Investigation of the static magnetic properties of the system $Mn_{1-x}Zn_xF_2$

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The static magnetic properties of single crystals of $Mn_{1-x}Zn_xF_2$, of tetragonal symmetry, at various concentrations x of the nonmagnetic Zn^{++} ion that replaces the magnetic Mn^{++} ion, have been investigated with a vibrating-specimen magnetometer over the magnetic-field range 0 to 60 kOe and over the temperature range 1.7 to 80 K. As a result of investigation of the magnetization curves $M(H)$ and the magnetic susceptibility of monocrystalline specimens of $Mn_{1-x}Zn_xF_2$ it was shown that, along with the usual properties of a uniaxial antiferromagnet, this system at concentrations $x > 30\%$ of the Zn^{++} ions possesses magnetic properties incompatible with its assignment to this class of antiferromagnets. A distinctive feature of the magnetic properties of $Mn_{1-x}Zn_xF_2$ at $x > 30\%$ is a strong temperature dependence of the transverse magnetic susceptibility $\chi_\perp^*(T)$ measured in weak magnetic fields, while the temperature dependence of the longitudinal magnetic susceptibility $\chi_\parallel(T)$ shows a maximum of the magnetic susceptibility, corresponding to a transition of the system to an ordered state. The question of the existence of a state of the "spin glass" type in this system is discussed.

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Single-crystal MnF_2, of the tetragonal symmetry D_{4h}^{14}, is one of the best studied easy-axis antiferromagnets.[1] The antiferromagnetic vector **L** in MnF_2 is oriented along its tetragonal axis. The elementary cell contains two magnetic Mn^{++} ions, located at the points (0;0;0) and $(\frac{1}{2};\frac{1}{2};\frac{1}{2})$.

The purpose of the present research was to investigate the static magnetic properties of the system $Mn_{1-x}Zn_xF_2$, in which the magnetic Mn^{++} ions in antiferromagnetic MnF_2 are replaced by nonmagnetic Zn^{++} ions, presumably in a random manner. Single-crystal ZnF_2 has tetragonal symmetry, and its elementary cell also contains two Zn^{++} ions at positions (0;0;0) and $(\frac{1}{2};\frac{1}{2};\frac{1}{2})$. The parameters of the elementary cells of MnF_2 and ZnF_2 and their melting points

	a, Å	*c*, Å	*t m*, °C
MnF_2	4.874	3.310	904
ZnF_2	4.703	3.133	920

are quite close to each other. An investigation of the magnetic properties of the system $Mn_{1-x}Zn_xF_2$ has been made by the methods of nuclear and of antiferromagnetic resonance,[2,3] but sufficiently detailed static magnetic measurements have not been made. It must be mentioned that an investigation of the magnetic properties of dilute systems has been made.[4] The authors of that paper studied the properties of the system Al_2O_3-Fe_2O_3-Ga_2O_3, in which nonmagnetic Al^{+++} and Ga^{+++} ions replace the magnetic Fe^{+++} ion. Recently there has occurred a development of research on investigation of the possibility of the existence of a spin-glass state in nonconducting systems[5-7] with a random distribution of magnetic ions. In the $Mn_{1-x}Zn_xF_2$ system under study, the random replacement of magnetic Mn^{++} ions by nonmagnetic Zn^{++} ions leads to the result that there is formed within it a random distribution of magnetic Mn^{++} ions, coupled to each other by antiferromagnetic exchange interaction between the sublattices and ferromagnetic exchange interaction within the sublattices of the original MnF_2. Such a distribution of negative and positive exchange bonds, as was pointed out in Refs. 5–7, could lead to a state of the spin-glass type.

According to published data, MnF_2 and ZnF_2 have nearly equal values of the elementary-cell parameters and of the melting temperature, but the values of the latter in different papers differ. In Ref. 8 single crystals of the solid solutions $Mn_{1-x}Zn_xF_2$ were obtained (where $x = 0.9; 0.48$), but in another paper[9] it is asserted that there exists a compound $ZnF_2 \cdot MnF_2$. Since we needed single crystals of $Mn_{1-x}Zn_xF_2$ over the whole range of concentration, we have to refine the character of the diagram of the condensed state of the system MnF_2–ZnF_2. For this purpose, differential thermal[1)] and x-ray phase[2)] analyses of specimens of various concentrations were carried out. The specimens were prepared from anhydrous MnF_2 and ZnF_2 that were first melted in an atmosphere of HF; thereafter, single crystals were grown in a helium atmosphere in the apparatus described earlier.[10]

The x-ray phase analysis showed that solid solutions exist in the system MnF_2–ZnF_2 over the whole range of concentrations, and that the lattice parameters of the solid solutions vary monotonically with variation of the concentration of the components.

