

Nuclear magnetic resonance of fluorine in $Mn_xZn_{1-x}F_2$ compounds at temperatures 4.2–300 K

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The transverse and longitudinal relaxation times and the NMR line profile were determined by the pulse method for fluorine nuclei in dilute antiferromagnets $Mn_xZn_{1-x}F_2$ at temperatures from 4 to 300 K. The decay of the nuclear magnetization as a result of a transition to an ordered state was nonexponential and was accompanied by a strong broadening of the NMR line which became asymmetric and split. The results of the measurements made it possible to identify the contributions of different types of the Mn ions, the exchange-isolated ions and those belonging to an infinite or a finite cluster.

INTRODUCTION

Experimental and theoretical investigations of amorphous magnetic materials, which are substances with a random spatial distribution of atoms, are vigorously pursued at present. This reflects a general tendency of the search for the laws governing disordered solids. A closely related subject is that of dilute antiferromagnets in which the crystal structure remains in the original form, but in which chaos is induced in the magnetic structure because of a random distribution of the magnetic ions in the crystal lattice. A low-temperature magnetic state of a system of this kind is ordered if the dilution is not too strong, but this state has a number of unusual features. The principal difference between such compounds and "conventional" magnetic materials is that, in addition to an infinite magnetic cluster, they contain a whole series of finite ordered regions of different sizes.

We have investigated a typical example of such structures, a classical two-sublattice antiferromagnet MnF_2 diluted with diamagnetic zinc ions. Compounds of this type exhibit a number of interesting phenomena such as the random field effect¹ and anomalies of the longitudinal and transverse magnetic susceptibility near the temperature T_N of the transition to an ordered state.²

One of the distinguishing properties of $Mn_xZn_{1-x}F_2$ solid solutions is the presence of "free" fluorine ions F_0 in the crystal lattice, i.e., of nuclei which do not have magnetic Mn ions in the immediate environment. Consequently, the NMR line of F_0 is not shifted in the paramagnetic and ordered antiferromagnetic phases. Moreover, investigations of the NMR of free fluorine are convenient because typical relaxation times are in the range of tens of microseconds, so that they can be determined readily by standard pulse methods. Consequently, it is possible to observe the NMR of F_0 in a wide range of temperatures. The relaxation times and the line profile are determined by the local field, the intensity and spectrum of which reflects the magnetic state of the electron system.

The published NMR investigations of $Mn_xZn_{1-x}F_2$ compounds have been carried out using continuous-wave and pulse methods. However, in most cases this has been done at liquid nitrogen and room temperature. As already

mentioned, the magnetic properties of such systems have anomalies at temperatures close to T_N . In the case of MnF_2 the Néel temperature is 67 K. It decreases linearly when Zn is added and vanishes for $Mn_{0.2}Zn_{0.8}F_2$. Therefore, we carried out a detailed investigation of these compounds by the NMR method in a wide range of temperatures from 4.2 to 300 K using samples with values of x ranging from 0.7 to 0.1.

EXPERIMENTS

An earlier study³ of the relaxation of $^{19}F_0$ in dilute $Mn_xZn_{1-x}F_2$ antiferromagnets at 300 and 77 K showed that the transverse relaxation time of the F_0 nuclei is 10–100 μs , depending on the Zn concentration. Therefore, in investigations of the nuclear relaxation by the pulse NMR methods it is necessary to use a relaxometer with a recovery time of 10–20 μs creating probe pulses of several microseconds in duration. On the other hand, the abrupt change in the dynamics of the electron spins of Mn, linked to form an infinite magnetic cluster, on transition to the ordered phase should be manifested strikingly in the nuclear relaxation. The Néel temperature of $Mn_xZn_{1-x}F_2$ varied from 0 to 67 K when x was increased from 0.2 to 1, so that an NMR relaxometer should operate in a wide range of temperatures, from room to liquid helium.

It is known that the transition at T_N broadens strongly the resonance line,⁴ so that the range of static magnetic fields used in the determination of the line profile should amount to a few kilo-oersted.

