Mn^{55} NMR investigation of the suppression of quantum fluctuations in quasi-one-dimensional antiferromagnets by a magnetic field

A. S. Borovik-Romanov,[a] S. V. Petrov, and A. M. Tikhonov
P. L. Kapitsa Institute of Physical Problems, Russian Academy of Sciences, 117334 Moscow, Russia

B. S. Dumesh
Institute of Spectroscopy, Russian Academy of Sciences, 142092 Troitsk, Moscow Region, Russia

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The NMR of Mn^{55} nuclei is measured in the quasi-one-dimensional antiferromagnets $CsMnBr_3$, $RbMnBr_3$, and $CsMnI_3$ in magnetic fields up to 8 T at temperatures in the range 1.3–4.2 K. The average moments of the magnetic sublattices and their field dependences, which turned out to be comparatively strong and different for magnetically nonequivalent Mn^{2+} ions, are determined from the hyperfine-field data obtained. As a result, the magnetizations of separate sublattices in an external magnetic field ~ 8 T differ by more than 5%. The results obtained agree qualitatively with the theory of the suppression of quantum fluctuations by a magnetic field. © *1997 American Institute of Physics.* [S0021-3640(97)01123-7]

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The investigation of the deviation of the average moments $\langle S\rangle$ of magnetic sublattices in antiferromagnets (AFs) from the nominal values S as a result of quantum fluctuations is one of the standard problems of the physics of antiferromagnetism. Although the general theory of this phenomenon was constructed quite long ago,[1] comparatively few reliable experiments have been performed. The problem is that in 3D antiferromagnets the reduction $(\langle S\rangle - S)/S \approx 2-5\%$ is small and difficult to measure.[b] The accuracy of the amplitude measurements is, as a rule, inadequate because of the need to make allowance for extinction effects in neutron diffraction. The other well-known method is measurement of the hyperfine fields at the nuclei of the magnetic ions. Thus, in ions of $3d$ elements

$$H_n = -\frac{A}{\gamma_n h}\langle S\rangle, \tag{1}$$

where A is the hyperfine constant, γ_n is the nuclear gyromagnetic ratio ($\gamma_n = 10.6$ MHz/T for Mn^{2+}), and h is Planck's constant. However, the reduction effect is masked by the uncertainty in the hyperfine constant A, determined from ESR on the same ions in an isomorphic nonmagnetic matrix.

TABLE I.

$\langle S \rangle$	Neutron diffraction	NMR	Other methods	Theory
$CsMnBr_3$	1.65 [Ref. 3]	1.8 [Ref. 4]	1.7 [Ref. 5]	1.82 [Ref. 6]
$RbMnBr_3$	1.8 [Ref. 7]	1.8 present		
$CsMnI_3$	1.85 [Ref. 8]	1.74 work	1.8 [Ref. 9]	1.8; 2 [Ref. 10]

Calculations[2] have shown that the hyperfine constant A in substances with a low concentration of magnetic ions is smaller than in pure magnets because of effects due to the transfer of an unpaired electron spin from one manganese ion to a neighboring one. Making allowance for covalence effects for the Mn^{2+} ion with six nearest neighbors gave a 2–4% increase in the hyperfine field, which limits the accuracy with which $\langle S \rangle$ in 3D magnets can be determined.

The situation is much better in the case of the investigation of quasi-one-dimensional magnets, where the expected spin reduction can reach 30% and can be measured by different methods. Moreover, in quasi-1D magnets the Mn^{2+} ion has only two nearest neighbors and therefore the contribution of the indirect hyperfine interaction to the local field at the nucleus of this ion should be less than the estimate indicated above.

Data on the magnitude of the average spins of Mn^{2+} ions in some quasi-1D AFs with triangular magnetic structure are given in Table I.[c)] One can see that the agreement of the results with one another and with the theoretical predictions is good. Moreover, as a result of the large spin reduction, it is now possible to study the suppression of quantum spin fluctuations (correspondingly, a decrease of the reduction) by an external magnetic field. Several recently published theoretical works are devoted to this question.[6,10,12,13] It was possible to explain some features of the field dependences of the magnetization in these substances by the mechanism of suppression of quantum fluctuations: the weak nonlinearity of the increase in magnetization in magnetic fields perpendicular to the plane of the triangle and the magnetization anisotropy above the reorientational phase transition.[6,12] The increase, associated with suppression of quantum fluctuations, of the average spin of the magnetic ions, which was found to be fully measurable[6,13] even in fields $H<0.1\ H_E$, was calculated.

On this basis, we undertook an investigation of Mn^{55} NMR in these substances. This makes it possible to measure directly the values and field dependences of the microscopic magnetic moments of Mn^{2+} ions.

