = 0.67$ and 0.8 for various temperatures and various orientations of **H**.

At $T > T_f = 11$ K the $M(H)$ dependence of the $Mn_{0.33}Zn_{0.67}F_2$ system is linear.[3] At temperatures $T < T_f$ the magnetic moment is observed to vary in a nonlinear way with the applied magnetic field, and there is no dependence on the orientation of **H**. In strong magnetic fields the $M(H)$ dependence can be described by $M(H) = M^* = \chi H$. At temperatures $T < T_N = 6.5 \pm 0.5$ K and in weak magnetic fields, an anisotropy of the magnetic moment $M(H)$ arises in magnetic fields **H** ∥ [001] (curve 1 in Fig. 1a) and **H** ∥ [100] (curve 2). At **H** ∥ [001] and $H < 5$ kOe, the $M(H)$ dependence is linear and can be described by the expression $M(H) = \chi_{\parallel} H$. At $H > 20$ kOe the $M(H)$ dependence is essentially the same as that found with **H** ∥ [100].

For the $Mn_{0.2}Zn_{0.8}F_2$ single crystal the dependence of the magnetic moment on the applied magnetic field is linear at $T > T_f = 6.5 \pm 0.5$ K: $M(H) = \chi(T)H$. At $T < T_f$ we see a nonlinear magnetic moment $M(H)$, which is independent of the orientation of **H** with respect to the crystal axes. In strong magnetic fields, the moment can be described by $M(H,T) = M^*(T) + \chi(T,H)H$.

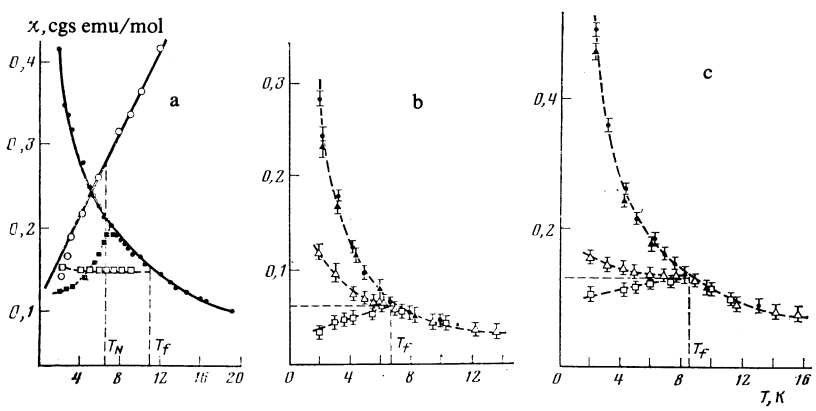

FIG. 2. Magnetic susceptibility versus the temperature in $Mn_{1-x}Zn_xF_2$ single crystals. *a*: $x = 0.67$. *b*: $x = 0.8$. *c*: $x = 0.75$. ●–$\chi^*(T)$ in weak fields, $\nu \approx 0$; □–$\chi(T)$ in strong fields, $\nu \approx 0$; ▲–$\chi^*(T)$ in weak fields, $\nu < 100$ Hz; △–$\chi^*(T)$ in weak fields, $\nu > 900$ Hz; ■–$\chi^*(T)$ in weak fields, **H** ∥ [001], $\nu \approx 0$; ○–$1/\chi^*$ in weak fields, **H** ∥ [100], $\nu \approx 0$.

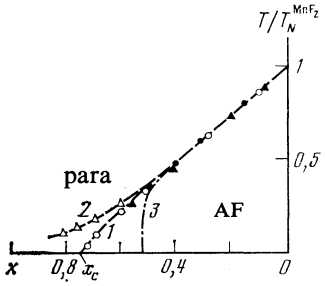

FIG. 3. The reduced temperatures T_N (curve 1) and T_f (2) versus the concentration of Zn^{+2} ions in $Mn_{1-x}Zn_xF_2$ single crystals. O, △–Present data; ●–data of Ref. 4; ▲–data of Ref. 19. Curve 3 is the proposed boundary of nonstationary states.

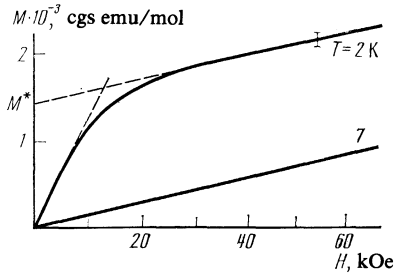

FIG. 4. Magnetic moment versus the applied magnetic field in $Co_{0.17}Zn_{0.83}F_2$ single crystals with $\mathbf{H}\perp[001]$.