We constructed a coherent pulse NMR relaxometer bearing in mind these requirements. The wide-band nature of the transmitter⁵ and receiver resulted in a "dead" time of 10 μs . The connections between the transmitter, working circuit, and receiver were similar to those described in Ref. 6 and are shown in Fig. 1. Signals to and from a working coil surrounding a sample in a cryostat passed along a coaxial line formed by two thin-walled stainless tubes with diameters 4 and 1 mm. The working coil with the sample was located inside two copper cans which were vacuum-insulated from one another and which could be filled with gaseous helium to provide thermal contact between the sample and the can walls. A heater, wound bifilarly on the inner can,

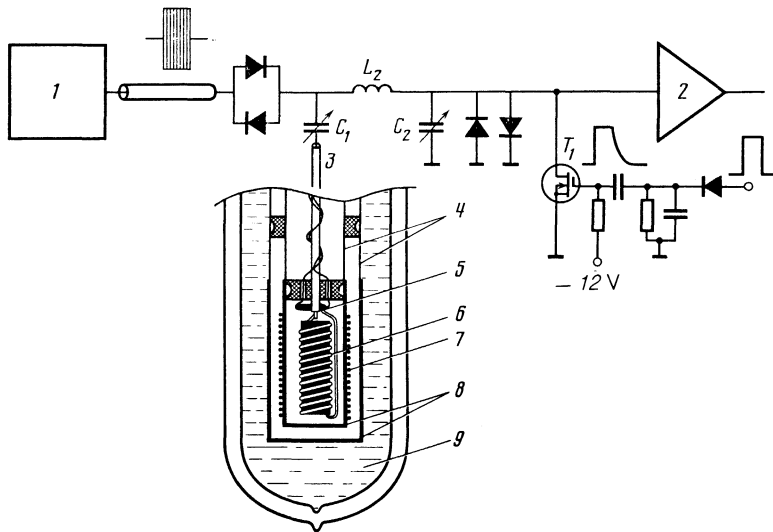


FIG. 1. Schematic representation of the connections between a transmitter and receiver and a working coil: 1) transmitter; 2) preamplifier; 3) low-temperature coaxial line; 4) stainless steel tubes; 5) semiconductor thermometer; 6) coil with samples; 7) heater; 8) copper cans; 9) liquid helium.

could increase the temperature from 4.2 to 300 K. The temperature of a sample was measured using a semiconductor thermometer and the errors were ± 0.1 K. The nuclear induction signal was first applied to a preamplifier,⁷ located on the cover of a Dewar flask, and was then passed to a direct-amplification receiver, a lock-in detector, and a V9-5 voltage converter. A static magnetic field was generated by a laboratory electromagnet⁸ and was varied linearly with time between 2 and 5 kOe. This field was stable to within $\sim 10^{-5}$.

The investigated polycrystalline samples were prepared in a platinum test tube which could be evacuated through a liquid nitrogen trap or filled with anhydrous HF (Ref. 9). At first powders of the fluorides MnF_2 and ZnF_2 were melted in a periodically replaced atmosphere (the test tube was alternately evacuated and filled with HF). This periodic change of the atmosphere ensured efficient desorption of moisture from the surface and thus ensured the purity of the original materials. The use of molten fluorides in the preparation of solid solutions of the required composition avoided the loss of the components during evacuation of the system and reduced the sorption surface of the fluorides. The composition of a sample was set by taking suitable proportions by weight. The weight of the initial components and the final samples agreed to within 0.5%.

RESULTS OF MEASUREMENT AND DISCUSSION

The fluoride MnF_2 is probably one of the most thoroughly investigated antiferromagnets. The NMR of ^{19}F in this compound was first obeyed by Shulman and Jaccarino back in 1957 (Ref. 10). They showed that the position of the resonance line and the nuclear relaxation time were governed primarily by a strong hyperfine interaction coupling the F nuclei with the three nearest magnetic Mn ions. In the paramagnetic phase, i.e., at temperatures $T > 67$ K, these hyperfine fields caused a shift of the NMR frequency (by $\sim 7\%$ at 77 K) and were responsible for the very short nuclear relaxation times, $T_1 \approx T_2 \approx 1 \mu\text{s}$. Transition to the ordered phase resulted in a large shift of the resonance frequency: at 4 K the resonance was observed at 160 MHz (Ref. 11).

