Observation of spin-reduction anisotropy in the quasi-one-dimensional antiferromagnet $CsMnI_3$

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The NMR of ^{55}Mn in the quasi-one-dimensional noncollinear antiferromagnet $CsMnI_3$ at $T=1.3$ K is investigated in magnetic fields up to ~ 40 kOe. Six NMR branches corresponding to six manganese spins per magnetic unit cell are observed. The NMR spectra correspond satisfactorily to the well-known magnetic structure of $CsMnI_3$, taking into account the dynamic frequency shift due to the interaction with the low-lying AFMR modes. The average spins $\langle S_A\rangle=1.86$ and $\langle S_B\rangle=1.74$ of the magnetically nonequivalent Mn^{2+} ions are determined from the measured values of the hyperfine fields. The results obtained agree qualitatively with the calculations of spin reduction in quasi-one-dimensional antiferromagnets [Y. Watabe, T. Suzuki, and Y. Natsume, Phys. Rev. B **52**, 3400 (1995)]. © *1998 American Institute of Physics.* [S0021-3640(98)01009-3]

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The properties of the crystal lattices of certain binary salts ABX_3 (A is an alkali metal, B is a 3*d* metal, and X is a halogen) make for a low dimensionality of the exchange structures formed by the B^{2+} ions. A large reduction of the average spins of the moments of magnetic ions is observed in the quasi-one-dimensional antiferromagnets (quasi-1D AFs) ABX_3 with a triangular magnetic structure. Thus, for compounds with Mn^{2+} magnetic ions ($^6S_{5/2}$ state) the average spin per ion is $\langle S\rangle\approx 1.8$, which makes it possible to study more subtle effects, for example, a change in reduction in strong magnetic fields as a result of the suppression of quantum fluctuations. In recent years a number of theoretical and experimental works have been devoted to this question.[1–3] It has been found that magnetically nonequivalent AF chains in easy-plane ''triangular'' quasi-1D AFs in strong magnetic fields have different average spins per ion.[4] According to the calculations in Ref. 5, the average spins of Mn^{2+} in magnetically nonequivalent AF chains in easy-axis triangular AFs (including $CsMnI_3$) can be different even in a zero magnetic field. The present work is devoted to verifying this assertion.

$CsMnI_3$ is a hexagonal crystal with symmetry space group D_{6h}^4. *All positions of*

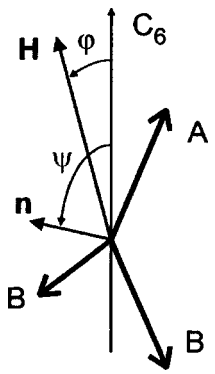

FIG. 1. Schematic diagram of the magnetic structure of $CsMnI_3$. Each AF chain is represented by one spin.

Mn^{2+} ions are crystallographically equivalent. The magnetic properties of $CsMnI_3$ can be described, to a first approximation, by a model Heisenberg Hamiltonian of a system of equivalent spins, taking into account the single-ion anisotropy and Zeeman energy of the magnetic moments in an external field **H**:

$$\mathcal{H}=2J\sum_i \mathbf{S}_i\cdot\mathbf{S}_{i+\Delta_z}+2J'\sum_i \mathbf{S}_i\cdot\mathbf{S}_{i+\Delta_\perp}+D\sum_i (S_i^z)^2-g\mu_B\mathbf{H}\cdot\sum_i \mathbf{S}_i, \tag{1}$$

where g is the g factor, μ_B is the Bohr magneton, $S=5/2$ for the Mn^{2+} ion; $J>0$, $J'>0$ are the antiferromagnetic exchange interaction integrals; and, $D<0$ is the anisotropy constant. The first term describes the exchange interaction along the C_6 axis; the second term describes the exchange interaction in a plane perpendicular to C_6. The distance between the Mn^{2+} ions along the axis is approximately half that in the plane and accordingly the exchange constants are $J=198$ GHz (Ref. 6) and $J'=1$ GHz (Refs. 6 and 7).

