Low-frequency noise in magnetic materials near the ordering temperature

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A SQUID magnetometer was used to measure zero-field magnetic noise in two- and three-dimensional magnetic materials [$MnSO_4$, $Mn_{0.28}Zn_{0.72}F_2$, K_2CuF_4, $(CH_3NH_3)_2 \cdot CuCl_4$, $Co(HCOO)_2 \cdot 2H_2O$] at frequencies in the range 0.01–10 Hz. A maximum of magnetic fluctuations, ≈ 0.3 K wide, was found in the region of the ordering temperature. In the case of the two-dimensional Heisenberg ferromagnets it was shifted toward higher temperatures relative to T_c and the magnetic moments in these ferromagnets were ordered in a plane. The rotation of spins to a plane occurred at various temperatures. The mean-square spectral power of the fluctuations obeyed closely the $1/f$ law and in some cases there was a large contribution from a uniform Nyquist noise.

INTRODUCTION

An equilibrium electrical noise due to fluctuations of the density of conduction electrons was discovered by Johnson[1] over sixty years ago in 1928. This was followed by a very general formulation of a fluctuation–dissipation theorem which states in particular that all real systems should exhibit also a magnetic noise. However, it is much more difficult to detect magnetic noise. This follows from simple calculations.[2] Let us assume that a measuring coil with an inductance L is filled completely with a material whose susceptibility is $\chi = \chi' - i\chi''$ and which is at a temperature T. Its impedance at the frequency ω is

$$Z = i\omega L(1+4\pi\chi). \tag{1}$$

The imaginary part χ'' of the susceptibility gives rise to a resistive part of the impedance

$$R = 4\pi\chi'' L\omega, \tag{2}$$

which, in accordance with the Nyquist theorem, creates the mean-square fluctuations of the voltage

$$\langle V^2 \rangle = 4kTR\Delta f. \tag{3}$$

The imaginary part of the susceptibility may be related to the static susceptibility $\chi(0)$ by introducing a relaxation time τ:

$$\chi'' = \chi(0)\,\omega\tau/(1+\omega^2\tau^2). \tag{4}$$

Substituting the reasonable values $\tau = 10^{-12}$ s, $\chi(0) = 0.1$, $L = 1\,\mu$H, and $f = 1$ Hz into Eqs. (2) and (4), we find that $R = 10^{-18}\ \Omega$. We can see immediately that at low frequencies it is much more difficult to record a magnetic noise than a corresponding electrical noise. We are speaking here of an equilibrium noise. In the case of a nonequilibrium process, particularly on application of an external field, magnetic fluctuations are many orders of magnitude stronger and they represent what is known as the Barkhausen noise.

It therefore follows that direct observation of an equilibrium magnetic noise is a very difficult experimental task and has in practice not been attempted. The frequency dependence of the relaxation time was deduced only from measurements of the ac susceptibility (usually between 10 Hz and 100 kHz) and from the thermomagnetic magnetization during cooling in a magnetic field (field cooling—FC) and in the absence of a field (zero-field cooling—ZFC).

Relaxation of the spins in ferromagnets lies in the gigahertz range and the associated noise is observed in ferrites.[3] The process of dipole relaxation in ferroelectrics is observed in the same frequency range.[4] However, the losses in ferromagnetic materials and the corresponding fluctuations are often manifested also at much lower frequencies because of the presence of defects in real crystals. Defects in ferromagnets pin domain walls to local energy minima and thermal fluctuations can induce activated motion of these walls. In conducting magnetic materials a local stochastic magnetic field causing vibrations of a domain wall may be induced by thermal motion of conduction electrons. The statistics of such thermal activated "jumps" of domain walls determines the spectral composition of the observed noise and describes satisfactorily the experimental results obtained for magnetically soft materials.[5]

Back in 1946 Bloch published his classical work on nuclear induction and showed that even in the absence of an external rf field a sample with N spins characterized by a magnetic moment μ induces a very weak fluctuation voltage in an induction coil and this voltage is proportional to $\mu N^{1/2}$. Almost 40 years later, in 1986, these temperature-independent fluctuations were observed by Hahn and his colleagues[6] for the ^{35}Cl nuclei in $NaClO_3$ at the frequency of a nuclear quadrupole resonance amounting to 30 MHz. A sample was placed in a superconducting induction coil which was part of an LCR circuit, and the induction currents were measured with a SQUID magnetometer. The resistive part of the circuit created the Nyquist noise; the spectrum of this noise had a Lorentzian profile because of the frequency properties of the resonance circuit, whereas the presence of the sample distorted this profile in the region of a nuclear quadrupole resonance: the frequency shifted because of the contribution of χ', and the noise power increased because of χ''.

In 1985 Ocio *et al.*[2] discovered, once again using the SQUID measurement technique, that the $1/f$ noise appeared in spin glasses. These experiments provided a direct proof of the theoretical models[7] based on nonequilibrium properties of these systems.

It follows from general considerations that fluctuations of the magnetization should increase strongly at a critical point where two tendencies compete: the ordering "energy" effects and the disordering "entropy" effects. The question of the magnitude of this noise enhancement at the phase

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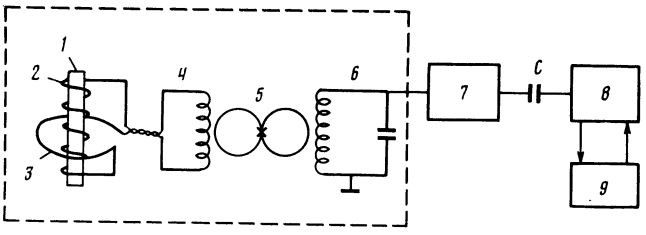

FIG. 1. Block diagram of the flux meter: 1) sample; 2) receiving coil of the flux transformer; 3) compensating coil in the superconducting magnetic flux transformer; 4) signal coil; 5) SQUID sensitive element; 6) hf circuit of the SQUID; 7) electronic unit of the SQUID; 8) digital voltmeter with an input resistance of 10^8 Ω; 9) DVK-3 computer. The components enclosed by the dashed box were located directly in the cryostat and kept at liquid helium temperature.

transition point in a real system and the width of the relevant region on the temperature scale have yet to be tackled. We used these general considerations in a direct experimental study of magnetic fluctuations in magnetic materials near the ordering temperature. The results are reported below. The preliminary announcement of the results obtained in a determination of fluctuations in the two-dimensional ferromagnet $(CH_3NH_3)_3 \cdot CuCl_4$ were published in Ref. 8.