Figure 2 shows the temperature dependence of the magnetic susceptibility of $Mn_{1-x}Zn_xF_2$ single crystals measured in applied magnetic fields of various magnitudes and orientations. We see that a susceptibility χ which depends weakly on the temperature appears at T_f. An anisotropy of the susceptibility χ^* for $\mathbf{H}\perp[001]$ and $\mathbf{H}\parallel[001]$ is observed beginning at $T_N < T_f$. For these single crystals, the susceptibility χ^* measured in weak fields with $\mathbf{H}\perp[001]$ typically increases with decreasing temperature.

Figure 3 shows the reduced temperatures T_N (curve 1) and T_f (curve 2) versus the concentration of Zn^{+2} ions in the $Mn_{1-x}Zn_xF_2$ compounds. At Zn^{+2} concentrations $x > x_c = 0.75 \pm 0.05$ we see no antiferromagnetic properties in this system, in agreement with Refs. 1, 4, and 19.

We studied the dependence of the magnetic moment on the applied magnetic field, $M(H)$, for $Co_{1-x}Zn_xF_2$ single crystals with $x = 0.72$ and 0.83 at various temperatures and in fields $\mathbf{H}$ in various orientations. Curves of $M(H)$ for $Co_{0.5}Zn_{0.5}F_2$ are shown in Ref. 3.

At $T > 8$ K the curves of $M(H)$ for $Co_{0.28}Zn_{0.72}F_2$ with $\mathbf{H}\parallel[100]$ and $\mathbf{H}\parallel[001]$ are described by linear expressions of the type $M(H) = \chi(T)H$. At $T < T_f = 8 \pm 0.5$ K in magnetic fields $\mathbf{H}\parallel[100]$ and $\mathbf{H}\parallel[001]$ we observe nonlinear $M(H)$ curves, which can be described in strong magnetic fields by an expression $M(H) = M^* + \chi H$ with various values of the magnetic moments M^* and the susceptibilities χ.

Figure 4 shows experimental results obtained for the $Co_{0.17}Zn_{0.83}F_2$ single crystal. At temperatures $T > T_f = 6.5 \pm 0.5$ K the $M(H)$ dependence is linear: $M(H) = \chi(T)H$. We see a change in the slope of the $M(H)$ curves in magnetic fields oriented along the tetragonal axis and perpendicular to it; this change corresponds to an anisotropy of the magnetic susceptibility of CoF_2 in the paramagnetic region. Figure 4 shows $M(H)$ curves for $\mathbf{H}\perp[001]$. At $T < T_f = 6.5$ K, we find a nonlinear $M(H)$ dependence which is independent, within 5%, of the orientation of $\mathbf{H}$ with respect to the crystal axes. In strong magnetic fields this dependence can be described by $M(H) = M^* + \chi H$.

Figure 5a shows the temperature dependence of the $Co_{0.17}Zn_{0.83}F_2$ susceptibility measured in weak (χ^*) and strong (χ) magnetic fields with $\mathbf{H}$ oriented perpendicular to the tetragonal axis.

In the experiments reported above the duration of an experiment was quite long (the time taken to sweep the magnetic field was $t \approx 5$ min) i.e., the typical experimental frequency was approximately zero. For a more detailed study of the magnetic properties of the $M_{1-x}Zn_xF_2$ compounds we studied the magnetic susceptibilities of these systems in weak magnetic fields, $H < 100$ Oe, as functions of the frequency of a modulating field.[20] Figure 6a shows the frequency dependence of the susceptibility of the $Mn_{0.2}Zn_{0.8}F_2$ system at various temperatures. We see from Fig. 6 that for

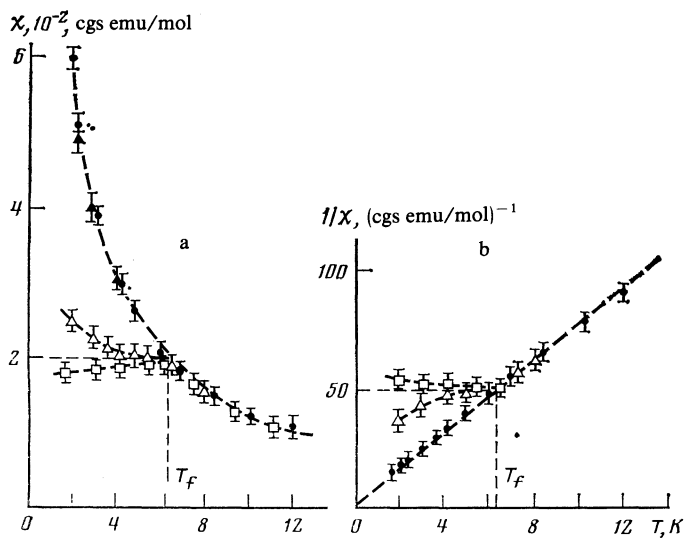

FIG. 5. Magnetic susceptibility (a) and reciprocal susceptibility (b) versus the temperature in a $Co_{0.17}Zn_{0.83}F_2$ single crystal. ●–χ^* ($H \to 0$, $\nu \approx 0$); ▲–χ^*($H \to 0$, $\nu < 20$ Hz); △–χ^*($H \to 0$, $\nu > 800$ Hz); □–χ ($H > 40$ kOe, $\nu \approx 0$).