The replacement of the magnetic Mn ions with the diamagnetic Zn in MnF_2 resulted first of all in the appearance of new resonances corresponding to the different magnetic environment of F. Our $\text{Mn}_x\text{Zn}_{1-x}\text{F}_2$ solid solutions contained F atoms without even one Mn in the first coordination sphere; they were represented by the unshifted NMR line F_0 . The fluorine atoms with the one, two, and three nearest magnetic neighbors should give rise to three additional lines: F_1 , F_2 , and F_3 . Such a splitting was indeed observed in the paramagnetic phase.³ Cooling of a sample below T_N should result, as in the case of MnF_2 , in a large shift of the resonances F_1 , F_2 , and F_3 , whereas the F_0 line should remain unshifted.

We determined the amplitude of the spin echo signal at 16 MHz when the external magnetic field was varied from 2 to 5 kOe. In the paramagnetic region we then observed only one symmetric line the width of which was determined mainly by the finite duration of the probe rf pulses. The lines corresponding to F_1 , F_2 , and F_3 were clearly characterized by relaxation times which were too short (this was due to the hyperfine fields) and were therefore not observed in our experiments. We plotted in Fig. 2 the measured values of the

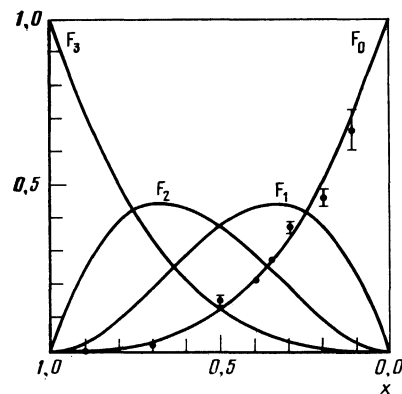


FIG. 2. Amplitude of the spin echo signal at 77 K reduced to $t = 0$ (●). The continuous curves represent the relative concentrations of F_0 , F_1 , F_2 , and F_3 . The experimental values are normalized to $x = 0.35$.

NMR signal intensity at 77 K as a function of the Mn concentration. The continuous lines in this figure are the dependences of the relative number of the free fluorine nuclei F_0 , and also of the nuclei F_1 , F_2 , and F_3 in the investigated compounds on the concentration of manganese. The results obtained represented effectively the concentration dependence of the intensity of the resonance due to free fluorine. At lower temperatures, the relaxation times of the F_1 , F_2 , and F_3 nuclei were not so short; we still did not observe any resonances apart from F_0 , but this was due to the large frequency shift mentioned above. Therefore, throughout the investigated temperature range from 300 to 4.2 K the observed NMR signal represented free fluorine.

The transverse relaxation time T_2 was deduced from the dependence of the spin echo amplitude on the delay between two probe pulses. At all temperatures above T_N and for all values of x the echo signal decayed exponentially:

$$M(t) = M(0) \exp(-2t/T_2), \quad (1)$$

where t is the time interval between the rf pulses.

The transverse relaxation of the F_0 nuclei in these compounds was due to the dipole interaction of these free nuclei with other free fluorines and with the fluorine nuclei coupled by the hyperfine fields to the Mn ions. The paramagnetic shift reduced considerably the contribution of the latter to T_2^{-1} and such a contribution was observed only at high Mn concentrations. The reduction in T_2 when x decreased was due to an increase in the concentration of the free fluorine nuclei. Since the nuclear dipole forces were independent of temperature, there was no significant change in T_2 as a result of cooling from 300 to 77 K. Some increase in T_2 (Fig. 3) observed on cooling was clearly due to an increase in the paramagnetic shift and a corresponding reduction in the contribution of the fluorine nuclei which had magnetic nearest neighbors. Similar results were obtained at 300 and 77 K by Yasuoka *et al.*¹² When a sample was cooled below T_N the resonance line was no longer symmetric and was greatly broadened, and the decay of the echo signal was no longer exponential, i.e., it was not described by Eq. (1), so that the transverse relaxation could not be represented by a definite value of T_2 .