APPARATUS

Figure 1 shows the basic layout used in measurements of spontaneous equilibrium fluctuations of the magnetization (magnetic noise). A sample was in a receiving part of a superconducting magnetic flux transformer, which was part of a differential system of coaxial coils. Any change in the magnetization of this sample altered the flux through the receiving system of the superconducting transformer, i.e., it gave rise to a current in its circuit. This current flowed through a signal coil and induced a magnetic flux in a sensitive component (SQUID) of a flux meter and this flux was converted by the SQUID electronics of the flux-blocking type into a feedback voltage V. Therefore, information on fluctuations of the spontaneous magnetization of the sample with time $M(t)$ was converted into a time-dependent voltage $V(t)$, which was measured with a digital voltmeter of the Shch-300 type (integrating voltmeter with an integration time of 20 ms for the input capacitance), controlled by a DVK-3 computer. The dc component of $V(t)$ was filtered off by a large-capacitance (20-μF) coupling capacitor C. The frequency characteristic of the flux meter was constant in the range 0.01–20 Hz.

The voltmeter readings were recorded at a frequency of 20 Hz and stored in the computer over a period of $\tau = 100$ s (in this time the computer memory accumulated 2048 readings). In view of the continuous variation of the feedback voltage, $V(t)$ was converted into a discrete series of values $V(t_k) = V_k$. At each temperature a total of 10 measurement cycles was carried out. The results obtained were then used to find the coefficients A_j and B_j in the Fourier expansion; the average values of these coefficients were obtained for 10 realizations and their variance was found. The unipolar spectral density of the feedback voltage

$$N^V(f_j) = [\tau(\overline{A_j^2 + B_j^2})/2]^{1/2} \qquad (5)$$

was converted, using the experimentally established relationship between the flux and the voltage, into the spectral density of the noise flux $N(f_j)$ in the SQUID aperture. The spectral density could be used to calculate the mean-square power of the magnetic fluctuations

$$S(f_j) = N^2(f_j)/(2L_{\text{eff}} K^2), \qquad (6)$$

where L_{eff} is the SQUID inductance in the presence of a superconducting magnetic flux transformer and K is the coefficient of coupling between the SQUID and the signal coil of the flux transformer. In our experiments the noise level in the empty system was $1.5 \times 10^{-4} \Phi_0$ Hz$^{-1/2}$ at the frequency of 1 Hz (here, Φ_0 is a magnetic flux quantum), corresponding to an energy resolution of 3×10^{-28} J/Hz. These values were obtained for the flux in the SQUID aperture.

We used a niobium symmetric SQUID with a point contact of the Zimmerman type; the SQUID inductance amounted to 5.9×10^{-10} H. The SQUID together with the components of the oscillatory circuit were mounted rigidly in a brass holder to which a low-temperature 50-Ω coaxial line was soldered; this line provided coupling to an electronic circuit. The coaxial line consisted of two thin-walled tubes (with internal diameters 7 and 1 mm) made of stainless steel and separated by insulating Teflon guides. The electrical conductivity was improved by silvering the inner tube; the hf coil in the oscillatory circuit consisted of a copper wire 0.15 mm in diameter wound on a polyethylene core.

The geometric parameters of the flux transformer were selected to ensure the maximum sensitivity of the apparatus, i.e., the maximum value of the signal/noise ratio.[9] The maximum-sensitivity condition was practically identical with the condition for the maximum flux transfer by the transformer in which the signal coil inductance should be equal to the inductance of the receiving coil. The mutual inductance M between the signal coil and the SQUID should also be maximal, i.e., the degree of overlap of the fluxes in the SQUID and signal coil apertures should be maximal and equal to the ratio of the squares of the diameters of these apertures. In our case this ratio was 0.7.

As pointed out already, we used a superconducting magnetic flux transformer and the coaxial type. The compensating coil was coaxial with the receiving coil and both were wound on quartz tubes with diameters 18.6 and 6.2 mm and consisted of 1 and 7 turns, respectively. The signal coil consisted of 50 turns wound on a polyethylene tube with a diameter of 1.4 mm. The whole superconducting magnetic flux transformer was a monolithic unit in order to avoid a vibration noise. The windings of the superconducting transformer were lead wires 0.3 mm in diameter coated by a BF-6 adhesive acting as an insulator. The calculated flux transfer coefficient was 0.018.

