Investigation of NMR in the quasi-one-dimensional antiferromagnetic $CsMnBr_3$

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The NMR spectrum of the quasi-one-dimensional easy-plane antiferromagnet $CsMnBr_3$ with a triangular magnetic structure has been studied. The measurements were performed in the decimeter microwave range in a special NMR spectrometer and in a wide range of magnetic fields at temperatures of 1.7 and 3.0 K. Three branches of the NMR spectrum were observed. One branch exhibits a very strong frequency-field dependence. This dependence can be explained, to a first approximation, by the existing theory of the interaction of the electronic and nuclear subsystems [E. A. Turov and M. P. Petrov, *Nuclear Magnetic Resonance in Ferro- and Antiferromagnets*, Halstead Press, N. Y., 1972]. To explain the behavior of the two other branches, a more complicated theoretical analysis is required. The observed shift of the NMR spectrum with increasing temperature also cannot be explained. The reduction of the spin moment of the magnetic ion Mn^{2+} due to magnetic fluctuations is determined to be 30%. © *1996 American Institute of Physics.* [S0021-3640(96)01715-X]

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1. INTRODUCTION

The properties of low-dimension magnets have been under active study in the last few years. An especially large reduction of the spin moment as a result of quantum fluctuations should be observed in them. One possible method for determining the magnitude of this reduction is to study the hyperfine fields at the nuclei of the magnetic ions by the NMR method. The NMR frequency of the nuclear moments of the magnetic ions is

$$\omega_n = \gamma_n H_n, \tag{1}$$

where γ_n is the gyromagnetic ratio. In magnetic insulators with $3d$ ions, H_n is proportional to the average spin $\langle S \rangle$ of the magnetic ion. In the absence of an external field

$$H_{n0} = -(A\langle S \rangle)/(\gamma_n \hbar), \tag{2}$$

where A is the hyperfine interaction constant. Therefore the decrease in the magnitude of the electronic magnetic moment will directly affect the resonance frequency.

The object of our investigations was the quasi-one-dimensional antiferromagnet $CsMnBr_3$. For the Mn^{2+} ion the gyromagnetic ratio $\gamma = 1.057$ MHz/kOe and $S = 5/2$. Correspondingly, the hyperfine field H_{n0} in three-dimensional magnets with Mn^{2+} ions fluctuates from 600 to 700 kOe.[1] The zero-point vibrations should substantially decrease the value of H_{n0} on account of the quasi-one-dimensionality of the antiferromagnetic Mn^{2+} chains in $CsMnBr_3$. One of the problems studied in the present work is to determine the difference of the magnetic moment of the Mn^{2+} ion from its nominal value. This difference characterizes the magnitude of the quantum fluctuations.

The NMR method has become very popular for investigating magnets. In application to antiferromagnetic crystals it has a number of aspects:[1] 1) on account of the high hyperfine field H_n, the NMR frequency is hundreds of MHz; 2) in antiferromagnets which possess a low-frequency AFMR branch, a very strong dynamic frequency shift (DFS), due to the coupled oscillations of the electronic and nuclear subsystems, is observed, and the crossing of the nuclear and electronic branches of the oscillations also produces a gap, whose magnitude is inversely proportional to the square root of the temperature, in the AFMR spectrum; and, 3) in magnetically ordered crystals, the absorption of the radio frequency field by the nuclei of magnetic ions is observed to intensify on account of the dynamic component of H_n.

From Chubukov's calculations[2] of the AFMR spectrum and also the experimental data obtained by Zalyaznik, Prozorova, and Petrov[3] it follows that $CsMnBr_3$ possesses a low-frequency AFMR branch with a cubic dependence of the frequency on the magnetic field. The interaction of the electronic oscillations with the three NMR modes has still not been investigated, either theoretically or experimentally. The clarification of the features of this interaction is the second problem addressed in the present work.