Below $T_{N2}=8.2$ K the magnetic structure consists of antiferromagnetic chains along the C_6 axis. In weak magnetic fields the spins of one third of the chains are directed along the axis (A spins), while in the remaining chains they make an angle $\Theta=51°\pm1°$ with the axis (B spins).[8,6] All Mn^{2+} spins are coplanar with one spin plane, if their small canting in an external field is neglected. There is no anisotropy in the hexagonal plane, so that when the magnetic field possesses a component oriented perpendicular to the C_6 axis, the normal to the spin plane is established parallel to this component. If a field is applied in the hexagonal plane, then such a structure is stable right up to a transition to the ferromagnetic state. For $\mathbf{H}\parallel C_6$ a spin-flop transition is observed in the field H_{sf} ($H_{sf}=54$ kOe at $T=2$ K); above the transition the spin of the neighboring chains apparently form a regular triangular structure oriented in a hexagonal plane. For an arbitrary orientation of the external field the spin plane rotates continuously so that[7]

$$\tan(2\psi)=\frac{H^2\sin(2\varphi)}{H^2\cos(2\varphi)-H_{sf}^2}, \tag{2}$$

where ψ is the angle between the normal **n** to the spin plane and the C_6 axis and φ is the angle between **H** and C_6 (see Fig. 1).

In accordance with the magnetic structure the ^{55}Mn NMR spectrum must consist of four branches, which in an approximation linear in H/H_n have the form

$$\frac{\omega_{n1,n2}}{\gamma_n} = H_{nA} \pm H\sin(\psi-\varphi), \quad \frac{\omega_{n3,n4}}{\gamma_n} = H_{nB} \pm H\sin(\psi-\varphi)\cos\Theta, \tag{3}$$

where $\gamma_n/2\pi = 1.06$ MHz/kOe is the gyromagnetic ratio for ^{55}Mn, $H_{nA,nB} = -A_0\langle S_{A,B}\rangle/\hbar\gamma_n$ are the hyperfine fields, and A_0 is the hyperfine interaction constant. We took into account that according to calculations[5] $\langle S_A\rangle \neq \langle S_B\rangle$. For $\varphi = \pi/2$ the terms linear in the field vanish and the twofold ($\omega_A \approx \gamma_n H_{nA}$) and fourfold ($\omega_B \approx \gamma_n H_{nB}$) degenerate branches remain.

The real NMR spectrum is much more complicated because of the dynamic frequency shift (DFS) due to the interaction with low-lying AFMR modes.[a)] In $CsMnI_3$ this phenomenon was detected from the appearance of a temperature-dependence gap in the spectrum ω_{e2} of the AFMR mode[10] and according to the strong field dependence of the NMR mode associated with it[4] in the case $\mathbf{H} \perp C_6$. In these works it is shown that the spectrum of coupled electron–nuclear oscillations can be described well by the solutions of the equation[9]

$$(\omega_{e2}^2 - \omega^2)(\omega_B^2 - \omega_2) - \omega^2\omega_T^2 = 0, \tag{4}$$

and the coupling frequencies $\omega_T \sim T^{-1/2}$ and $\omega_B(0)/2\pi \approx 390$ MHz at $T = 1.3$ K are determined. Unfortunately, in this geometry it was not possible to find the NMR mode corresponding to the spins of the A chains. For this reason, we performed an experiment with $\mathbf{H} \parallel C_6$, where the mode composition of the NMR spectrum should be substantially richer.

All experiments were performed with a wide-band cw NMR spectrometer with a reentrant resonator and frequency modulation, described in detail in Ref. 11. The spectra were obtained by passing through resonance in the magnetic field at $T = 1.3$ K. The samples were single-crystalline and were grown by the Bridgman method. The samples were oriented according to natural cleavage surfaces along binary planes. To prevent hydration the samples were coated with a protective film of rubber cement and stored in a helium atmosphere. The intensity of the magnetic field of the superconducting solenoid was measured with a Hall sensor, which was calibrated according to the NMR signal on ^{1}H protons contained in the cement.