Low-temperature part of the flux meter. In normal operation of the flux meter and in the course of precision measurements it was necessary to ensure that the flux meter was properly protected from external alternating and constant magnetic fields. The external magnetic fields were attenuated first of all by a two-layer screen made of Permalloy annealed in hydrogen and located outside a glass liquid-nitrogen Dewar. The helium Dewar had an additional lead superconducting screen inside of which there was an evacuated copper jacket sealed with indium and containing a low-temperature unit (Fig. 2). This unit was connected to a cap

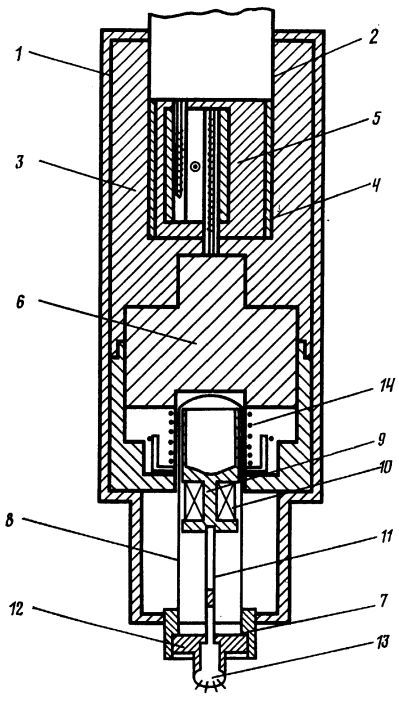

FIG. 2. Construction of the low-temperature unit: 1) copper can; 2) thin-walled tube 16 mm in diameter made of stainless steel; 3), 4) superconducting lead screen; 5) SQUID holder; 6) Teflon holder in the superconducting magnetic flux transformer; 7) platinum tube; 8) test tube; 9) heat conductor; 10) heater; 11) support; 12) flange; 13) bead; 14) receiving coil of the superconducting magnetic flux transformer.

by a thin-walled stainless steel tube 2 to which a copper can 1 was soldered. A copper heat sink linked this can to a helium bath. A third cylindrical lead screen was placed so as to fit tightly inside the can (the tight fitting was needed to avoid mechanical displacements). A niobium SQUID was placed in the upper part of the stainless steel tube so that its aperture for the signal coil was located on the axis of the system. The signal coil was attached to the upper part of a Teflon insert 6, in the lower part of which was bonded a thin quartz tube on which the receiving coil 14 of the superconducting magnetic flux transformer was wound.

The lower part of the can 1 carried a soldered platinum tube 7 whose open end was facing downward and bonded to a test tube 8 made a chemical glass with a wall thickness of 0.15 mm. A copper holder with a sample was introduced from below into this test tube in the same way as was done by Khlyustikov.[10] The upper part of the holder was a hollow cylinder 10-mm long with an internal diameter 5 mm and a wall 0.3 mm thick. The cylinder had 10 narrow longitudinal cuts which prevented the onset of vortex currents whose magnetic field coincided with the receiving coil axis. The lower part of the holder carried a bifilarly wound heater which was impregnated with an epoxy resin. The power was supplied to the heater from small batteries in order to avoid any additional strays in the flux meter. The holder of the sample was attached to the can by a thin stainless steel tube 11 with a wooden rod in its middle in order to increase the thermal resistance.

The temperatures were measured with a thermocouple made of copper and thermocouple-grade gold. The warm junction of the thermocouple was soldered to the copper

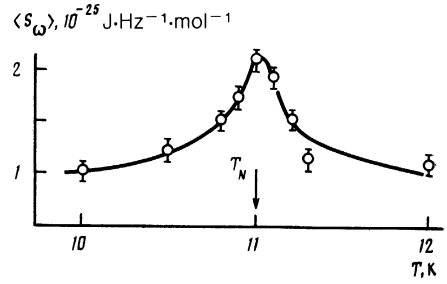

FIG. 3. Temperature dependence of the mean-square power of magnetic fluctuations in $MnSO_4$, averaged over the frequency interval 0.01–10 Hz.

holder of the sample, whereas the cold end was soldered to a flange 12 which was kept at liquid helium temperatures.

The sample holder was thermally insulated by high vacuum which was established in the test tube when atmospheric air in it was frozen out. Hermetic sealing of the test tube took place after inserting the sample: the flange 12 together with the holder well sealed with a low-melting-point solder. Leads supplying the power to the heater and the thermocouple leads were introduced into the high-vacuum part of the system through an epoxy resin bead. The temperature in the low-temperature unit was determined to within 0.01 K, which was the change in the temperature during an experiment.

EXPERIMENTAL RESULTS

Our experimental results were in the form of the spectral density of the fluctuations N_ω and of the mean-square power of the fluctuations S_ω calculated from the spectral density. All the results were obtained for fluctuations of the flux within the SQUID aperture and they were normalized to 1 mole of the material. No corrections for the shape of a sample and its coupling to the receiving coil of the superconducting magnetic flux transformer were made because of ambiguities in the correction procedure. The samples were made of ferromagnetic and antiferromagnetic substances with different magnetic structures.

$MnSO_4$. Anhydrous manganese sulfate is an antiferromagnet with the orthorhombic crystal structure and its three-dimensional magnetic structure is a helicoid with a period of 30 Å; the Néel temperature is $T_N = 11$ K. Our experiments were carried out on a polycrystalline sample with a mass of about 150 mg. We determined the temperature dependence of the mean-square power of magnetic fluctuations in this substance (Fig. 3) averaged over the investigated frequency range 0.01–10 Hz. The fluctuation maximum corresponded to the Néel temperature for $MnSO_4$ and the spectral density of the fluctuations resembled the $1/f$ dependence.

$Co(HCOO)_2 \cdot 2H_2O$. The crystal structure of this compound is monoclinic and the lattice parameters are $a = 8.6$ Å, $b = 7.06$ Å, and $c = 9.2$ Å. The magnetic Co^{2+} ions in the (100) plane, known as the A plane, are coupled by a strong antiferromagnetic exchange interaction characterized by $J_{AA} = 4.3$ K. The magnetic ions in the (200) plane, known as the B plane, are not coupled to one another and behave as paramagnetic ions, but they are coupled to the ions in the next plane by an exchange interaction with $J_{AB} = 0.6$ K. It therefore follows that the system is similar to a sandwich of paramagnetic ions enclosed between planes with the

antiferromagnetic ordering.[11] The phase transition at $T_N = 5.1$ K in $Co(HCOO)_2 \cdot 2H_2O$ is due to an Ising anisotropy of the intraplane interaction J_{AA} between the Co^{2+} ions in the A plane. This compound has a strongly anisotropic g factor, characterized by the ratio $g_\parallel / g_\perp \approx 3$,[12] so that its magnetic properties correspond to the Ising model with $d = 2$.