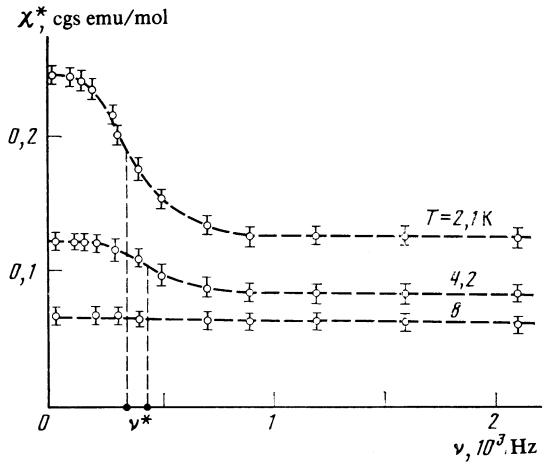

FIG. 6. Magnetic susceptibility of an $Mn_{0.2}Zn_{0.8}F_2$ single crystal versus the frequency at various temperatures.

$Mn_{0.2}Zn_{0.8}F_2$ at temperatures $T<T_f$ there is a sharp decrease in the susceptibility at frequencies $\nu\approx 400$ Hz from a high value χ' ($\nu<200$ Hz) to a value χ'' ($\nu>700$ Hz) which is 1.5 times lower than χ' at $T=4.2$ K. It can also be seen from Fig. 6 that as the temperature is lowered the low-frequency region over which the susceptibility $\chi'(\nu)$ remains constant becomes slightly narrower. Figure 2b shows the temperature dependence of χ' at frequencies $\nu<100$ Hz. We see that this behavior (the filled triangles) is essentially the same as the behavior $\chi^*(T)$ found earlier (filled circles) on the magnetometer ($\nu\approx 0$). Also shown in Fig. 2b is the temperature dependence of the susceptibility χ^* measured at frequencies $\nu>900$ Hz (the open triangles). We see from this figure that, although χ^* does increase somewhat at $\nu>700$ Hz with decreasing temperature $T<T_f$, there is a sharp change in the dependence at the point $T=T_f$. At $T>T_f$ there is no inflection point on the $\chi^*(\nu)$ curve, and the $\chi^*(T)$ dependence is the same as that found previously. Figure 2c shows the temperature dependence of the susceptibility of the $Mn_{0.25}Zn_{0.75}F_2$ crystal measured at various strengths of the applied field and at various frequencies. This study of the frequency dependence of the susceptibility χ of the $Mn_{0.33}Zn_{0.67}F_2$ crystal shows that in the temperature interval $T_N<T<T_f$ there is a state analogous to that which arises in $Mn_{0.2}Zn_{0.8}F_2$ at $T<T_f$ (Fig. 2b). At lower temperatures, $T<T_N$, $Mn_{0.33}Zn_{0.67}F_2$ acquires antiferromagnetic properties, while the frequency dependence of the weak-field susceptibility χ^* remains the same. A study of the frequency dependence of the weak-field susceptibility χ^* in the $Co_{1-x}Zn_xF_2$ system with $x=0.18$ showed that the dependence is similar to that shown in Fig. 6, with a characteristic frequency $\nu\approx 20$ Hz.

DISCUSSION OF RESULTS

A fair number of studies [8–13] have now been published on spin glasses and dilute antiferromagnets in which the $\pm$ exchange interaction has a random, fluctuating distribution, and the orientational distribution of the anisotropy axes of each of the interacting magnetic ions is random. One of the goals of these studies is to determine whether the freezing point T_f in spin glasses is a static phase transition or a consequence of a "dynamic" increase in the relaxation time of the system, with an experimental duration quite long in comparison with the times for system restructuring at the given temperatures. Let us attempt a qualitative interpretation of the experimental results on the $Mn_{1-x}Zn_xF_2$ single crystals, shown in Figs. 1–6.

We must first determine whether magnetic clusters form as the result of a possible nonuniform distribution of the Mn^{+2} magnetic ions in the $Mn_{1-x}Zn_xF_2$ crystal lattice. If such clusters do form, we need to identify the role which they play in the magnetic properties of these systems. By "noninteracting magnetic clusters" we mean systems of "rigidly" bound magnetic moments of Mn^{+2} ions which can freely rotate around the crystal axes. We need to determine the conditions under which the paramagnetic constant can be conserved in the Curie law for the weak-field susceptibility χ^* of the $Mn_{1-x}Zn_xF_2$ system as the temperature is lowered to $T<T_f$. We need to explain the frequency dependence of the susceptibility $\chi^*(\nu)$ at $T<T_f$ and to determine those states of the Mn^{+2} magnetic ions in $Mn_{1-x}Zn_xF_2$ which arise in both weak and strong magnetic fields.