The differential thermal analysis also corroborated the existence of a continuous series of solid solutions in the system MnF_2–ZnF_2. Each specimen grown and investigated was placed in x-ray apparatus to determine its crystallographic axes. The accuracy of determination of the axes of the single crystals was no worse than 2°.

The investigations of the magnetization of single crystals of $Mn_{1-x}Zn_xF_2$ were made on a vibrating-specimen magnetometer[11] over the temperature range 1.5 to 70 K and the magnetic-field range 0 to 60 kOe. Temperatures below 4.2 K were attained by evacuation of helium vapors in the solenoid cryostat.[11] The $Mn_{1-x}Zn_xF_2$ specimens under investigation, having been

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oriented on the x-ray apparatus, were placed in the magnetometer in such a way that it was possible to investigate the magnetization curves $M(H)$ both for orientation of the applied magnetic field perpendicular to the tetragonal axis ($\mathbf{H}\perp C_4$) and for orientation of the field along the tetragonal axis of the single crystal. The accuracy of orientation of the crystallographic axes of the $Mn_{1-x}Zn_xF_2$ single crystals with respect to the axes of the measurement cells in the magnetometer was not worse than 2–3°.

RESULTS OF THE MEASUREMENTS

Figures 1(a)–(f) show magnetization curves $M(H)$ of single crystals of $Mn_{1-x}Zn_xF_2$ at temperature $T=4.2$ K.

Curves 1 in Figs. 1(a)–(f) represent the variation of the magnetic moment of the specimen with the magnetic field **H** when **H** is applied perpendicular to the tetragonal axis of the single crystal. Curves 2 in Figs. 1(a)–(f) represent the $M(H)$ relation of the specimen when **H** is applied along the tetragonal axis of the single crystal. The magnetization curves $M(H)$ for $\mathbf{H}\perp C_4$ and $\mathbf{H}\parallel C_4$ for pure MnF_2 ($x=0$), shown in Fig. 1(a), are taken from Ref. 1. It is evident from Fig. 1 that with increase of the concentration of the nonmagnetic Zn^{++} ion, anomalies appear on the magnetization curves $M(H)$ of the system $Mn_{1-x}Zn_xF_2$ both when $\mathbf{H}\perp C_4$ and when $\mathbf{H}\parallel C_4$. With increase of the concentration x of Zn^{++} ions in MnF_2, a nonlinear increase $M(H)$ occurs on the magnetization curve $M(H)$ for $\mathbf{H}\perp C_4$ in weak fields, $H<10$ kOe. For example, for the specimen with ion concentration $x=0.6$ the magnetization curve $M(H)$ of the specimen under investigation has a nonlinear character for $\mathbf{H}\perp C_4$ in magnetic fields up to 10 kOe, while in magnetic fields larger than 10 kOe the $M(H)$ relation can be described by the expression $M(H)=M^*(x)+\chi_\perp H$, where the magnetic susceptibility $\chi_\perp=(1\pm0.2)\cdot10^{-2}$ cgs/emu/mol is independent of the magnetic field.

When the magnetic field **H** is oriented along the tetragonal axis C_4 (curves 2 in Fig. 1), the plot of the magnetic moment versus applied magnetic field shows a phase transition due to flipping of the magnetic moments of the sublattices of Mn^{++} ions. The value of the magnetic field at the phase transition, as is evident from Fig. 1, depends strongly on the concentration of Zn^{++} ions. For a specimen with ion concentration $x=0.6$, with $\mathbf{H}\parallel C_4$ and a value of the magnetic field $H<10$ kOe, the $M(H)$ relation is described by the linear expression $M(H)=\chi_\parallel=(1.7\pm0.2)\cdot10^{-3}$ cgs emu/mol. In the magnetic-field range $20<H<40$ kOe, a strong nonlinear increase of the $M(H)$ relation is observed; and when $H>40$ kOe, the $M(H)$ relation for $\mathbf{H}\parallel C_4$ coincides with the $M(H)$ relation for the magnetic moment of the specimen for $\mathbf{H}\perp C_4$. The character of the phase transition in magnetic fields $20<H<40$ kOe when $\mathbf{H}\parallel C_4$ suggests that in this field range there occurs something like a flip of the magnetic Mn^{++} sublattices of the system $Mn_{1-x}ZnF_2$.