Our sample of this compound was a polycrystalline powder which was used to fill the copper cylinder in the holder. The noise spectrum of this compound was predominantly of the Nyquist nature, although a slight increase in the noise was observed at very low frequencies ($f < 0.1$ Hz). As in the case of $MnSO_4$, the fluctuation maximum was observed at the Néel point.

$(CH_3NH_3)_2 \cdot CuCl_4$. This compound is a typical ferromagnet with the easy-plane anisotropy.[13,14] Crystals of this compound go over to the monoclinic structure at $T < 250$ K and the angle of this structure is 92°; it consists of $CuCl_4$ layers separated by two CH_3NH_3 layers.[15] The ferromagnetic exchange interaction between the magnetic Cu^{2+} ions ($s = 1/2$) in a layer is almost of the Heisenberg nature with $J = 19.6$ K and the weak ($\sim 1\%$) anisotropy of this exchange tends to align the spins in the basal plane. This easy-plane anisotropy has the effect that at low temperatures the compound $(CH_3NH_3)_2 \cdot CuCl_4$ behaves as a two-dimensional XY ferromagnet. A very weak uniaxial planar anisotropy and a weak exchange between the spins in the neighboring planes give rise to the ferromagnetic order which appears at $T_c = 8.9$ K. The anisotropy of the g factor is characterized by $g_\parallel / g_\perp = 1.06$ ($g_\parallel$ is aligned along the c axis and $g_\perp$ corresponds to the plane). The phase diagram of this ferromagnet has been investigated in detail.[16]

Our single crystals were thin $4 \times 5 \times 0.15$ mm platelets. We carried out two series of experiments: 1) the (100) planes of the crystals were parallel to the receiving coil axis and in this case the projection of the magnetic moment $M_\parallel$ onto the (100) plane was recorded preferentially; 2) the (100) plane was perpendicular to the receiving coil axis so that the axial component of the magnetic moment $M_\perp$ was recorded preferentially. The total mass of our crystals was 8 mg.

1)$M_\parallel$. As already mentioned, in this case the crystal plates were placed inside the copper cylindrical holder parallel to its axis. Figure 4 shows the temperature dependence of the mean-square power of the fluctuations, averaged over the frequency range 0.01–10 Hz. We can see immediately a shift of the maximum of the fluctuations away from T_c by 0.4 K toward higher temperatures. We checked that this shift was not due to a temperature gradient between the holder and the crystals in an experiment in which the upper part of the cylindrical copper holder was covered by a copper cap. This ensured a thermal equilibrium inside the holder. The results confirmed that the maximum was shifted along the temperature scale. The absolute value of S_ω then decreased by two orders of magnitude because of the screening of the magnetic fields by copper. There could be doubts about calibration of the thermocouple, but the exact coincidence of the transition temperature with the maxima of fluctuations in the case of $MnSO_4$ and $Co(HCOO)_2 \cdot 2H_2O$ demonstrated the correctness of the calibration process. A possible reason for the anomaly (Fig. 4) will be considered later in a discussion of the results.

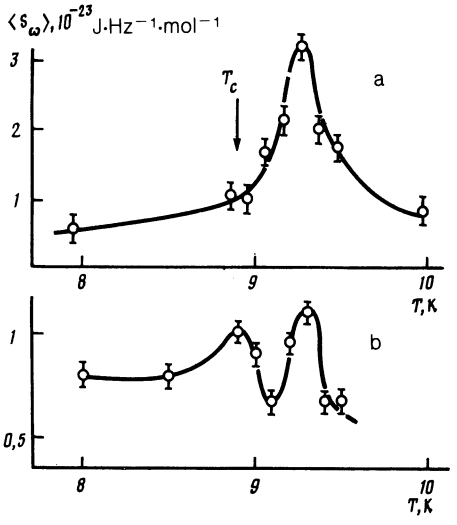

FIG. 4. a) Mean-square power of fluctuations of $M_\parallel$ parallel to the (100) plane component of the magnetic moment in a sample of $(CH_3NH_3)_2 \cdot CuCl_4$, averaged over the frequency interval 0.01–10 Hz. b) Same power but for $M_\perp$ when the (100) plane in crystals was perpendicular to the axis of the receiving coil of the superconducting magnetic flux transformer.

The frequency dependence of the mean-square power of the fluctuations observed at 9.3 K is plotted in Fig. 5. We can see that the noise spectrum of this compound was basically of the Nyquist nature.

2)$M_\perp$. The temperature dependence of the power of transverse fluctuations (Fig. 4b) exhibited unexpectedly two maxima: one at the transition temperature and the other at the maximum of $M_\parallel$.

K_2CuF_4. The interest in this compound has appeared because of the anomalies exhibited by $(CH_3NH_3)_2 \cdot CuCl_4$. Crystals of K_2CuF_4 could also be regarded quite accurately as two-dimensional ferromagnets with the easy-plane anisotropy. The properties of this compound were described in detail in Ref. 17. The dimensions of our crystal were $2.5 \times 1.3 \times 0.8$ mm. As in the preceding case, we determined $M_\parallel$ and $M_\perp$. The mean-square spectral power of the fluctuations practically followed the $1/f$ law (Fig. 5). We again observed a shift of the maximum of the $M_\parallel$ fluctuations toward higher temperatures relative to T_c, but it was not so clear and amounted to just 0.1–0.2 K (Fig. 6). We also plotted in Fig. 6 the results of measurements of the fluctuations of $M_\perp$; once again the fluctuations of $M_\perp$ exhibited two maxima.