The formation of arbitrary static clusters at $T<T_f$ should cause a pronounced change at $T\approx T_f$ in the constant $C=N\langle\mu\rangle^2/3k$ in the Curie law

$$\chi=N\langle\mu\rangle^2/3kT$$

or the Curie-Weiss law

$$\chi=N\langle\mu\rangle^2/3k(T-\Theta),$$

where N is the number of magnetic ions, and μ is the magnetic moment of the ion. In experiment, however, we do not see this pronounced change. The conservation of the constant C in the Curie law at $T<T_N$ and $T>T_f$ can be explained if the number of uncompensated magnetic ions in the clusters which form is $\sqrt{n}$, where n is the number of magnetic ions in the clusters. The magnetic moment of each static cluster is then $\mathbf{M}_{cl}=\sqrt{n}\boldsymbol{\mu}$. In the Curie law or the Curie-Weiss law for the susceptibility of these noninteracting clusters we have

$$\chi=(N/n)\langle\sqrt{n}\mu\rangle^2/3k(T-\Theta).$$

After some simple manipulations of this expression we find that the Curie-Weiss law for the susceptibility of the system has the same form at $T>T_f$ in the paramagnetic state as at $T<T_f$ in the state with clusters ($\mathbf{M}_{cl}=\sqrt{n}\boldsymbol{\mu}$). As the magnetic field is strengthened to a substantial level, these noninteracting "static" clusters rotate in such a manner that all their magnetic moments come to satisfy $\mathbf{M}_{cl}\parallel\mathbf{H}$. Experimentally here we should see a magnetic moment satisfying

$$M^*=(N/n)\sqrt{n}\mu=(N/\sqrt{n})\mu.$$

We see from the experimental results in Fig. 1b that the magnetic moment M^* found by extrapolating $M(H)$ in strong magnetic fields to $H\to 0$ is $M^*\approx M_0/3$, where the magnetic moment $M_0=N_\mu$ is the known saturation magnetic moment of Mn^{+2} ions in $Mn_{1-x}Zn_xF_2$. This value of M^* leads to a rather small number (≈ 9) of Mn^{+2} ions in a noninteracting cluster. The probability for a static transition in such a

cluster is extremely small, expecially if three uncompensated ions are present.

The most plausible model is that of a "nonstationary" spin glass, according to which at $T<T_f$ the system can go into some rather large set of energetically equivalent states which differ in spin orientation. At $T<T_f$, even with a uniform distribution of Mn^{+2} ions, the crystal can then break up spatially into regions of a certain radius which are determined by each of the equivalent states and which differ in the local orientational distribution of the magnetic moments. Since all the local states are equivalent, the state of the crystal as a whole can be characterized by a certain lifetime τ. The walls of each of the states are continuously in motion in the crystal. As time elapses, each given region of the crystal goes through a succession of the allowed local states; each new state arises in a random manner with a certain probability. In this dynamic model, with a random motion of the walls, and under the condition that each state contains n magnetic ions, the quantity $\sqrt{n}$ is the number of uncompensated magnetic ions, while $\sqrt{n}\mu$ is a "random," fluctuating magnetic moment of the state. Since the local states are assumed noninteracting, the constant C in the Curie law in this model remains constant as the temperature is lowered to $T<T_f$, and as the transition occurs from the paramagnetic state of the crystal to the nonstationary state which we have just described. We should point out that the crystal as a whole does not have a magnetic moment in the absence of a magnetic field according to this model, in agreement with experiment at $T<T_f$.

With increasing magnetic field H, the energetic equivalence of the states is lost, and the crystal enters a single state characterized by some energetically favored distribution of the orientations of the ion magnetic moments with respect to the orientation of the applied magnetic field. The field dependence of the magnetic moment of the crystal is $M(H)=M^*+\chi_H$ in this case, but the magnetic moment M^* is no longer $(N/\sqrt{n})\mu$, as in the case of static clusters, but instead the magnetic moment of the new magnetic state of the crystal as a whole. The susceptibility χ characterizes some average exchange interaction between randomly distributed magnetic ions.