$CsMnBr_3$ possesses a hexagonal lattice and is an easy-plane antiferromagnet at $T < T_N = 8.3$ K. The strong exchange interaction J along the spin chains, which are parallel to the C_6 axis, establishes antiferromagnetic order in them. The anisotropy energy in $CsMnBr_3$ (characterized by $H_a = 2.4$ kOe) establishes the direction of all spins in all chains perpendicular to the C_6 axis. The weak exchange interaction J' ($J/J' = 460$) between spins lying in the same plane gives rise to a triangular 120° magnetic structure on account of the fact that the magnetic ions Mn^{2+} are arranged in the planes into a hexagonal network. The magnetic structure of $CsMnBr_3$ consists of six sublattices; these are shown schematically in Fig. 1. The neighboring layers perpendicular to the C_6 axis each contain three pairs of antiparallel sublattices. The magnetizations $M_i^{\pm}$ of these pairs are rotated relative to one another by an angle $\alpha = 120°$.[2,4]

The behavior of $CsMnBr_3$ in a magnetic field was studied by Chubukov.[2] In a field H applied along the Y axis in the basal plane, the magnetizations $M_1^{\pm}$ of one pair of sublattices are oriented perpendicular to the applied field H. In these sublattices the field

$$H_n^0 = H_{n0}[1 + (1/2)(H/H_{n0})^2 + H^2/(H_{n0}H_E)], \tag{3}$$

which is identical for M_1^+ and M_1^-, acts on the nuclei of the magnetic ions. Here H_{n0} is the hyperfine field in the absence of an external field and $H_E = 1530$ kOe is the exchange field, whose value was obtained from static data.[5]

In contrast to the first pair of sublattices ($M_1^{\pm}$), the other two pairs ($M_2^{\pm}$ and

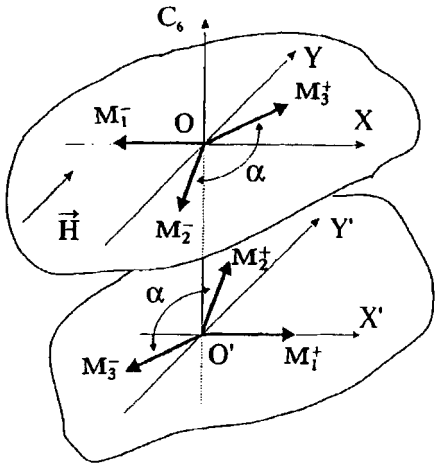

FIG. 1. Schematic diagram of the magnetic structure of $CsMnBr_3$.

$M_3^{\pm}$) start to rotate toward one another under the action of a field applied along Y. According to Ref. 2, the magnetic field acting on the nuclei of these sublattices is given by

$$H_n^{\pm}=H_{n0}[1+(1/2)(H/H_{n0})^2+H^2/(H_{n0}H_E)]\pm H\sqrt{1-[(1/2)(1+z/(2-z))]^2}. \quad (4)$$

Here H_n^+ is the field in the canted sublattices, whose magnetizations M_2^+ and M_3^+ are directed along the applied field, and H_n^- is the field in the sublattices whose magnetizations M_2^- and M_3^- are directed oppositely to the applied field, $z=(H/H_c)^2$, and $H_c=64$ kOe is the spin-flop field in which the magnetic structure transforms from a six-sublattice structure into a quasi-two-sublattice structure. The value given for H_c was obtained in static experiments[5,6] and is confirmed in the present work. The formulas (3) and (4) hold for $H<H_c$. Increasing the field further cause all sublattices to rotate smoothly toward the direction of the magnetic field to the point of complete destruction of the antiferromagnetic structure by a spin-flip transition.

The NMR frequency is proportional to the field at the nucleus. Therefore, on the basis of what we have said above, it can be expected that the NMR spectrum in the experimental material in fields $H<H_c$ will consist of three branches:

$$\omega_n^0=\gamma H_n^0, \quad \omega_n^-=\gamma H_n^-, \quad \omega_n^+=\gamma H_n^+. \quad (5)$$

These three branches are shown in Fig. 2 by the curves a, b and c, respectively. We chose $H_{n0}=388$ kOe, which corresponds to $\omega_{n0}=410$ MHz and agrees best with our experimental data.