$Mn_{0.28}Zn_{0.72}F_2$. The last decade has seen a major increase in interest in dilute antiferromagnets of the $M_xZn_{1-x}F_2$ type, where M = Mn, Fe, or Co. This is due to the fact that such systems do not have the translational symmetry properties and the question of the possibility and nature of the order–disorder transition in these systems is of fundamental importance. We selected MnF_2 diluted with Zn because its properties had been investigated in detail already.[18–21] As already mentioned, in the case of spin glasses we could expect a typical $1/f$ dependence of the mean-square power of the fluctuations. We found that in $Mn_xZn_{1-x}F_2$ compounds with the Mn ion concentrations close to critical the temperature and frequency dependences of the magnetic susceptibility exhibited a number of singularities in the vi-

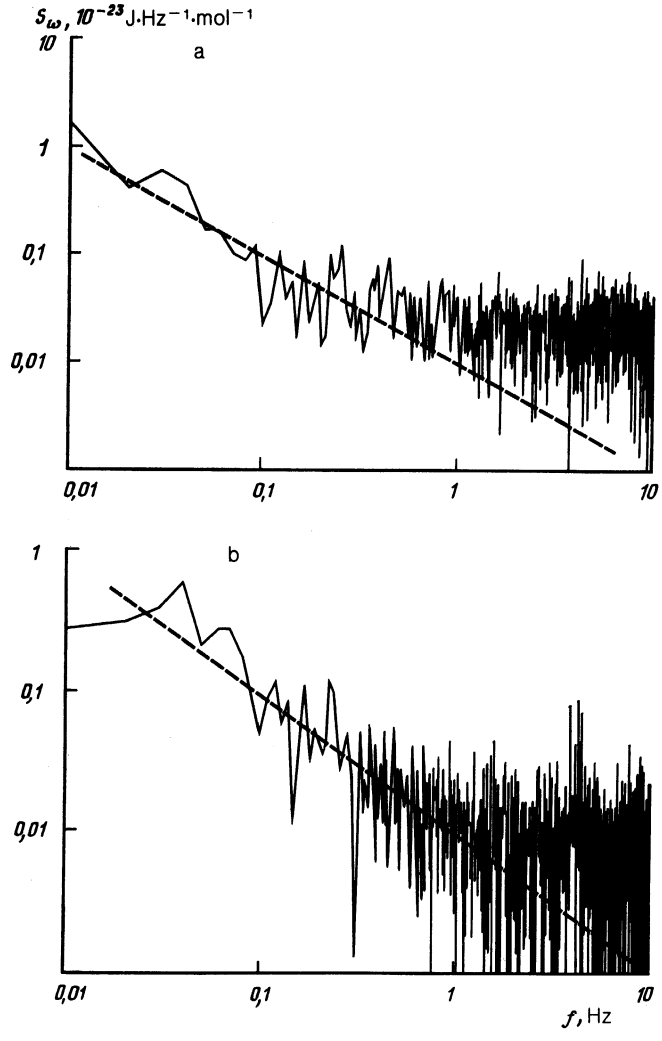

FIG. 5. Frequency dependence of the mean-square power of fluctuations of $M_\parallel$ in $(CH_3NH_3)_2$·$CuCl_4$ at 9.3 K (a) and in K_2CuF_4 at 6.3 K (b). The dashed line represents the $1/f$ dependence.

cinity of the ordering temperature.[19] It was not clear whether these results indicated the presence of the spin glass state.

We investigated a polycrystalline sample of $Mn_{0.28}Zn_{0.72}F_2$, i.e., the dilution of the sample was close to the percolation threshold. According to NMR measurements, the Néel temperature of this compound was 7.1 K. We plotted in Fig. 7 the temperature dependences of the mean-square power of the fluctuations averaged over the frequency ranges 0.01–0.1 and 1–10 Hz. The nature of these dependences varied; in the range 1–10 Hz we observed, as before, a clear maximum at $T = T_N$, whereas at ultra-low frequencies we found that cooling enhanced the fluctuations near T_N, which then became constant right down to $T \approx 6$ K. The noise spectrum observed at 7.1 and 6.5 K is reproduced in Fig. 8. At $T = 7.1$ K the $1/f$ part of the noise extended approximately to just 0.1 Hz and at higher frequencies the value of S_ω became constant, whereas at 6.5 K the $1/f$ noise range was at least an order of magnitude wider extending right up to 1 Hz.

DISCUSSION OF RESULTS

a) Frequency dependence of the mean-square power of fluctuations

The frequency dependence of the mean-square power of fluctuations in all our samples was to a greater or lesser extent similar to the $1/f$ noise. As is well known, the $1/f$ noise is observed in a very wide range of objects: it represents the current noise of conductors and the spectrum of fluctuations associated with the response to external excitation of real disordered systems.[22] Therefore, observation of the $1/f$ fluctuations in magnetic materials is not surprising. The general origin of this noise in a great variety of systems is postulated to be an exponentially wide distribution of relaxation times of the fluctuating parameter. The fluctuation–dissipation theorem provides the direct relation between fluctuations and relaxation processes. An exponentially wide range of relaxation times is usually attributed to microscopic local defects, but a uniform distribution of the activation energies

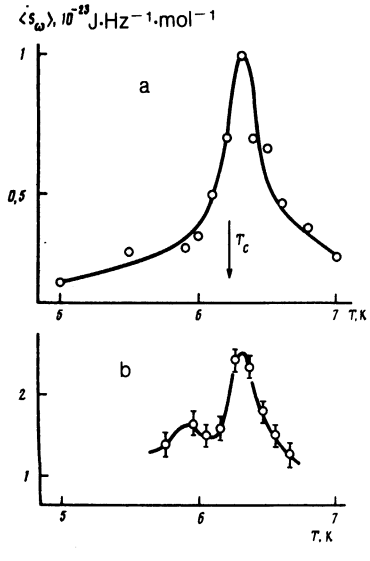

FIG. 6. Mean-square power of fluctuations of $M_\parallel$ (a) and $M_\perp$ (b) in a crystal of K_2CuF_4 averaged over the frequency interval 0.01–10 Hz.