The ^{55}Mn NMR signal was observed in a wide frequency range 250–450 MHz in magnetic fields 15–40 kOe. It consisted of several lines of width $\sim$1–5 MHz, corresponding to six possible NMR modes. The signal spectra for $\varphi < 0.5°$ and $\varphi \approx 7°$ are presented in Figs. 2 and 3. One can see that five branches are observed. We have enumerated the branches in order of decreasing frequency. In weak fields the branches *3* and *5* converge to ω_B, while branches *1* and *4* converge to $\omega'/2\pi \approx 417$ MHz. Their spectrum is close to $\omega_{1,4} = \omega' \pm \gamma_n H$ (dashed lines in the figures), making it possible to attribute these branches to oscillations of the *A* spins.

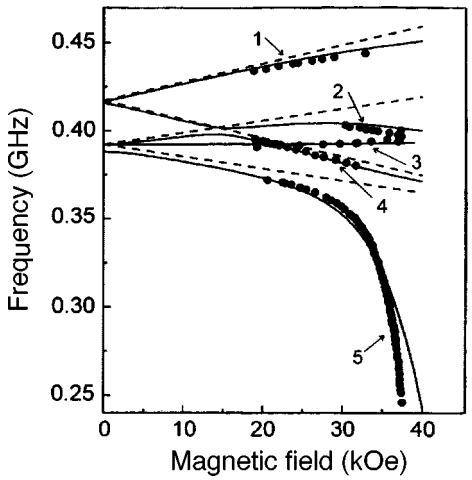

FIG. 2. ^{55}Mn NMR spectrum in $CsMnI_3$ at $T=1.3$ K and $\varphi<0.5°$: Dots — experiment, dashed lines — unshifted spectrum (3), solid lines — calculation using Eqs. (7) and (8).

For a quantitative description of the spectra it is necessary to take into account the dynamic frequency shift due to the interaction with the low-frequency AFMR modes ω_{e2} and ω_{e3}. Their spectrum in the range of fields of interest to us can be described, to a first approximation in $\varphi \ll 1$, by the formulas[7]

$$\omega_{e2}=\frac{\gamma_e\sqrt{\eta}H_{sf}H\varphi}{\sqrt{H_{sf}^2-H^2}}, \quad \omega_{e3}=\frac{\omega_{e3}(0)H_{sf}\sqrt{\eta}}{\sqrt{\eta H_{sf}^2+H^2}}\left(1-\frac{H^2}{H_{sf}^2}\right)^2\left[1+O\left(\frac{H^2}{H_{sf}^2}\varphi^2\right)\right], \tag{5}$$

where γ_e is the electron gyromagnetic ratio, $\eta=0.89$ is a phenomenological parameter,

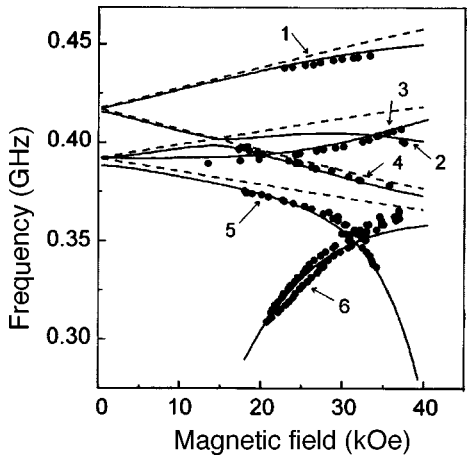

FIG. 3. ^{55}Mn NMR spectrum in $CsMnI_3$ at $T=1.3$ K and $\varphi\approx0.7°$: Dots — experiment, dashed lines — unshifted spectrum (3), solid lines — calculation using Eqs. (7) and (8).

and $\omega_{e3}(0)/2\pi = 35$ GHz is the gap in the spectrum of this mode at $H = 0$. It is easy to see that a strong dependence on the angle φ occurs only for ω_{e2}. This makes it possible to distinguish the nuclear modes associated with ω_{e2}.