We investigated magnetization curves of $Mn_{1-x}Zn_xF_2$ in magnetic fields $\mathbf{H}\perp C_4$ and $\mathbf{H}\parallel C_4$ at various temperatures from 1.5 to 70 K. By processing the $M(H)$ relations obtained for specimens with various concentrations x at various temperatures, we plotted magnetic susceptibility relations $\chi(T)$ for the different orientations of the applied magnetic field **H** and for various values of the magnetic field.

In Figs. 2(a)–(f), curves 1 represent the variation

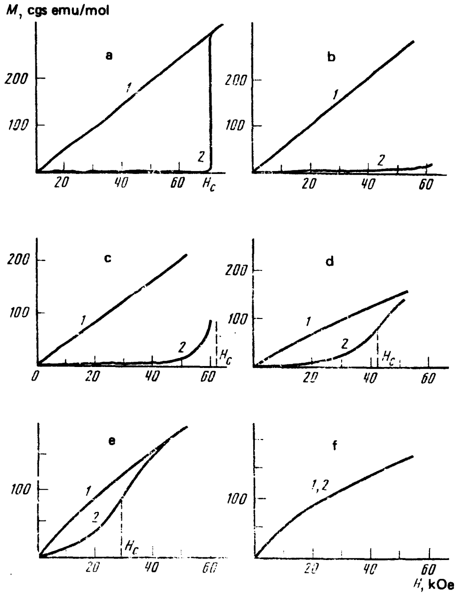

FIG. 1. Variation of magnetic moment of single crystals of $Mn_{1-x}Zn_xF_2$ with applied magnetic field, when $H\perp C_4$ (Curves 1) and when $H\parallel C_4$ (Curves 2), for the following concentrations x of nonmagnetic Zn^{++} ions: a) 0; b) 0.1; c) 0.28; d) 0.46; e) 0.6; f) 0.7. In Fig. 1f, Curves 1 and 2 coincide.

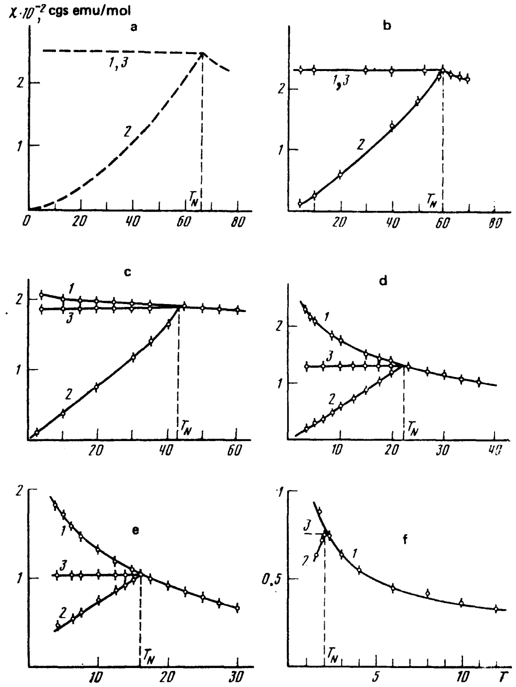

FIG. 2. Temperature dependence of magnetic susceptibility of a single crystal of $Mn_{1-x}Zn_xF_2$. Curves 2, magnetic field oriented along tetragonal axis, the relation $\chi_\parallel(T)$. Curves 1 and 3, magnetic field $H\perp C_4$: Curves 1, in weak magnetic fields $H<1$ kOe, the relation $\chi_\perp^*(T)$; Curves 3, in strong magnetic fields $H>50$ kOe, the relation $\chi_\perp(T)$. For Figs. 2a–f, $x=0, 0.1, 0.28, 0.46, 0.6, 0.7$ respectively. In Figs. 2a and 2b, Curves 1 and 3 coincide.