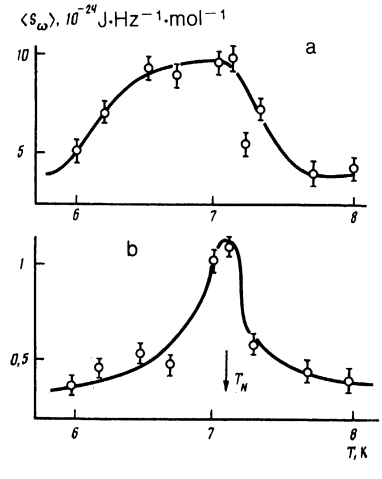

FIG. 7. Temperature dependence of the mean-square power of magnetic fluctuations in $Mn_{0.28}Zn_{0.72}F_2$ averaged over the frequency intervals 0.01–0.1 Hz (a) and 1–10 Hz (b).

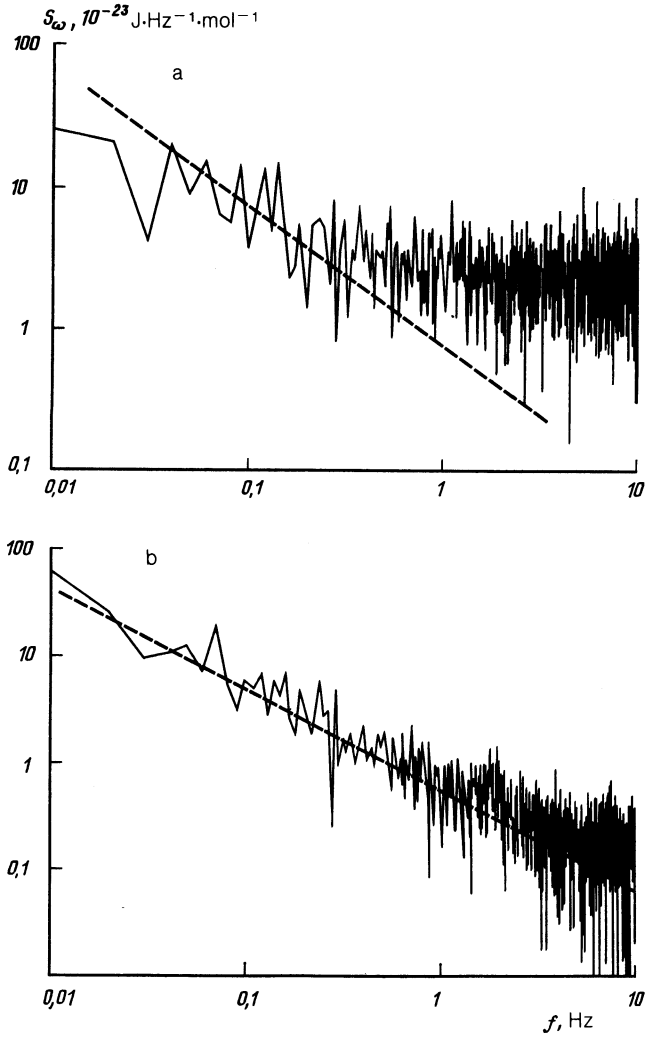

FIG. 8. Spectrum of the magnetic noise in an antiferromagnet of the $Mn_{0.28}Zn_{0.72}F_2$ composition at temperatures 7.1 K (a) and 6.5 K (b).

has to be ensured. It is this that causes difficulties in the interpretation of specific experiments. As pointed out already, this has been confirmed experimentally for spin spectra and the discovery of the $1/f$ noise in these glasses is a confirmation of the theoretical predictions.

The exponentially wide range of relaxation times appears also in models which include extended defects, such as dislocations, grain and phase boundaries, and domain walls in magnetic materials.[23] The crux of the matter is that extended defects have a large number of interacting degrees of freedom and they interact with randomly distributed local defects and with one another.

There have been several experimental investigations demonstrating the existence of 1f vibrations in magnetic materials. As a rule, it is assumed that they are due to an inhomogeneity of the ordered structure. The temperature and frequency dependences of the susceptibility of $Co(HCOO)_2 \cdot 2H_2O$ were reported in Ref. 24. At frequencies below 1 MHz it was found in Ref. 24 that a new low-frequency mode appeared near T_N; the amplitude of this mode was maximal near T_N and then fell as a result of cooling. Throughout the investigated temperature range the contribution of this 1f mode increased on reduction in the frequency. In the range 1.5–60 MHz this mode had a resonance near T_N. This was attributed in Ref. 24 to splitting of the investigated system into a large number of weakly coupled subsystems, so that the hf mode represented vibrations in the subsystems where the long-range order was established, whereas fluctuations between the weakly coupled subsystems was responsible for the 1f dispersion mode, but as a result of cooling below T_N the bonds became frozen and the amplitude of these vibrations decreased.

The real and imaginary parts of the magnetic susceptibility were determined[25] in the frequency range 0.0005–10 Hz for $CoCl_2$ intercalated in graphite. This substance provided a good model of an XY ferromagnet with a triangular structure. However, the structure of this system was quite special: many two-dimensional clusters of finite dimensions (islands) formed in the $CoCl_2$ planes. Therefore, the transition of this system to the ordered phase was of two-stage nature: first to be ordered were the islands and they assumed a two-dimensional order at a temperature T_{cu}, which was followed by three-dimensional ordering of all the clusters at T_{cl}. In the temperature interval between T_{cu} and T_{cl} there were slow magnetic fluctuations of the system, since the magnetization of the clusters relative to one another could vary. The dynamic susceptibility χ' depended weakly on the frequency and was maximal at T_{cl}. The imaginary part of the susceptibility increased in a step-like manner: the rise of χ'' began from T_{cu}, which was followed by a plateau, but at T_{cl} the value of χ'' began to rise again. However, χ'' was practically independent of the frequency and, therefore, on the basis of the fluctuation-dissipation theorem the authors of Ref. 25 concluded that they observed for the first time the $1/f$ noise in regular magnetic structures. The noise was attributed to an inhomogeneity of the interisland interactions, although other factors could also be at work. The temperature dependence of $\chi''(\omega)$ of $CoCl_2$–GIC exhibited practically no increase in χ'' near T_{cu} and T_{cl}.