The decay of the longitudinal magnetization of the F_0 nuclei was due to the fluctuating dipole magnetic fields of the second-nearest and further magnetic nuclei. The dynamics of the electron spins depended in turn on the magnetic environment of the spins, i.e., it varied depending on whether a given spin was part of an infinite magnetic cluster, a finite cluster, or was not exchange-coupled to other electron spins. Therefore, the value of T_1 for dilute antiferromagnets depend strongly on x and T .

The longitudinal relaxation on $Mn_xZn_{1-x}F_2$ at 300 K was studied using the free induction signal in the 180–90° sequence. At low temperatures a strong inhomogeneous broadening of the NMR line suppressed the free induction signal so that we determined T_1 by the usual three pulse method: we measured the amplitude of the echo depending on the time interval between a 180° pulse and two probe pulses.

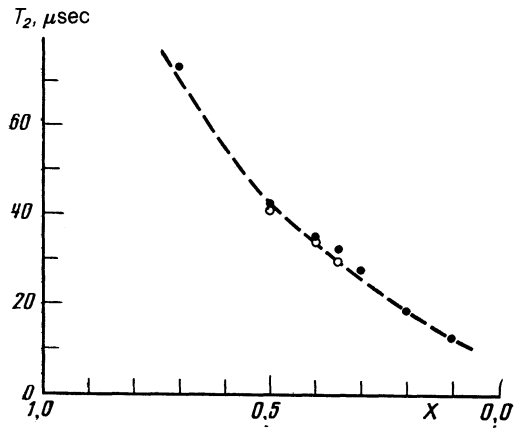


FIG. 3. Dependence of the transverse relaxation time on the concentration of Mn at $T = 300$ K (○) and 77 K (●).

In our experiments we found that at temperatures $T > T_N$ the decay of the longitudinal magnetization of F_0 in slightly dilute compounds, i.e., in the range $x \geq 0.4$, was practically exponential:

$$M(t) = M(\infty) [1 - 2 \exp(-t/T_1)]. \quad (2)$$

In the case of samples with a high Zn concentration we noticed a deviation from this law (Fig. 4). This behavior of $M(t)$ was recently investigated experimentally¹² and studied theoretically by Thayamballi and Hone.¹³ We shall now consider briefly the main results of this theory. The decay of the nuclear magnetization at a site r_i

$$P(r_i, t) = [M(r_i, \infty) - M(r_i, t)] / M(r_i, \infty) \quad (3)$$

is described by the expression

$$\partial P(r_i, t) / \partial t = -P(r_i, t) \sum_j T_1^{-1}(r_{ij}), \quad (4)$$

where $T_1^{-1}(r_{ij})$ is the rate of the nuclear relaxation resulting from the interaction with an electron spin at a site r_j . This expression is simplified by dropping the term corresponding to spin diffusion, because it becomes important only for $x < 0.1$. We can see that the magnetization at each nucleus r_i decays exponentially:

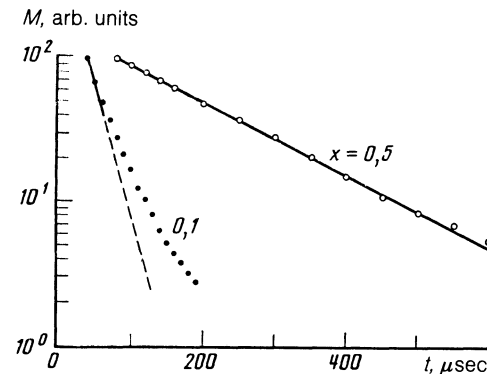


FIG. 4. Decay of the longitudinal nuclear magnetization at 77 K in $Mn_{0.1}Zn_{0.9}F_2$ (●) and $Mn_{0.5}Zn_{0.5}F_2$ (○).