It can be seen from this discussion that the formation of static clusters is a particular case of this model for a nonuniform distribution of Mn^{+2} ions in the crystal. In the $Mn_{1-x}Zn_xF_2$ samples, clusters of this type apparently form at concentrations $x\approx 0.6$–0.8, the constant C of the Curie-Weiss law for the susceptibility $\chi^*(T)$ to change somewhat (by 20%) with change of the Zn^{++}-ion concentration. The static clusters do not determine the particular features in the magnetic properties of these systems, but they may be the centers at which time-varying states arise in the crystal. According to the dynamic model described above, we would expect the susceptibility of the system in weak magnetic fields to become dependent on the frequency at $T<T_f$. We would expect to see different results in measurements of $\chi^*(T)$ at times $t\gg\tau$ and $t\ll\tau$, where τ is the lifetime of an individual local state.

For comparison we consider the questions which are presently being resolved in research on the spin-glass state. References 8–13 deal with the stability of the spin-glass state which arises at $T<T_f$ in a system of magnetic ions which interact with each other in accordance with the Hamiltonian

$$\mathcal{H}=\sum_{ij}J_{ij}\mathbf{S}_i\mathbf{S}_j$$

where the exchange interaction J_{ij} has a Gaussian distribution. It can be concluded from these studies that the spin-glass state is apparently unstable and highly degenerate in the orientation of the magnetic moments of the interacting magnetic ions. In contrast with the usual paramagnetic state in such a system, we do not have the symmetry element $\mathbf{S}_i\rightarrow-\mathbf{S}_i$ at $T<T_f$. Considering only an isolated magnetic ion, we conclude that its magnetic moment can be in some set of equivalent states which are separated from each other by energy barriers.[10–12] The system of magnetic ions as a whole may be in some set of equivalent magnetic states with different orientations of the individual magnetic moments.[10,11] At temperatures T below the freezing point T_f, the metastable states which arise can have a finite, possibly quite long, lifetime τ. This circumstance might lead to a quasistatic phase transition in an experiment briefer than the lifetime of the metastable states, τ. This conclusion can also be reached in a model with a random distribution of anisotropy axes[9] of individual, randomly distributed magnetic ions. The Hamiltonian of such a system can be written in the form

$$\mathcal{H}=\sum_{ij}J_{ij}\mathbf{S}_i\mathbf{S}_j-D\sum_i(\mathbf{n}_i\mathbf{S}_i)^2,$$

where $\mathbf{n}_i$ is an arbitrary vector and D is a constant.

It thus follows from these qualitative arguments regarding the magnetic properties of dilute antiferromagnets that the questions which can be answered for spin glasses[8–13] are analogous to those which we must resolve for dilute antiferromagnets. A study of such systems requires a study of the frequency dependence of their magnetic susceptibility. We see from Fig. 6 that in dilute $M_{1-x}Zn_xF_2$ antiferromagnets with $x\geqslant x_c$ exhibit at temperatures $T<T_f$ the characteristic nonlinear frequency dependence of the weak-field susceptibility χ^*.

Figure 7 shows the temperature dependence of $1/\chi^*$ for

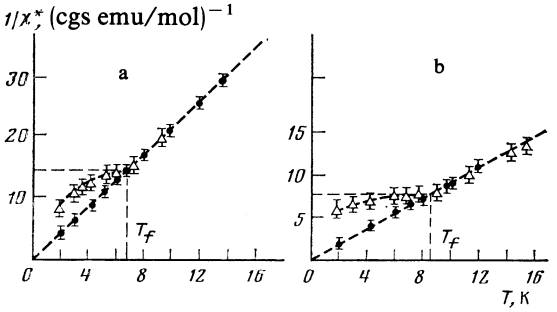

FIG. 7. Reciprocal susceptibility measured in weak magnetic fields versus the temperature for $Mn_{1-x}Zn_xF_2$ single crystals at various frequencies. a: $x=0.8$. b: $x=0.75$. ●–$\chi^*(H\rightarrow 0,\ \nu\rightarrow 0)$; Δ–$\chi^*(H\rightarrow 0,\ \nu>900$ Hz).

$Mn_{1-x}Zn_xF_2$ ($x = 0.8$ and $x = 0.75$) and $Co_{0.17}Zn_{0.83}F_2$ single crystals (see also Fig. 5b). These results were measured at various values of the applied magnetic field H and at various frequencies of the modulating magnetic field. Figure 2a shows the temperature dependence of $1/\chi^*$ for an $Mn_{0.33}Zn_{0.67}F_2$ single crystal.

The results shown for $Co_{0.17}Zn_{0.83}F_2$ in Fig. 5 were obtained in a magnetic field $\mathbf{H}\perp[001]$. In experiments in a field $\mathbf{H}\|[001]$ in the temperature range studied we observed an anisotropy on the order of 5% in the susceptibility χ, but this anisotropy is slightly less pronounced than that in the susceptibility of antiferromagnetic CoF_2 in the paramagnetic state at high temperatures.[21] The slightly weaker anisotropy of the susceptibility can probably be attributed to an insufficiently broad temperature interval in our experiments.