of the magnetic susceptibility $\chi_{\perp}^{*}(T)$ when the applied magnetic field **H** is oriented perpendicular to the tetragonal axis C_4, obtained by processing the magnetization curves $M(H)$ in weak magnetic fields, $H < 1$ kOe. Curves 2 in Figs. 2(a)–(f) represent the variation of the magnetic susceptibility $\chi_{\parallel}(T)$ for orientation of the applied magnetic field **H** along the tetragonal axis, also obtained by processing of magnetization curves $M(H)$ in weak magnetic fields, $H < 1$ kOe. Curves 3 in Figs. 2(a)–(f) represent the variation of the magnetic susceptibility $\chi_{\perp}(T)$, obtained by processing of magnetization curves $M(H)$ in strong magnetic fields, $H > 50$ kOe. Figure 2(a) shows, for comparison with the experimental data, the relations $\chi_{\perp}(T)$ and $\chi_{\parallel}(T)$ for pure MnF_2, obtained in Ref. 1.

The greatest difference of the magnetic susceptibility relations of the system $Mn_{1-x}Zn_xF_2$ from the magnetic susceptibility of antiferromagnetic MnF_2 is observed on the curve showing the perpendicular magnetic susceptibility relation $\chi_{\perp}^{*}(T)$. In antiferromagnetic MnF_2 the value of the perpendicular magnetic susceptibility $\chi_{\perp}(T)$ at a temperature below the phase-transition point is independent of temperature, whereas in a diluted system $Mn_{1-x}Zn_xF_2$ there appears a strong dependence of the magnetic susceptibility on temperature (curves 1 of Fig. 2). The variation of the magnetic susceptibility $\chi_{\parallel}(T)$ of the system $Mn_{1-x}Zn_xF_2$ for orientation of the applied magnetic field along the tetragonal axis C_4 has a clearly expressed maximum, dependent on the concentration of Zn^{++} ions, and characteristic of an antiferromagnetic transition. At Zn^{++} ion concentrations $x > 0.7$, both the magnetization curves $M(H)$ and the magnetic susceptibility curves $\chi(T)$ are independent of the orientation of the applied magnetic field with respect to the crystallographic directions of the specimen and have the form represented in Figs. 1(f) and 2(f).

DISCUSSION OF RESULTS

Replacement of a magnetic Mn^{++} ion in the tetragonal antiferromagnet MnF_2 by a nonmagnetic Zn^{++} ion does not introduce into its magnetic properties any peculiarities directly due to the Zn^{++} ion. The system $Mn_{1-x}Zn_xF_2$ may be regarded as a tetragonal crystal in which the magnetic Mn^{++} ions have been distributed quite at random and the interactions between these magnetic ions have been preserved. The magnetic properties of such a system are determined solely by the properties of the sytem of Mn^{++} ions. The peculiarity of the magnetic properties of the system $Mn_{1-x}Zn_xF_2$ that distinguishes it from the pure antiferromagnet MnF_2 is, as has already been indicated, the strong nonlinear increase of the magnetic susceptibility $\chi_{\perp}^{*}(T)$ of a single crystal with increase of its temperature, when the magnetic field is applied perpendicular to the tetragonal axis. In the antiferromagnetic state of MnF_2, the antiferromagnetic vector **L** is oriented along the tetragonal axis C_4. A peculiarity of easy-axis antiferromagnets with Mn^{++} ions is the temperature independence of the perpendicular magnetic susceptibility $\chi_{\perp}(T)$ and the strong temperature dependence of the parallel magnetic susceptibility $\chi_{\parallel}(T)$.[1] At $T=0$, $\chi_{\parallel}=0$; at $T=T_N$, $\chi_{\parallel}=\chi_{\perp}$ [Fig. 2(a)]. Thus it may be concluded that a single crystal of $Mn_{1-x}Zn_xF_2$ with $x > 0.25$ is not a simple antiferromagnet. But it must be noted that antiferromagnetic properties also persist in this system. The presence of a sharp maximum in the variation of the magnetic susceptibility when the applied magnetic field is oriented along the tetragonal axis (Fig. 2), and also the phase transition accompanied by a flip of the magnetic moments of the sublattices as determined from the variation of the magnetic moment with the applied magnetic field H when $\mathbf{H} \parallel C_4$, are characteristic of an antiferromagnetic of the "easy axis" type when there is a component of the antiferromagnetic vector along the applied magnetic field **H**. But the character of the phase transition suggests that, in addition to a component of the antiferromagnetic vector along the applied magnetic field, along the tetragonal axis, components of the antiferromagnetic vector are possible in the plane perpendicular to this axis. It is evident from Fig. 1 that a phase transition involving flipping of a component of the antiferromagnetic vector **L** occurs not discontinuously, as in pure MnF_2 ($\mathbf{L} \parallel C_4$), but smoothly over a certain range of values of the magnetic fields. Such a phase transition is characteristic of an antiferromagnet in which the total antiferromagnetic vector **L** is oriented at an angle to the applied magnetic field; that is, at an angle to the tetragonal axis C_4.