$$P(r_i, t) = \exp\left(-t \sum_j T_1^{-1}(r_{ij})\right). \quad (5)$$

The total magnetization measured experimentally

$$P(t) = \sum_i P(r_i, t) \quad (6)$$

is the result of averaging over all the electron and nuclear configurations, which is the reason for the nonexponential decay. The main conclusion of the theory of Ref. 13 is that for $x \approx 1$, i.e., when almost all the magnetic ions combine to form an infinite magnetic cluster, the magnetization decay is exponential:

$$P(t) \approx \exp\left(-t \sum_j T_1^{-1}(r_j)\right). \quad (7)$$

If $x \approx 1$, i.e., when all the spins are exchange-isolated, the decay is nonexponential:

$$P(t) \approx \exp\left\{-x \sum_j (1 - \exp[-t/T_1(r_j)])\right\}. \quad (8)$$

If we assume that the relaxation of the isolated nuclei F_0 is due to the electron-nuclear dipole interaction and if we ignore its angular dependence, i.e., if we assume that

$$T_1^{-1} = \alpha/r^6, \quad (9)$$

we can find the exact expression for $P(t)$ if we replace summation with integration. It is found that for short times the decay of the magnetization is still exponential:

$$P(t) \approx \exp(-t/T_1), \quad (10)$$

whereas after longer times

$$P(t) \approx \exp[-(t/T_1)^n]. \quad (11)$$

It therefore follows that the observed nonexponential decay of the nuclear magnetization at low Mn concentrations is due to relaxation involving single paramagnetic ions and is in agreement with the theory of Ref. 3.

The values of T_1 we obtained for short times, i.e., when the magnetization decay was exponential, are plotted in Fig.

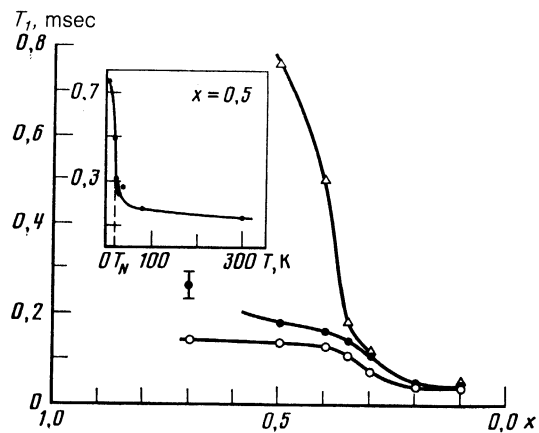


FIG. 5. Dependence of the longitudinal relaxation time T_1 on the concentration of Mn at $T = 300$ K (\circ), 77 K (\bullet), and 4.2 K (Δ). The inset shows the temperature dependence of T_1 for $Mn_{0.5}Zn_{0.5}F_2$.

5 for different values of x at temperatures 300 , 77 , and 4.2 K. We can see that at concentrations below the critical value $x_c = 0.2$, i.e., when the system did not have an infinite magnetic cluster, the relaxation time T_1 was indeed independent of temperature. In the range $x > x_c$, the value of T_1 increased as a result of cooling and a steep rise of T_1 occurred on transition to the ordered phase. In the temperature range from 300 to 77 K there was no change in the nature of the decay. However, below T_N the samples with high Mn concentrations exhibited not only a strong increase in T_1 , but also a considerable derivation from the exponential decay law. If the experimental results of $P(t)$ were approximated by the expression

$$P(t) = \exp[-(t/T_1)^n], \quad (12)$$

it was found (see Fig. 6) that at 300 K the power exponent was $n = 1$ for $Mn_{0.4}Zn_{0.6}F_2$. At 4.2 K the exponent was $n = 1$ during the initial period and $n = 0.64$ for longer times t . Such a strong temperature dependence of T_1 could be explained by allowing for two contributions to the longitudinal relaxation process: the relaxation involving exchange-isolated electron spins and that involving an infinite cluster. The