Our results differed qualitatively because we observed a strong enhancement of fluctuations in the region of the ordering temperature for all the investigated magnetic materials and this was an expected consequence of a second-order phase transition.

A comparison of the values of the mean-square power of magnetic fluctuations (Figs. 3, 4, 6, and 7) showed that, firstly, in the case of ferromagnetic compounds it was approximately 100 times stronger than for antiferromagnets. In principle, this could be expected because in the case of ferromagnets there is a nonzero spontaneous moment, whereas in the case of antiferromagnets the appearance of a finite average magnetic moment is entirely due to partial antiferromagnetic ordering of a sample. Secondly, the level of fluctuations in $Mn_{0.28}Zn_{0.72}F_2$ is considerably higher (by a factor of about 25) than in $MnSO_4$, although both these substances are three-dimensional antiferromagnets and they contain the same magnetic ions. In estimating the difference between the fluctuations we allowed for the degree of dilution in the case of $Mn_{0.28}Zn_{0.72}F_2$. Such an enhancement of fluctuations in dilute systems could naturally be attributed to the existence of a large number of isolated clusters exhibiting a large uncompensated magnetic moment.

The mean-square power of fluctuations resembled the $1/f$ noise, but it was clearly different for different magnetic compounds: in the case of K_2CuF_4 the spectrum obeyed ac-

curately the $1/f$ dependence and we observed clearly a transition to the Nyquist white noise in the case of $Mn_{0.28}Zn_{0.72}F_2$. Therefore, we should rather speak of an increase in the power of fluctuations at ultralow frequencies, i.e., of large-scale fluctuations of the magnetic moment of a sample. It seems to us that such a universal enhancement of large-scale fluctuations near the phase transition is due to the different relaxation of magnetic fluctuations with different wave vectors, as pointed out in Ref. 26. In the phase transition region there is no long-range order and the ordering of spins occurs only in regions of finite dimensions which are not coupled to one another. Therefore, the spin-wave excitations are also spatially localized. This means that the resultant large-scale fluctuations of the magnetic moment, exceeding the dimensions of the ordered regions, are weakly damped and are effectively magnetostatic oscillations of the magnetic moment.

We must not forget that real crystals always contain a variety of defects, such as impurities, dislocations, domain walls, etc. If there is a local change in the order parameter in the vicinity of a defect, then the size of the region perturbed by the defect increases strongly near T_c because of a rapid rise of the correlation length at $T \to T_c$. A region distorted by a defect is characterized by a stronger dissipation of energy and, consequently, in accordance with the fluctuation–dissipation theorem it is a source of noise. Since the size of this region increases at $T \to T_c$, it follows that the contribution of defects to the dissipation processes increases. It is practically impossible to estimate quantitatively the contribution of defects to the magnetic noise and this can be done only experimentally by introducing impurities or various defects.

b) Characteristics of fluctuations in two-dimensional magnetic materials

We investigated three representatives of the class of two-dimensional magnetic materials, one of the Ising type $Co(HCOO)_2 \cdot 2H_2O$ and two Heisenberg magnetic materials $(CH_3NH_3)_2 \cdot CuCl_4$ and K_2CuF_4. The structure and excitation spectra of two-dimensional magnetic systems have a number of special features distinguishing them qualitatively from three-dimensional magnetic materials (see, for example, Ref. 27). Berezinskiĭ and, independently, Kosterlitz and Thouless predicted the existence of magnetic vortices in XY magnetic materials, i.e., they predicted excitations with a nonzero circulation of the spin fields $\mathbf{S}(x)$ around a singular point (center of a vortex). At low temperatures such vortices combined to form strongly coupled "neutral molecules" consisting of vortices with opposite circulations. On increase in temperature the number of such molecules and their characteristic size both increase. At temperatures $T > T_c$ a finite density of free vortices remains in the system. The phase transition in the two-dimensional XY model can be regarded as a transition from a neutral gas to a plasma in a two-dimensional Coulomb gas and it is usually called the Berezinskiĭ–Kosterlitz—Thouless (BKT) transition. From the point of view of the spin field geometry this is a topological transition.

There are no ideal two-dimensional magnetic materials: all of them are quasitwo-dimensional because of an interaction between the layers and a uniaxial anisotropy in the plane which lifts the degeneracy in this plane. These two interactions suppress strongly vortex spin excitations and induce a transition from a long-range order phase at a finite temperature (according to the Mermin–Wigner theorem the long-range order is absent in the two-dimensional XY model at $T \neq 0$). Nevertheless, many characteristic features of the BKT transitions have been observed also in quasitwo-dimensional magnetic systems. For example, an experimental study of quasielastic neutron scattering in K_2CuF_4 yielded the temperature dependence of the correlation radius of spins in a plane.[28] Even at temperatures above $T_c = 6.25$ K all the way up to $T \approx 6.6$ K a correlation was found not only in a plane, but also between the layers, so that the three-dimensional long-range order was established.