All three substances ($CsMnBr_3$, $CsMnI_3$, $RbMnBr_3$) possess a closely similar crystal structure.[14] The Mn^{2+} ions are surrounded by octahedra of halogen atoms, and these octahedra, joined at a common face, form chains along the C_6 axis. These chains are packed hexagonally in the basal plane of the crystal, and the voids thus arising are filled with alkali-metal atoms. The unit cells in $CsMnBr_3$ and $CsMnI_3$ contain two formula units and possesses D_{6h}^4 symmetry. All Mn^{2+} ions are crystallographically equivalent.[d)] The distance between neighboring Mn^{2+} ions along the chains is approximately half the distance between neighbors in the plane. Correspondingly, the value of the exchange

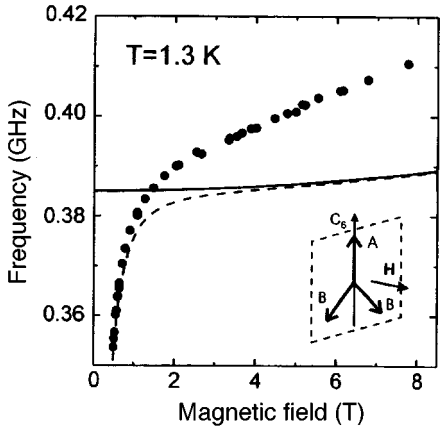

FIG. 1. Mn^{55} NMR spectrum of $CsMnI_3$ at $T=1.3$ K and with $\mathbf{H}\perp C_6$. Solid line — ''unshifted'' NMR spectrum with $H_n=$ const; dashed line — allowance for the DFS of NMR. Inset: Arrangement of Mn^{2+} spins with $\mathbf{H}\perp C_6$.

integral J between them is several hundreds of times larger. Nonetheless, magnetic ordering with $T_N\approx 10$ K arises on account of interchain exchange J'. The Mn spins in the chains are ordered antiferromagnetically and the mutual polarization of the chains is determined by J' and the anisotropy. Triangular ordering occurs in all substances — in weak fields the spins of neighboring ions in the plane lie on the sides of isosceles triangles (in $RbMnBr_3$ in fields $H>3$ T).

The NMR of Mn^{55} was measured at temperatures 1.3–4.2 K with a cw NMR spectrometer, similar to the one employed in Ref. 15, in the frequency range 200–450 MHz and in magnetic fields 0.5–8 T. All measurements were performed on single-crystalline samples, placed in a helium bath and oriented so that the external and high-frequency magnetic fields were mutually perpendicular and lay in the basal plane. As a rule, the absorption line was recorded by scanning the magnetic field. Preliminary results on NMR in $CsMnBr_3$ were published in Ref. 4; a more complete article is published in Ref. 16.

The anisotropy in $CsMnI_3$ is of the easy-axis type. For this reason, the triangles of Mn^{2+} spins lie in a plane passing through the C_6 axis. When a magnetic field perpendicular to the C_6 axis is switched on, the planes of the triangles rotate so that the spins are perpendicular to $\mathbf{H}$. The Mn^{55} NMR spectrum is presented in Fig. 1. To a first approximation, it should be described by the formula

$$\frac{\omega_n}{\gamma_n}=|\mathbf{H}_n+\mathbf{H}|=H_n\left[1+\frac{H^2}{H_n^2}\left(1-\frac{2H_n}{H_E}\right)\right]^{1/2}. \tag{2}$$

Here H_E is the exchange field and H is the external magnetic field. We took account of the fact that the Mn^{2+} spins are tilted with respect to the external field by the small angle $\sim H/H_E$ ($H_E\approx 140$ T). This dependence with $H_n=$ const is presented in Fig. 1 (solid line).

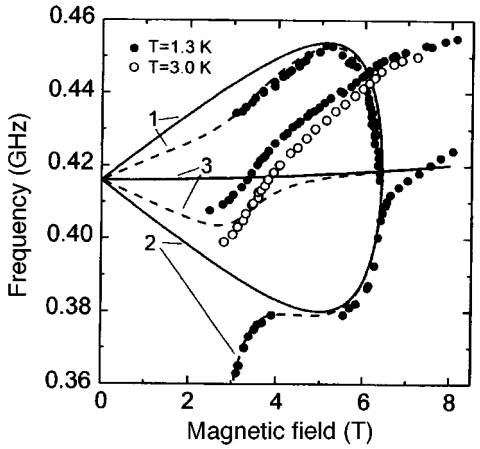

FIG. 2. Mn^{55} NMR spectrum of $CsMnBr_3$ with $\mathbf{H} \perp C_6$, $T=1.3$ K (●), $T=3.0$ K (○) (only the middle branch is shown). Solid line — ''unshifted'' NMR spectrum with $H_n=$ const; dashed line — allowance for DFS of NMR.