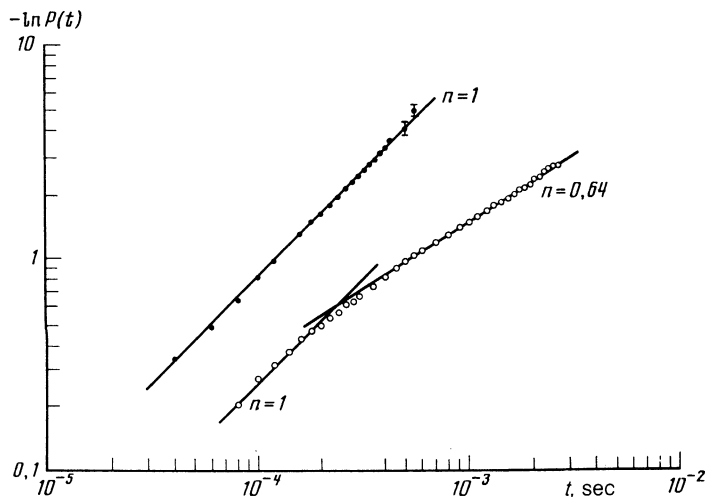


FIG. 6. Time dependences of the longitudinal magnetization of $Mn_{0.4}Zn_{0.6}F_2$ at $T = 300$ K (\bullet) and $T = 4.2$ K (\circ). The exponent n corresponds to the approximation of the curves in accordance with Eq. (12).

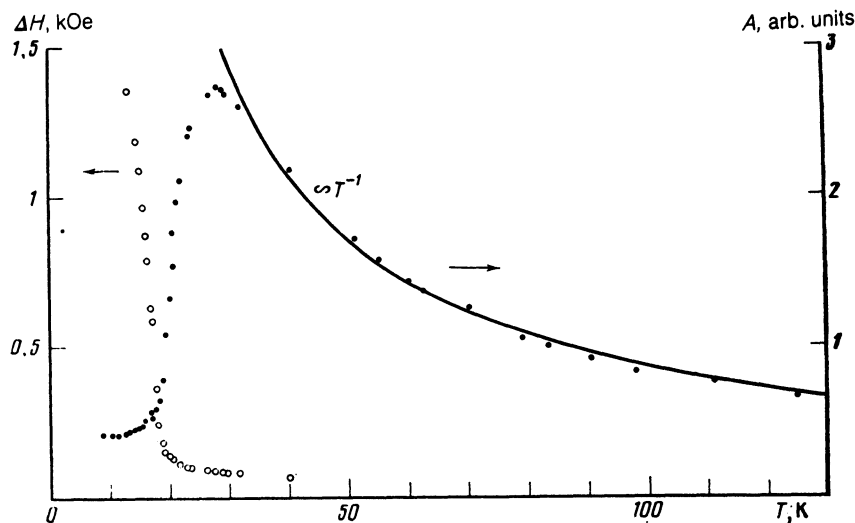


FIG. 7. Temperature dependences of the amplitude of the spin echo signal (●) and of the NMR line width at midamplitude (○) for $Mn_{0.4}Zn_{0.6}F_2$.

contribution of the exchange-isolated spins at temperatures $T \gg T_N$ is

$$T_1^{-1} \propto \omega_e^{-1} x(1-x)^8, \quad (13)$$

whereas the infinite cluster contributes

$$T_1^{-1} \propto \omega_e^{-1} x^{1/2}. \quad (14)$$

Since the exchange frequency ω_e is several orders of magnitude higher than ω_c (ω_c^{-1} is the characteristic decay time of the autocorrelation function of the exchange-isolated electron spins), it follows that for $x < 0.4$ the main contribution to the longitudinal relaxation comes from the isolated spins, whereas for $x > 0.4$ the relaxation is dominated by the infinite cluster.³ Cooling from 300 to 77 K creates a short-range order in the finite cluster and this reduces fluctuations of the electron dipole fields due to the exchange-coupled spins, and consequently, increases T_1 at high values of x . On the other hand, the relaxation of the isolated-electron spins is almost independent of temperature and, therefore, T corresponding to low values of x remains constant at all temperatures. The "freezing" of the electron spins exchange to form an infinite cluster at temperatures $T \rightarrow 0$ effectively excludes them from the nuclear relaxation process and this is why T_1 rises strongly on transition to the ordered phase. The relaxation then occurs because of the exchange-coupled spins, and,

therefore, the nuclear relaxation decay is nonexponential for longer times, as in the case of a very dilute antiferromagnet at temperatures $T > T_N$.