Figure 3(a) shows the variation of the phase-transition point T_N of single crystals of $Mn_{1-x}Zn_xF_2$ with the concentration x of Zn^{++} ions. The phase-transition point was determined from the position of the maximum of the magnetic susceptibility $\chi_{\parallel}(T)$. The same figure shows data obtained in Ref. 3. Figure 3(b) shows the variation of the phase-transition field H_c with the concentration of Zn^{++} ions when the magnetic field is oriented along the tetragonal axis and $T=4.2$ K. The value of the flip field was determined from the point of inflection of the magnetization curve $M(H)$. The regular variation of the phase-transition point with the concentration suggests that in the single crystals of $Mn_{1-x}Zn_xF_2$ studied, there is a quite random distribution of Zn^{++} ions and Mn^{++} ions.

The mean value of the component of the antiferromagnetic vector in the plane perpendicular to the tetragonal axis, as a function of the concentration x of Zn^{++} ions, can be estimated from the experiments represented in Figs. 1 and 2.

As has already been indicated, when the magnetic

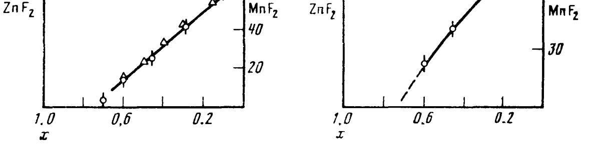

FIG. 3. a—Variation of the temperatures T_N of the magnetic phase transition of $Mn_{1-x}Zn_xF_2$ with the concentration x of Zn^{++} ions: ○) results of the present paper; △) results of Ref. 3. b—Variation of the "flip field of the magnetic sublattices" (H_c) of $Mn_{1-x}Zn_xF_2$ with the concentration x of Zn^{++} ions; $T=4.2$ K.