In weak fields the spectrum is deformed by the interaction with the Goldstone branch of the AFMR (so-called dynamic frequency shift (DFS) of NMR). The NMR spectrum under the condition $\omega_n^2 \ll \omega_e^2$ is described well by the expression[17]

$$\frac{\omega_n^2}{\gamma_n^2} = H_n^2 \left(1 + \frac{\omega_T^2}{\omega_e^2} \right)^{-1}. \tag{3}$$

Here ω_e is the unshifted AFMR frequency and ω_T is the coupling frequency. The frequencies ω_e and ω_T were taken from the AFMR data presented in Ref. 9. Although Eq. (3) was introduced for two-sublattice AFs, the calculation performed in Ref. 9 showed that for $CsMnI_3$ it holds up to terms $\approx 10^{-5} H_n^2$. However, in strong fields, where the DFS is negligibly small, a substantial increase of the NMR frequency is observed. This increase can be interpreted, in accordance with Eq. (2), as an increase in the hyperfine field. The field dependence $H_n(H)$ obtained is presented in Fig. 3 (see below).

In $CsMnBr_3$ the spins lie in the basal plane. When an external field is applied, the spins become oriented in a manner so that the field lies in the direction of the bisector of the triangle on whose sides the spins lie. As the field increases, the angles at the base of the triangle start to decrease as[18]

$$\cos(\alpha) = \frac{1}{2 - H^2/H_C^2}, \tag{4}$$

where $H_C = 6.4$ T is the reorientational phase transition field. A collinear structure consisting of antiferromagnetically ordered ferrimagnetic planes (with spin ratio 2:1) arises above the transition. To within the tilt angles $\sim H/H_E$ ($H_E \approx 150$ T), all spins are perpendicular to the magnetic field.

The NMR spectrum in $CsMnBr_3$ is presented in Fig. 2. It consists of three branches,

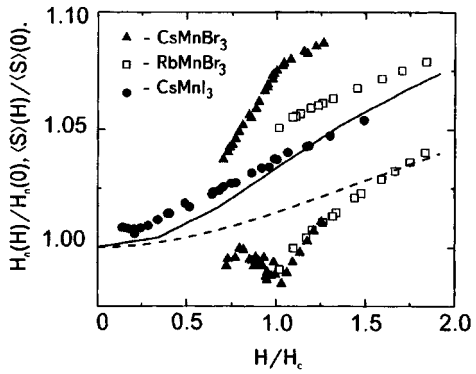

FIG. 3. Field dependences of the hyperfine field at Mn^{55} nuclei with $\mathbf{H}\perp C_6$, $T=1.3$ K in $CsMnBr_3$ (Δ), $RbMnBr_3$ ($\square$), and $CsMnI_3$ ($\bullet$). Dashed line — $\langle S\rangle(H/H_C)$ in $CsMnBr_3$ with $\mathbf{H}\|C_6$;[6] solid line — $\langle S\rangle(H/H_C)$ for $CsNiCl_3$ with $\mathbf{H}\perp C_6$.[13]

corresponding to different relative arrangements of the hyperfine and external fields,

$$\frac{\omega_{1,2}}{\gamma_n}=H_n\left[1+\frac{H^2}{H_n^2}+2\frac{H}{H_n}\left(\pm\sin(\alpha)-\frac{H}{H_E}\cos^2(\alpha)\right)\right]^{1/2}, \tag{5}$$

$$\frac{\omega_3}{\gamma_n}=H_n\left[1+\frac{H^2}{H_n^2}\left(1-\frac{2H_n}{H_E}\right)\right]^{1/2}, \tag{6}$$

for $H>H_C$ and constant H_n a single branch, described by Eq. (6) (solid curve *3* in Fig. 2), remains. The dashed lines indicate the NMR spectrum with allowance for the DFS, calculated in Ref. 16. One can see that up to H_C the branches *1* and *2* agree satisfactorily with the calculation, while the frequency of the branch perpendicular to the magnetic field increases with field similarly to $CsMnI_3$. Above H_C the increase in the frequency of this branch slows down, though appreciable growth of the bottom branch is observed for spins which in weak fields comprised the lateral faces of the triangle. The corresponding field dependences $H_n(H)$ are presented in Fig. 3. This figure also shows the dependences $H_n(H)$ on Mn^{55} nuclei for the collinear phase of $RbMnBr_3$ in fields $H>H_C\approx 4$ T. This is also an easy-plane AF, in which a complicated spin structure, incommensurate with the lattice, is realized in weak fields, but in $H\approx 3$ T it transforms into a commensurate phase with triangular spin ordering and subsequently behaves just as in $CsMnBr_3$.[11] One can see that similarly to $CsMnBr_3$ the nonequivalent Mn^{2+} spins in the magnetic plane are characterized by different values of H_n, which depend quite strongly on the external field.