Figure 7 shows the measured values of the amplitude of the spin echo signal and of the line width at midamplitude obtained for $Mn_{0.4}Zn_{0.6}F_2$. Similar measurements were made for samples of all the concentrations. The line profile was determined by slow variation of the static magnetic field and plotted automatically. We can see from Fig. 7 that the echo signal amplitude increased in accordance with the Curie law as a result of cooling, since it was proportional to the nuclear susceptibility. At some temperature known to be higher than T_N there was a strong deviation from the T^{-1} law. The reason for this deviation was that the nuclear susceptibility increased simultaneously with an increase in the electron paramagnetic susceptibility and, consequently, the local field at the F_0 nuclei responsible for the inhomogeneous line broadening also increased. When the line width became greater than the rf field in the profile, the amplitude of the echo signal decreased, i.e., there was a deviation from the Curie law.

The appearance of the long-range order on transition to the antiferromagnetic phase strongly broadened the resonance line. This is manifested clearly in Fig. 8, which gives the measured values of the line width at half-maximum ob-

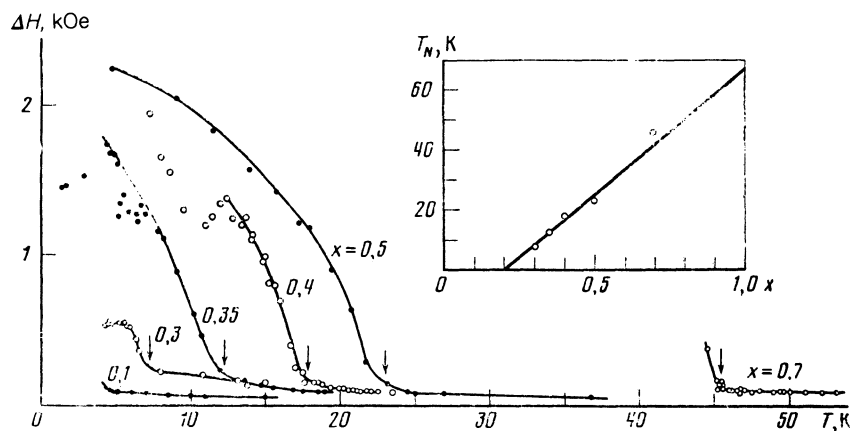


FIG. 8. Temperature dependences of the NMR line width plotted for different Mn concentrations. Here, T_N is the temperature at which a strong broadening of the NMR line begins (identified by an arrow). The inset shows a comparison of the values of T_N obtained in this way with the predictions of the theory of Ref. 14 (continuous line).

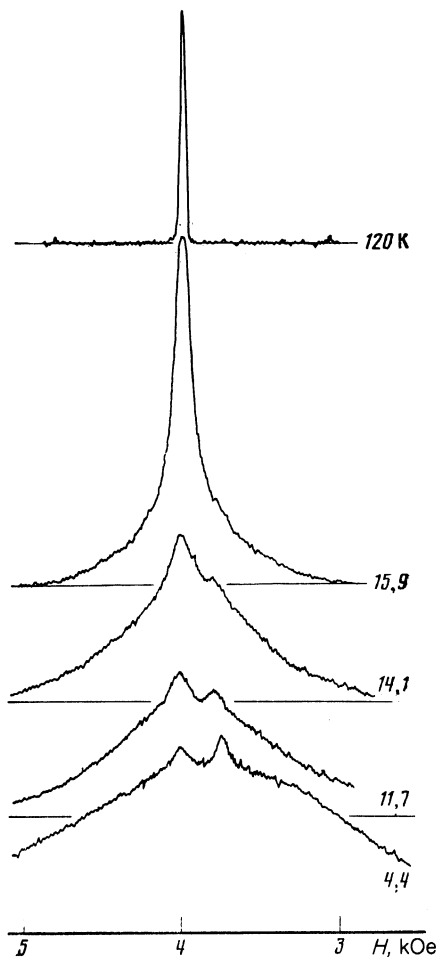


FIG. 9. Profile of the NMR line of $\text{Mn}_{0.4}\text{Zn}_{0.6}\text{F}_2$ at various temperatures.