field $\mathbf{H}$ is at an angle to the antiferromagnetic vector $\mathbf{L}$, there occurs a smooth rotation of $\mathbf{L}$ into a direction perpendicular to $\mathbf{H}$. Equations for such a rotation of the antiferromagnetic vector $\mathbf{L}$ were obtained in Ref. 1 for known values of the effective exchange field H_E and uniaxial-anisotropy field H_{AE}. Knowing the value of the magnetic susceptibility $\chi_\perp$ and the value H_c of the flip field of the magnetic moments of the sublattices, one can determine, for specimens with various concentrations of Zn^{++} ions, their effective exchange field $H_E = M_0/\chi_\perp$ and uniaxial-anisotropy field $H_{AE} = H_c$. Having calculated the equation of rotation of the antiferromagnetic vector $\mathbf{L}$ for known H_E and H_{AE}, one can estimate the mean value $\bar{\theta}$ of the angle between the direction of the antiferromagnetic vector $\mathbf{L}$ and the applied magnetic field $\mathbf{H} \| C_4$. This mean value $\bar{\theta}$ of the angle can also be determined by comparing the value of the perpendicular magnetic susceptibility $\chi_\perp(\mathbf{H}\perp\mathbf{L})$ and the value of the magnetic susceptibility $\chi_\|(0) = \chi_\perp \sin^2\theta$ (Ref. 1) obtained by extrapolation of the $\chi_\|(T)$ relation to $T=0$. At concentrations $x=0.6$, the mean angle $\bar{\theta}$ between the direction of the antiferromagnetic vector $\mathbf{L}$ and the axis C_4 has a value of the order of 15°. The antiferromagnetic vector $\mathbf{L}$ for a system with a random distribution of magnetic ions may be defined as before: $\mathbf{L} = (\mathbf{M}_1 - \mathbf{M}_2)/2M_0$, where M_1 and M_2 are the magnetic moments of the ions of different sublattices, but not necessarily in a single elementary cell. It must be noted, however, that the experiments presented do not constitute a direct proof that the antiferromagnetic vector $\mathbf{L}$, in the system $Mn_{1-x}Zn_xF_2$ with $0.3 < x < 0.7$, is oriented at an angle to the tetragonal axis; the angle θ was calculated on the assumption of this possibility. From this experiment it follows only that in the system $Mn_{1-x}Zn_xF_2$, as compared with the pure antiferromagnet MnF_2, the component of $\mathbf{L}$ along the tetragonal axis is conserved. The experiments presented in Figs. 1 and 2 point to the possibility of the appearance in $Mn_{1-x}Zn_xF_2$ of a component of $\mathbf{L}$ ($\mathbf{L}_\perp$) in a direction perpendicular to the tetragonal axis. In view of the randomness of the distribution of Mn^{++} and Zn^{++} ions, it may be supposed that there is a random distribution of the component $\mathbf{L}_\perp$ in the (001) plane.[5] Such a possibility exists in spin glasses;[4-6] but for an accurate determination of this, neutron-diffraction experiments are necessary. Investigation of the magnetization curves $M(H)$ of $Mn_{1-x}Zn_xF_2$ in strong magnetic fields $H > 40$ kOe, Fig. 1, shows that at Zn^{++} ion concentrations $x > 0.45$, at such values of the magnetic fields, the antiferromagnetic vector $\mathbf{L}$ always sets itself perpendicular to the applied magnetic field, for arbitrary orientation of $\mathbf{H}$ with respect to the axis of the single crystal. Here the measured magnetic susceptibility $\chi_\perp(T)$ of Fig. 2 (curves 3), just as in antiferromagnets, is independent of temperature.

The most interesting experimental fact obtained in investigation of a single crystal of $Mn_{1-x}Zn_xF_2$ is the temperature dependence $\chi_\perp^*(T)$ of the magnetic susceptibility, obtained in weak magnetic fields $H < 1$ kOe at a temperature below the temperature T_N of the maximum of the magnetic susceptibility $\chi_\|(T)$. The temperature dependence of the inverse susceptibility $1/\chi_\perp^*$ is determined by a linear expression over the whole temperature range: $1/\chi_\perp^* = \alpha(T - T^*)$, where T^* is a quantity dependent on the concentration of nonmagnetic ions.

That the single crystals investigated are not simple two-phase mixtures of an antiferromagnet and a paramagnet is indicated by the investigation of the magnetic-moment variation $M(H)$ for orientations $\mathbf{H}\perp C_4$ and $\mathbf{H}\| C_4$. If the single crystals under investigation were such two-phase mixtures, a nonlinear $M(H)$ relation would be observed for $\mathbf{H}\| C_4$ in weak fields, analogous to the nonlinear $M(H)$ relation for $\mathbf{H}\perp C_4$, and an anomaly would also be observed on the magnetic susceptibility curve $\chi_\perp^*(T)$ at the phase-transition point T_N (Fig. 2). Similar variations $\chi_\perp^*(T)$ of the magnetic susceptibility with temperature have been observed[12] in investigation of the properties of Fe_2TiO_5. The authors of this paper, who investigated not only the static magnetic properties of these single crystals but also, by the neutron-diffraction method, the magnetic structure, did not detect long-range magnetic order in this material but did determine the presence in it of short-range magnetic order. This result enabled them to assert that the material studied by them can be classified as an "anisotropic spin glass" with basic antiferromagnetic interaction.[5] From our experiments on investigation of $Mn_{1-x}Zn_xF_2$ single crystals it may be concluded that possibly the system investigated, for $x > 0.3$, belongs to the anisotropic spin glasses. At Zn^{++} ion concentrations $x > 0.7$ [Fig. 1(e)], a paramagnetic law of increase of $\chi(T)$ is observed in weak fields down to the lowest temperature obtainable in the apparatus (1.5 K). Further investigation of the paramagnetic law of increase of the magnetic susceptibility $\chi_\perp^*(T)$, obtained in weak magnetic fields for $\mathbf{H}\perp C_4$ at various concentrations of the nonmagnetic Zn^{++} ions in $Mn_{1-x}Zn_xF_2$, requires lower temperatures.