It follows from Figs. 7 and 5b that the temperature dependence of $1/\chi^*$ can be described by $1/\chi^* \propto T$ over the temperature range studied, with a constant whose value depends on the particular $M_{1-x}Zn_xF_2$ sample. It can also be seen from these figures that in experiments in magnetic fields $H \to 0$ at frequencies $\nu \approx 0$ the values of $1/\chi^*$ deviate from a $\propto T$ law at temperatures $T > T_f$. The slope of this curve decreases slightly with increasing temperature, indicating a nonzero Curie temperature Θ in the Curie-Weiss law for the magnetic susceptibility of these $Mn_{1-x}Zn_xF_2$ single crystals. To determine the value of Θ in the Curie-Weiss law for the susceptibility of these crystals, we need experiments at temperatures $T \gg T_f$. Over the temperature interval studied, the observed nonlinearity of $1/\chi^*$ is very slight. The transition to a time-varying magnetic state with decreasing temperature in this case is accompanied by a change in the behavior of the susceptibility $\chi^*(T)$ of these crystals from the Curie-Weiss behavior observed at $T > T_f$ to a Curie law at $T < T_f$.

Comparison of the curves of $\chi^*(T)$ for the $Mn_{0.2}Zn_{0.8}F_2$ and $Mn_{0.25}Zn_{0.75}F_2$ single crystals shows that the increase in the susceptibility χ^* measured at high frequencies is due to the presence in the $Mn_{1-x}Zn_xF_2$ of some unbound paramagnetic Mn^{+2} ions, which are surrounded exclusively by Zn^{+2} ions. The typical relaxation rate of such ions is $\sim 10^5$ Hz. Most of the Mn^{+2} ions in the $Mn_{1-x}Zn_xF_2$ lattice are in a nonparamagnetic state at temperatures below T_f. This conclusion can be reached from the circumstance that at frequencies $\nu \ll \nu^*$ the temperature dependence $\chi^*(T)$ can be described by $\chi^* = A/T$, while at frequencies $\nu \gg \nu^*$ it can be described by $\chi^* = \chi_0^* + B/T$, where $\chi_0^* = \chi_0^*(T_f)$, and A and B are constants satisfying $B \approx 0.08A$. This state is presumably also a highly degenerate, nonstationary spin-glass state.[8-13]

The behavior of the susceptibility in weak magnetic fields at low and high frequencies shows that no static ordering is observed in the $Mn_{1-x}Zn_xF_2$ system. The reason lies in the degeneracy of the states which arise at $T < T_f$ and which differ in the distribution of the orientations of the magnetic moments of the interacting Mn^{+2} magnetic ions.

The frequency dependence of the weak-field susceptibility χ^* can be described by (Fig. 6).

$$\chi^* = \chi'' + \Delta\chi/[(1-r) + re^{\omega\tau}],$$

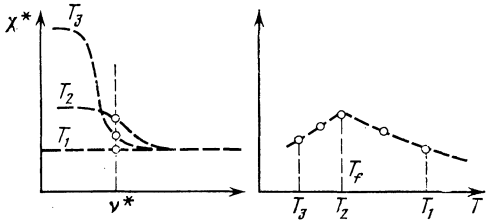

FIG. 8. Sketch of the maximum which arises in the magnetic susceptibility $\chi^*(T)$ of the compound $Mn_{0.2}Zn_{0.8}F_2$ in measurements at frequencies $\nu \approx \nu^*$ and temperatures $T \approx T_f$. Here $T_3 < T_2 < T_1$.

where χ'' is the high-frequency susceptibility, $\omega = 2\pi\nu$, and r and τ are independent of the temperature. The frequency (ν^*) at which the inflection point occurs on the $\chi^*(\nu)$ curve characterizes the lifetime of certain local states which arise in a random fashion in the crystal at $T < T_f$. A study of the frequency dependence of the weak-field susceptibility $\chi^*(\nu)$ shows that $\chi(T)$ increases at $\nu > 900$ Hz because of 2–3% of the Mn^{+2} ions which are in a paramagnetic state. By studying $\chi^*(T)$ at frequencies $\nu \approx \nu^*$ near the inflection point on the $\chi^*(\nu)$ curve, and taking into account the shift of the inflection point ν^* toward lower frequencies with decreasing temperature (Fig. 6), we can find the maximum in the susceptibility $\chi^*(T)$ at $T = T_f$.

Figure 8 sketches the appearance of a maximum in $\chi^*(T)$ near the temperature T_f in measurements at frequencies $\nu \approx \nu^*$. The shift of the $\chi^*(T)$ maximum from the frequency observed in classical spin glasses[11] can be explained by studying the $\chi^*(\nu)$ dependence at various temperatures in the frequency range $\nu \approx \nu^*$; the accuracy of the calculations is not great, however, since they incorporate only the paramagnetic increase in the susceptibility $\chi^*(T)$ measured at $\nu > 900$ Hz. The range over which the temperature T_f can vary[11] as a function of the frequency in the frequency interval which we used does not exceed 0.5 K. This result can be attributed to some nonuniformity of the distribution of interacting magnetic ions in the samples studied.