In summary, strong growth of the hyperfine field on Mn^{55} nuclei is observed in all three materials with the application of an external magnetic field. This dependence is different for magnetically nonequivalent ions and leads to splitting of the NMR in the collinear magnetic phase. Such a growth cannot be explained by a change in the hyperfine constant of the ion itself on account of magnetostriction, since the orbital contribution to it $A_L\sim(g-2)\approx 0.004$ is very small (g is the g factor of the ion) and the contri-

bution due to core polarization depends extremely weakly on the distance up to the ligands.[19] The well-known instability arising in the crystal structure of these compounds as a result of the shift in the neighboring octahedral chains relative to the C_6 axis also has a weak effect on the hyperfine constant, since it does not change the nearest neighbor environment of the magnetic ions. The nature of the contribution of the indirect hyperfine interaction of neighboring magnetic ions is close to that of the exchange interaction. For this reason, the change in A due to reorientation of neighboring Mn spins in the plane should be J'/J times less than the correction calculated in Ref. 2. For this reason, it can be asserted that the change in the average spins $\langle S\rangle$ of the Mn^{2+} ions makes the main contribution to the change in the hyperfine fields.

Thermal fluctuations of the spins also make a definite contribution to $\langle S\rangle$. However, they are small at temperatures $T\approx 1.3$ K. According to our data on the temperature dependence of H_n in $CsMnBr_3$ at $H=0$, $\langle S\rangle(0)-\langle S\rangle(1.3\text{ K})\leqslant 0.01\langle S\rangle(0)$ (Ref. 16). Moreover, temperature fluctuations become frozen out when $\hbar\omega_e(H)>kT$, i.e., in comparatively weak magnetic fields. The field dependence of the frequency of the middle branch of Mn^{55} NMR in $CsMnBr_3$ at $T\approx 3$ K is presented in Fig. 2. One can see that it is appreciably steeper in weak fields, and for $H>6.0$ T the temperature correction becomes very small.

It is difficult to make a quantitative comparison between our results and the theory of the suppression of quantum fluctuations, since no calculations have been performed for our experimental situation. The dashed curve in Fig. 3 shows the dependence $\langle S\rangle \times(H/H_C)$ calculated in Ref. 6 for $CsMnBr_3$ but with $\mathbf{H}\|C_6$ (in this geometry all Mn^{2+} spins are equivalent and there is no splitting). The solid curve shows the $\langle S\rangle(H/H_C)$ ($\mathbf{H}\perp C_6$)for $CsNiCl_3$ (analog of $CsMnI_3$) from Ref. 13. One can see that the increase in magnetization of the sublattices corresponds in order of magnitude to our experiment.

In Ref. 10, it was pointed out that in quasi-one-dimensional AFs with easy-axis anisotropy the magnetic ions are nonequivalent even in the absence of an external field, since only one third of them are oriented parallel to the easy axis C_6 (spins A) and the remaining spins are tilted from the axis by an angle $\sim 50°$ (spins B) (see inset in Fig. 1). In consequence the average spins are different, the difference $\langle S_A\rangle-\langle S_B\rangle\approx 0.2$ for $CsMnI_3$. The corresponding splitting of Mn^{55} NMR ≈ 50 MHz is close in order of magnitude to the splitting we observed in $CsMnBr_3$ and $RbMnBr_3$. Unfortunately, the NMR line corresponding to A spins in $CsMnI_3$ is very weak and we could not detect it.[e)]

In summary, we have measured the field dependences of the average spins of Mn^{2+} ions in quasi-one-dimensional AFs $CsMnI_3$, $CsMnBr_3$, and $RbMnBr_3$. These dependences were found to be not only strong enough to be observed by the NMR method but also different for magnetically nonequivalent Mn^{2+} ions. The results obtained are in qualitative agreement with the theory.[6,10,13]

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[a)]Deceased.

[b)]The reduction in AFs with spin 1/2 should be much greater, but experiments with such ions (Cu^{2+}) are difficult to interpret because of the difficulty of taking into account accurately the effect of the large orbital magnetic moment $L=2$. For this reason, in what follows, we shall discuss substances with Mn^{2+} ions ($^6S_{5/2}$ state).

[c)]The magnetic properties of these compounds are discussed in greater detail in Ref. 11.

[d)]The structure in $RbMnBr_3$ is more complicated because of orthorhombic distortions.[11]

[e)]While this paper was being prepared for publication, we observed this NMR branch. Its frequency in the absence of a magnetic field equals 417 MHz.

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