Thus as a result of the investigations of the static magnetic properties of single crystals of $Mn_{1-x}Zn_xF_2$, it may be concluded that the system investigated possesses properties of an antiferromagnet of the "easy axis" type; but the strong nonlinear increase $\chi_\perp^*(T)$ of the perpendicular magnetic susceptibility obtained in weak magnetic fields cannot be explained on the basis of this assumption. Most probable is the existence in this system of a state of the antiferromagnetic spin-glass type, as was suggested in Refs. 5–7.

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Nuclear relaxation and nuclear-nuclear double resonance in systems with inhomogeneous EPR broadening

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Nuclear relaxation and nuclear-nuclear double resonance are considered in an electron-nuclear spin system in which the degree of inhomogeneity of the EPR broadening can be varied. The case closest to the qualitative experimental results [J. van Houten, W. Th. Wenckebach, and J. J. Poulis, Physica **92B**, 201, 210 (1977) and **100B**, 35 (1980); J. van Houten, Dissertation, Leiden (1979)] is singled out from among several limiting cases. Good quantitative agreement between theory and experiment is found.

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1. INTRODUCTION

A number of investigations have been made[1-3] of the relaxation of the protons of the water of hydration in copper-Tutton's salt containing a certain amount of D_{20}:

$$(\mathrm{Cu}_f,\ \mathrm{Zn}_{1-f})\mathrm{Cs}_2(\mathrm{SO}_4)_2\cdot 6(\mathrm{H}_y,\ \mathrm{D}_{1-y})_2\mathrm{O},$$

where $f\approx 0.5\%$, and y ranges from 6 to 100%, as well as nuclear-nuclear double resonance with participation of protons, deuterons, and cesium nuclei.

The copper Tutton's salt crystal contain Cu^{2+} ions with electron ($S=\frac{1}{2}$) and nuclear ($I^{\mathrm{Cu}}=3/2$) spins. In addition, there are the spins of the protons ($I_p=\frac{1}{2}$), of the deuterons ($I_d=3/2$), and of the cesium nuclei $I_{\mathrm{Cs}}=7/2$). Since the Cu^{2+} ions occupy two magnetically nonequivalent positions in the lattice, the EPR spectrum of Cu^{2+} consists of two sets of lines that coincide if the constant magnetic field is directed along the crystal axis K_1 or K_3. Each of the two sets consists of four lines due to the hyperfine interaction of the electron and nuclear spins of the Cu^{2+} ions. The EPR lines are inhomogeneously broadened by the hyperfine interaction of Cu^{2+} with ligand protons and deuterons.

The most essential feature of the experimental results is the dependence of the proton-relaxation time T_{1p} and of the nuclear-nuclear double resonance coefficient Q on the orientation of the constant magnetic field relative to the crystal axes K_1 and K_3. This phenomenon was explained[1-3] on the basis of the assumption that in the bottleneck in the proton relaxation to the lattice are two thermal contacts: 1) the contact of the proton Zeeman subsystem with the electron dipole-dipole pool (EDDP); 2) the contact of the proton Zeeman subsystem with the "difference" Zeeman energies of the electron spins, which is effected with the aid of a three-spin process with participation of two electron spins and one nuclear spin [first described by Kessenikh and Manenkov[4] and usually called electron-nuclear cross relaxation (CR)]. It was assumed that as a result of the effective electron cross relaxation, the EDDP and the difference Zeeman electron energies combine into a single "non-Zeeman" pool [usually called the local-field pool (LFP)[5]].

This model, however, did not describe the experimentally observed[1-3] overall decrease of T_{1p} in the angle region near the axes K_1 and K_3, and did not explain the presence of a maximum in the angular dependence of the nuclear-nuclear double resonance coefficient Q. To resolve the latter contradiction it was proposed[3] that the EDDP and the difference Zeeman energies are not in equilibrium with each other in the nuclear-nuclear double resonance process.

The purpose of the present paper is a study of the nuclear relaxation of nuclear-nuclear double resonance in spin systems in which it is possible to vary the de-

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