A detailed investigation of the FMR spectra of quasitwo-dimensional easy-plane ferromagnets of the $(CH_3NH_3)_2 \cdot CuCl_4$ and K_2CuF_4 compositions and a determination of the H–T phase diagrams were reported in Ref. 17. The results obtained were described qualitatively (practically without any fitting parameters) on the basis of the BKT theory allowing for the contribution of spin waves and vortices to the destruction of the magnetic order. It should be pointed out that although the theory of spin waves describes satisfactorily these experimental results only down to ≈ 3 K, the scaling theory of plane degenerate systems provides a good agreement in a wide range of temperatures right up to $T \approx T_c$. It was shown in Ref. 17 that the anisotropy of the FMR spectra of $(CH_3NH_3)_2 \cdot CuCl_4$ relative to the direction of the magnetic field was retained right down to 16 K, which was well above the transition temperature.

Interesting features were exhibited also by the temperature dependences of the magnetic parts of the specific heats of the compounds of formic acid with the chemical formula $M(HCOO)_2 \cdot 2H_2O$ (Ref. 12). In the case of an Ising antiferromagnet of the $Co(HCOO)_2 \cdot 2H_2O$ type the usual anomaly of the specific heat was observed at T_N, whereas isotropic $Mn(HCOO)_2 \cdot 2H_2O$ had an asymmetric specific heat curve and at $T > T_N$, right up to $T = 2T_N$, there was a wide "shoulder." The Fe and Ni ions had specific heat curves of intermediate nature.

Two-dimensional magnetic materials investigated by us exhibited similar features. In the case of the Ising-type antiferromagnet with the composition $Co(HCOO)_2 \cdot 2H_2O$ it was found that magnetic fluctuations were maximal at T_N, whereas in the case of the Heisenberg planar magnetic materials of the $(CH_3NH_3)_2 \cdot CuCl_4$ and K_2CuF_4 types this maximum was shifted toward higher temperatures. It was natural to attribute this difference to the existence of vortex excitations mentioned earlier. In the case of the easy-axis two-dimensional ferromagnets there were no vortex excitations and there were only spin waves which destroyed the order in a plane. In the case of the easy-plane two-dimensional ferromagnet the phase transition was initiated by dissociation of vortex pairs.

The BKT transition should occur at a lower temperature than that due to spin waves. Nevertheless, the influence of spin-wave excitations on the destruction of the magnetic order in planes should still be observed. We can assume that the maximum of magnetic fluctuations in the two-dimensional XY magnetic materials was observed by us at the same temperature at which there should have been a phase transition if it had been due to spin waves and had there been no vortex excitations in the system. On the other hand, we should mention that, for example, in the case of

$(CH_3NH_3)_2 \cdot CuCl_4$ the estimates based on the anisotropy of the FMR spectra indicated that a pure spin-wave transition should occur at 16 K, whereas the observed shift was only 0.4 K.

The results of our experimental study of two-dimensional Heisenberg ferromagnetic crystals involving measurements of $M_\perp$, representing the axial component of the magnetic moment, revealed two features: 1) the absolute value of the noise of $M_\perp$ was much less than the noise of $M_\parallel$, indicating that the magnetic moments were oriented mainly in the (100) planes; 2) the temperature dependences of fluctuations had two maxima, one of which coincided with the maximum of the $M_\parallel$ fluctuations and the other was lower on the temperature scale. The existence of the maximum coinciding with the maximum of the fluctuations of $M_\parallel$ on the temperature scale was most probably due to insufficient sensitivity of the receiving coil of the superconducting magnetic flux transformer specifically to the perpendicular (transverse) component of the magnetic moment in view of the finite dimensions of the coil, i.e., this was due to the edge effects. The second maximum shifted downward on the temperature scale indicating that the rotation of the spins to a plane and their ordering in a plane occurred at different temperatures.

c) Fluctuations in a dilute antiferromagnet of the $Mn_{0.28}Zn_{0.72}F_2$ composition

As pointed out already, the interest in dilute antiferromagnets is due to their unusual properties near the Néel point T_N and at concentrations close to the critical value. As demonstrated in Ref. 19, as unusual state appeared in these compounds at $T > T_N$.

The results of our measurements of magnetic fluctuations in $Mn_{0.28}Zn_{0.72}F_2$ (in this case the critical concentration of the Mn ions destroying the transition to the antiferromagnetic state was ~ 0.2) differed considerably from the results for all the other magnetic materials investigated by us: singularities appeared in the spectrum of magnetic fluctuations at temperatures below the transition point. It is clear from Figs. 7 and 8 that between 6 and 7 K the level of fluctuations at ultralow frequencies was much lower than at high frequencies and the fluctuation spectrum was transformed from the Nyquist to the $1/f$ noise type. Using the theoretical justification of the noise in spin glasses, we can assume that the spin-glass phase of this compound is observed in the relevant range of temperatures. However, such a spectrum had been observed for almost all the magnetic materials so that this conclusion was clearly ambiguous. An experimental study of fluctuations in polycrystalline materials with different concentrations of the magnetic ions and also in single crystals should be investigated in order to throw light on this problem.

CONCLUSIONS

An experimental study of lf equilibrium magnetic fluctuations in a number of ferromagnets and antiferromagnets was carried out in zero field and it showed that the noise was maximal near the ordering temperature. The fluctuation spectrum changed from the purely $1/f$ dependence for K_2CuF_4 to the Nyquist type in $Mn_{0.28}Zn_{0.72}F_2$. The absolute power of fluctuations in ferromagnets was approximately 100 times greater than in antiferromagnets. In the case of two-dimensional XY ferromagnets it was found that, firstly, the fluctuation maximum was located above T_c and, secondly, rotation of the spins to a plane and their ordering in the plane occurred at different temperatures. All the characteristic features of the frequency and temperature dependences of the lf magnetic fluctuations penetrating into magnetic materials near the phase transition temperature are still unfortunately qualitative. Undoubtedly, more detailed experimental investigations are needed and a more detailed theoretical analysis should be provided.

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