2. MEASUREMENT PROCEDURE

To find the NMR spectrum of $CsMnBr_3$, we constructed a special NMR spectrometer with continuous pumping and a high-Q resonance circuit ($Q\simeq 300$) with a modified

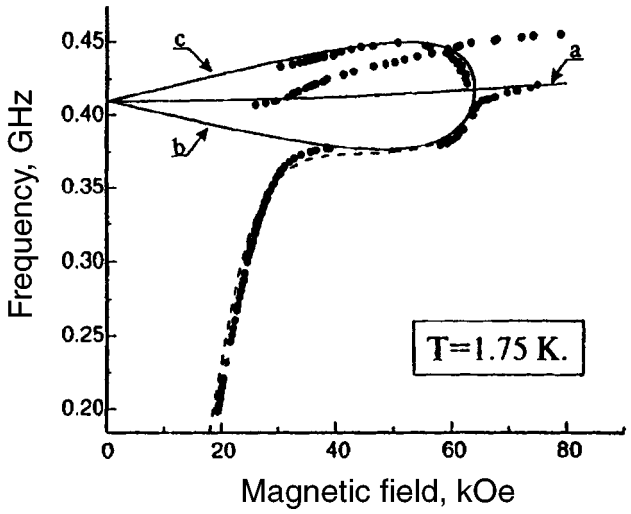

FIG. 2. NMR spectrum: dots (●)—experimental data; solid lines—spectrum calculated neglecting any dynamic interaction between the oscillations of the nuclei and the electrons; dashed curve —theoretical calculation of the behavior of the lower NMR branch taking account of the interaction only between the lower NMR branch and the lower AFMR branch.

loop-gap type tunable resonator.[7] Except for some details, the operating principle of the spectrometer is described in Ref. 8.

The frequency of the microwave signal of the generator was modulated at a frequency of 100 kHz and the signal at the first harmonic was used to maintain the generator frequency at the peak of the resonance curve of the resonator with the aid of an electronic tracking circuit. The frequency of the second harmonic was used to record the absorption in the resonator. The magnitude of the applied magnetic field was registered with a Hall sensor. All data were recorded with a computer and an ADC. To excite the nuclear resonance oscillations and obtain the maximum NMR gain, the field of the solenoid and the microwave field were applied perpendicular to one another in the basal plane of the $CsMnBr_3$ crystal. The C_6 axis of the sample was oriented relative to the solenoid axis with an accuracy of about 5°; this did not increase the error much in determining the resonance field. The investigations were performed in the temperature range 1.7–3 K. The temperature was monitored with a mercury manometer and was maintained stable to within 0.05 K. All measurements were performed in the frequency interval 200–500 MHz. The stability of the resonance frequency over the sweep time of the magnetic field was better than 0.1 MHz. All frequency–field dependences were obtained by sweeping the external magnetic field. The $CsMnBr_3$ crystals were prepared by the method described in Ref. 3.

3. EXPERIMENTAL RESULTS AND DISCUSSION

The main experimental results obtained at $T=1.75$ K are displayed in Fig. 2 (●). If there is no interaction between the nuclei and the electrons, then we should observe three

NMR branches, corresponding to the solid curves in Fig. 2. As one can see from the figure, three branches are indeed observed in the real NMR spectrum. However, the lower branch exhibits a very strong frequency–field dependence which saturates in a field of 40 kOe at a frequency of the order of 380 MHz and then merges with the curve b. The two other branches do not exhibit such a strong dependence, though their behavior is characteristic.