Binder[10] has derived an expression for the magnetic susceptibility which would be observed in the limit $\nu \to 0$ for N randomly distributed magnetic ions with a randomly distributed interaction:

$$\chi^*(H,T) = \frac{1}{NkT}\sum_{ij}[\langle S_iS_j\rangle_T]_{av} - \left\{3\frac{H^2}{N(kT)^3}\sum_{ijkl}\left[\langle S_iS_j\rangle_T\langle S_kS_l\rangle_T - \frac{1}{3}\langle S_iS_jS_kS_l\rangle_T\right]_{av}\right\},$$

where $[\ldots]_{av}$ is an average over the distribution of interacting magnetic ions.

This expression can be simplified in the case of a symmetric distribution of a $\pm$ exchange interaction, $p(J_{ij}) = p(-J_{ij})$, where $p(J_{ij})$ is the probability for one sign or the other of the exchange interaction between magnetic ions i and j:

$$\chi^*(H,T) = \frac{C}{T}\left\{1 - 6\left(\frac{H}{kT}\right)^2\sum_{ij}[\langle S_iS_j\rangle_T]_{av}^2 + o(H^3)\right\}.$$

The overall dependence of the susceptibility on the tempera-

ture and the magnetic field is determined by the H and T dependence of the correlation function $[\langle S_i S_j \rangle_T]_{av}$. For a two-dimensional Edwards-Anderson model, for example, Binder[10] derived the following expression for $\chi(H,T)$:

$$\chi^*(H, T)=\chi_0\{1-KH^2/T^6+O(H^3)\}, \quad T\to 0, \quad H\to 0,$$

where χ_0 is the paramagnetic susceptibility, and K is a constant.

In our interpretation of the experimental results on $Mn_{0.2}Zn_{0.8}F_2$ we write the magnetic susceptibility as the following function of the magnetic field:

$$\chi^*(H, T)=\chi_0[1-KH^\alpha/T^\beta]. \quad (1)$$

In the limit $H\to 0$, $\nu\to 0$, this function becomes qualitatively the same as that which we found in the experiments whose results are shown in Fig. 2 and also in some experiments carried out previously.[1-3]

To determine the constants α and β in (1) we plotted $\ln M(H)$ and $\ln(\chi^*/\chi_0-1)$ versus $\ln H$ at constant T, and we plotted $\ln(\chi^*/\chi_0-1)$ versus $\ln T$ at constant H. For the $Mn_{0.2}Zn_{0.8}F_2$ single crystal we found that the dependence of the magnetic moment on the applied magnetic field at $H>2$ kOe and a constant temperature can be described by $M(H)=\chi H^\gamma$, where $\gamma=2/3\pm 1/6$. The behavior of the susceptibility of the crystal studied can be described by expression (1) with the value $\beta=6\pm 1$ and with a value for α which ranges from 1.6 to 2.1, depending on the temperature. The observed T dependence of α may mean that $\chi(H,T)$ is a more complicated function of H and T than as represented in (1). The behavior of the magnetic moment which we measured for $Mn_{0.2}Zn_{0.8}F_2$ as a function of the applied field agrees with calculations[12] carried out to determine the dependence of the magnetic moment of a spin glass on the applied magnetic field and the temperature in the Edwards-Anderson model with a short-range interaction. According to our experiments, and in agreement with Ref. 12, the dependence $M(H)$ for $Mn_{0.2}Zn_{0.8}F_2$ can be described by $M(H)=\chi H^\gamma$, again with $\gamma=2/3\pm 1/6$.

As the magnetic field is increased in the temperature range $T<T_f$, the single crystals go into a stable state[11] determined by a random distribution of the components of the magnetic moments perpendicular to the applied magnetic field. According to the experimental results, the magnetic moment $M(H,T)$ of the sample in this rather strong field can be described by $M(H,T)=M^*+\chi H$, where M^* is the magnetic moment in the **H** direction, and χ is the average susceptibility of this system, which is different from the antiferromagnetic susceptibility. In the experiments on $Mn_{0.2}Zn_{0.8}F_2$ a stable state of this sort arose at $H>30$ kOe (Fig. 1). The possibility of a transition to a stable spin-glass state with increasing magnetic field was predicted by Fischer[11] on the basis of a theoretical analysis and by Kinzel and Binder[12] on the basis of Monte Carlo calculations.