tained for different values of x , where the arrows identify the postulated values of T_N . These values are shown in the inset and the straight line represents a calculation for the $\text{Mn}_x\text{Zn}_{1-x}\text{F}_2$ system.¹⁴

Cooling of a sample below T_N resulted in a nonmonotonic variation of the line width, as shown in Fig. 8 for $x = 0.4$ and 0.35 . This unusual behavior of the line width was due to a change in the line profile, as demonstrated clearly in Fig. 9. Below T_N the line became asymmetric and split. This NMR line profile could be explained qualitatively as follows. Cooling increased the local magnetization in the direction of the external field so that the field at the F_0 nuclei, equal to the sum of the external field H_0 and the local field H_{loc} due to the Mn ions in the second and third coordination spheres, increased on the average and the center of gravity of the line shifted toward lower values of H_0 .

The observed splitting of the NMR line could not be due to the contribution of the F_1 , F_2 , or F_3 nuclei because the resonance frequency shift caused by the hyperfine interaction was much greater.¹¹ Therefore, it was due to the dipole interaction of the fluorine nuclei F_0 with the magnetic Mn ions in, for example, the second coordination sphere. The amplitude of this field should depend on temperature and its order of magnitude should be

$$H_{\text{loc}} \approx \langle \mu \rangle / r^3. \quad (15)$$

The average magnetic moment $\langle \mu \rangle$ depended on whether a given ion belonged to an infinite ordered cluster or a finite cluster, or whether it was an isolated paramagnetic spin. In the former case at temperatures $T \ll T_n$, the average magnetic moment should be

$$\langle \mu \rangle \approx g\mu_B [S(S+1)]^{1/2}. \quad (16)$$

In the case of an isolated paramagnetic moment, we should have

$$\langle \mu \rangle = \frac{g^2 \mu_B^2 S(S+1) H_0}{3kT}. \quad (17)$$

The local field at the fluorine nuclei created by the electron moment located in the second coordination sphere should, at $T = 4.2$ K and for $H_0 = 4$ kOe, amount to 0.9 and 0.1 kOe, respectively. The magnetic field of the spins belonging to a finite cluster would obviously have an intermediate value. We can see from Fig. 9 that the splitting at $T = 4.2$ K was approximately 0.2 kOe, which agreed in order of magnitude with the above estimate. However, in view of this indeterminacy one could not say which configuration of the electron moment did result in the observed splitting. The splitting of the F_0 line at temperatures $T < T_N$ was significant for all values of x , but it was exhibited particularly clearly for $x = 0.4$.

CONCLUSIONS

We investigated experimentally the NMR of free fluorine in dilute $\text{Mn}_x\text{Zn}_{1-x}\text{F}_2$ antiferromagnets over a wide range of temperatures from 4.2 to 300 K using samples with the Mn concentrations from 0.1 to 0.7. Measurements of the longitudinal and transverse relaxation times and of the resonance line profile made it possible to identify the contributions made by different types of Mn ions, the exchange-isolated ions and those belonging to an infinite cluster. This was manifested particularly clearly at low temperatures. Our experiments showed that the longitudinal relaxation in samples with values of x below the percolation limit was independent of temperature and nonexponential, and was due to fluctuating dipole fields generated by exchange-isolated paramagnetic Mn ions. The longitudinal relaxation in samples with high values of x at temperatures $T > T_N$ was due to the dipole interaction of the F_0 nuclei with an infinite magnetic cluster and the nuclear magnetization decayed exponentially. At temperatures $T < T_N$ the nuclear relaxation involved exchange-isolated paramagnetic spins and was of the same nonexponential nature as in the case of strongly dilute antiferromagnets. The longitudinal relaxation time rose steeply when antiferromagnetic long-range order appeared.

The width of the NMR line caused by the scatter of the local dipole fields increased strongly as a result of cooling below T_N . The line became asymmetric and manifested clearly the appearance of another resonance due to the dipole fields of the Mn ions located in the second coordination sphere.

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