The lower branch of the spectrum is described quite well by the Turov–Kuleev theory for two-sublattice antiferromagnets,[9] assuming that only the lower AFMR branch interacts with the lower branch of the NMR spectrum. According to Ref. 9, the shifted NMR frequency Ω_n is

$$\Omega_n = \sqrt{\frac{(\omega_n^-)^2\omega_e^2}{\omega_T^2+\omega_e^2}}. \tag{6}$$

In this formula ω_n^- is the unshifted lower NMR branch obtained from Eqs. (3) and (4); the value $\omega_T = 6.5$ GHz for $T = 1.75$ K was obtained from the data of Ref. 10 on the width of the gap in the AFMR spectrum; and the approximate formula from Ref. 2 was used for the unshifted AFMR frequency ω_e:

$$\omega_e = \gamma_e \frac{H^3}{H_c^2}\sqrt{\frac{3}{4}}. \tag{7}$$

The computational results obtained using Eq. (6) (Fig. 2, dashed line) gave very good agreement.

A more accurate calculation of the frequencies of coupled oscillations in the lower AFMR mode and on all three NMR branches in fields far from H_c, where the triangular magnetic structure is distorted very little, was performed in Ref. 10. In fields up to 40 kOe, the results of this calculation satisfactorily describe our data on all three branches.

The interaction with the electronic oscillations has very little effect on the behavior of the two other branches of the spectrum. The upper branch c is scarcely shifted at all. The behavior of the middle branch is especially strange in fields above 40 kOe. It is surprising that above the spin-flop field H_c, where to a first approximation $CsMnBr_3$ should behave as a two-sublattice antiferromagnet with one NMR frequency, we observe two frequencies. This anomaly could be due to the anomaly in the static properties, where in fields above H_c a difference is observed in the magnetizations for $H_\parallel$ and $H_\perp$.[5]

Even stranger behavior of the NMR spectrum was observed as the temperature increased. One can see from Fig. 3 that as the temperature increases, the spectrum drops appreciably in frequency, attesting to the decrease in the spontaneous electronic moment of the magnetic ions Mn^{2+}. According to the theory of the DFS,[2] the NMR line should shift with increasing temperature to lower fields, whereas we observed the directly opposite behavior. This cannot be explained either by a decrease in the magnetization of the sublattices or a decrease in H_c.

All this shows that an additional theoretical analysis of the properties of $CsMnBr_3$ is required.

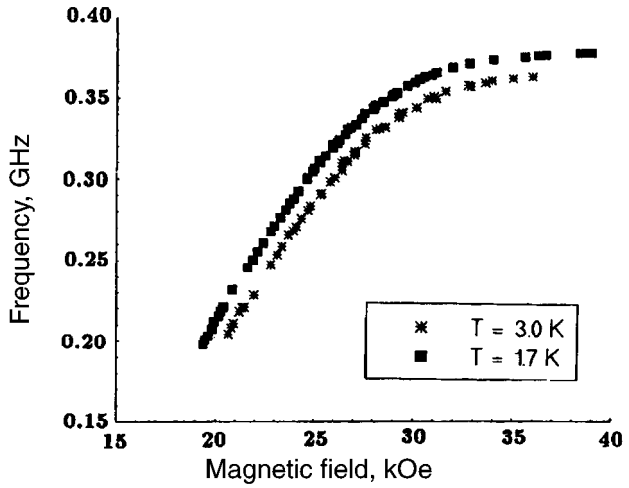

FIG. 3. Spectra of part of the low-frequency NMR branch at $T=1.7$ and $T=3$ K.

It definitely follows from our data that at temperature $T=1.75$ K the unshifted frequency equals 420 MHz. As noted in the introduction, the hyperfine field at the Mn^{2+} nuclei in normal three-dimensional magnets equals 600–700 kOe and for such compounds the typical unshifted NMR frequency equals 600–700 MHz. Therefore, according to our data, the spin moment reduction $\delta S/S=(S-\langle S\rangle)/S$ in $CsMnBr_3$ equals $(30\pm5\%)$. The error given is associated with the uncertainty in the value of the hyperfine constant for this material. Our value agrees with the data obtained by other methods.[4,5]

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