As the concentration of Zn^{+2} ions in $Mn_{1-x}Zn_xF_2$ is reduced to $x<x_c$ the nonstationary state is also observed at temperatures $T<T_f$. It can be seen from Fig. 2a that for $Mn_{0.33}Zn_{0.67}F_2$ this prevails at $T<12$ K. At $T<T_N$, the nonstationary state is retained upon the appearance of antiferromagnetic properties for this compound: A nonstationary antiferromagnetic state arises. A fluctuating magnetic moment in an antiferromagnetic state of this sort arises in the (001) plane of the crystal.[2]

Hertz[13] has derived a theory for the frequency dependence of the magnetic susceptibility of a spin glass in the Edwards-Anderson model, working from the equations of motion

$$\frac{\partial S_i}{\partial t}=-\gamma_0\frac{\partial \mathcal{H}}{\partial S_i}+\eta_i(t),$$

where the effective Hamiltonian of the system is

$$\mathcal{H}=\frac{1}{2}\sum_{ij}J_{ij}S_iS_j+\sum_i\left[\frac{1}{2}r_0S_i^2+\frac{1}{8}uS_i^4+h(t)S_i\right].$$

Here J_{ij} is the exchange interaction between nearest neighbors, which has a Gaussian distribution; $\eta_i(t)$ is a Langevin noise, which satisfies the condition

$$\langle\eta_i(t)\eta_j(t')\rangle=2T\gamma_0\delta_{ij}\delta(t-t');$$

r_0 and u are constants; and $h(t)$ is the magnetic field. Hertz derived the average dynamic susceptibility $G_{ij}(\omega)$ and the spin correlation function $C_{ij}(\omega)$ for spin glasses. Comparison reveals a qualitative agreement between the theoretical predictions of Ref. 13 and our experimental data on the frequency dependence of the susceptibility and the conclusions reached from these data.

In contrast with $Mn_{1-x}Zn_xF_2$, $Co_{1-x}Zn_xF_2$ exhibits not only a random distribution of the exchange interaction but also a random distribution of the Dzyaloshinskiĭ interaction[16] in the (001) plane. For $Co_{0.28}Zn_{0.72}F_2$ we see a difference between the magnetic moments $M(H,T)$ in the field orientations $\mathbf{H}\parallel[100]$ and $\mathbf{H}\parallel[001]$, but this difference disappears as the concentration of Zn^{+2} ions is raised to $x=0.85$ in $Co_{1-x}Zn_xF_2$ (Fig. 4). The magnetic moment $M(H,T)$ is independent within 10% of the orientation of H with respect to the crystal axes. A study of the magnetic susceptibility as a function of the temperature, the magnetic field, and the frequency showed that again in the $Co_{1-x}Zn_xF_2$ system (Fig. 5) a time-varying state with a random distribution of interacting moments arises at $x>0.8$ and $T<T_f$. With increasing magnetic field, a stationary state with a susceptibility χ and a magnetic moment M^* sets in (Fig. 4). The characteristic frequency of the time-varying state of this $Co_{0.17}Zn_{0.83}F_2$ single crystal is $\nu^*\approx 20$ Hz; this frequency has so far hindered a detailed study of this compound.

Figure 3 shows the results of our previous measurements[1,2] and of measurements by other workers[4,19] of the temperature (T_N) at which $Mn_{1-x}Zn_xF_2$ develops antiferromagnetic properties, plotted against the concentration of nonmagnetic Zn^{+2} ions in these compounds. Also shown in this figure are the values which we found for the temperature (T_f) of the transition to the time-varying, spin-glass magnetic state in $Mn_{1-x}Zn_xF_2$ from the onset of the frequency dependence of the susceptibility, $\chi^*(\nu)$, and from the appearance of a slightly temperature-dependent susceptibility χ. We should point out again that the temperature T_f (curve 2 in Fig. 3) is determined by the transition region $T_f\pm 0.5$ K

between the paramagnetic state and the state of a time-varying spin glass.

In summary, the results of this study show that a time-varying state with randomly distributed magnetic moments of the Mn^{+2} and Co^{+2} ions arises in single crystals of the compounds $Mn_{1-x}Zn_xF_2$ ($M = Mn^{+2}$, Co^{+2}) at concentrations $x > x_c = 0.7$–0.8 of the nonmagnetic Zn^{+2} ion and at temperatures $T < T_f(x)$ in the absence of a magnetic field. This time-varying state is distinct from the usual paramagnetic state. AT temperatures $T \leqslant T_f(x)$ the relaxation time of the system changes, and we observe the characteristic dependence of the susceptibility χ on the measurement frequency. A corresponding effect—a sharp change in the relaxation time of the system at a certain temperature T_f—has been observed by Mezei[22] in a study of the dynamics of the spin glasses Cu + 1%, 5%, and 10% Mn^{+2} ions. As the applied magnetic field is increased, a stationary state with randomly oriented magnetic moments with respect to the orientation of the magnetic field arises in the compounds which we studied.

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