Comparing Figs. 2 and 3 shows that branches *1*, *4*, and *5* remain practically unchanged, while mode *3* increases appreciably in high fields and mode *2* practically vanishes, but there appears a low-frequency branch *6* which decreases with decreasing field. We attribute the vanishing of the mode *2* to a purely instrumental effect, since the weak signal from this mode is difficult to observe against the background of a strong signal from the adjacent mode *3*. The NMR signal of mode *6* consists of two overlapping lines. We attribute this to the twinned nature of the crystal with a weak disorientation of the C_6 axis and we also believe that it attests to a strong angular dependence of the spectrum of this mode. Therefore the NMR branches *3* and *6* of nuclear spins in the B positions are related with the electronic mode ω_{e2}. This corresponds to the polarization of this mode.[12] Hence it can be concluded that the modes ω_{e2} and ω_{e3} interact independently with NMR.[b)]

To describe the DFS of the NMR we employed the equation

$$(\omega_e^2 - \omega^2) = \omega^2 \omega_T^2 \sum_i \frac{\rho_i}{\omega_{ni}^2 - \omega^2}, \tag{6}$$

where the summation extends over the ''unshifted'' ω_{ni} NMR branches interacting with ω_e, while ρ_i is the fraction of nuclear spins in the ith unshifted NMR branch among the total number of nuclei involved in the interaction. Although this equation was proposed for describing the DFS in ''triangular'' AFs with easy-plane anisotropy,[11,13] it is much more general. First, it is a natural extension of Eq. (4). Second, it describes well the DFS of NMR not only in triangular $CsMnBr_3$[11] but also in all cases of multiple-sublattice AFs known to us (four-sublattice 3D AFs $CsMnF_3$ and $CsMnCl_3$).

On this basis we obtain the NMR spectra for the branches *1*, *2*, *4*, and *5* from the equation

$$(\omega_{e3}^2 - \omega^2) = \frac{\omega^2 \omega_T^2}{6}\left(\frac{1}{\omega_{n1}^2 - \omega^2} + \frac{1}{\omega_{n2}^2 - \omega^2} + \frac{2}{\omega_{n3}^2 - \omega^2} + \frac{2}{\omega_{n4}^2 - \omega^2}\right), \tag{7}$$

and we obtain the NMR spectra for the branches *3* and *6* from the equation

$$(\omega_{e2}^2 - \omega^2) = \frac{\omega^2 \omega_T^2}{2}\left(\frac{1}{\omega_{n3}^2 - \omega^2} + \frac{1}{\omega_{n4}^2 - \omega^2}\right), \tag{8}$$

where ω_{e2} and ω_{e3} are the unshifted AFMR frequencies from Ref. 7, the coupling frequency $\omega_T/2\pi \approx 6$ GHz at $T = 1.3$ K (it is also the temperature-dependent gap in the AFMR spectrum) was obtained in Ref. 10, and ω_{ni} are the unshifted NMR frequencies from Eq. (4). The computational results are presented in Figs. 2 and 3. One can see that they describe well all modes of the NMR spectrum,[c)] for both $\varphi < 0.5°$ and $\varphi = 7°$. We have introduced the new constant $\omega_A/2\pi = 417$ MHz. Therefore we have completely described the NMR spectrum in $CsMnI_3$ with the DFS of the NMR taken into account.

From the hyperfine fields which we have obtained and the hyperfine constant $A_0 = (-1.49 \pm 0.04) \times 10^{-18}$ erg (Ref. 14), known from ESR data on Mn^{2+} in $CsMgI_3$, we

find $\langle S_A \rangle = 1.86$ and $\langle S_B \rangle = 1.74$, which is close to the value obtained from neutron scattering[8,6,15] $\langle S \rangle \approx 1.8$. The calculation in Ref. 5 gives $\langle S_A \rangle = 1.8$ and $\langle S_B \rangle = 2.0$. The difference compared with our results appears to be due to the inadequacy of the description of the magnetic properties of $CsMnI_3$ in the single-ion anisotropy model with a Hamiltonian of the form (1). The problem is that according to Ref. 5 the difference $\langle S_A \rangle - \langle S_B \rangle$ depends strongly on the ratio $|D|/J'$, changing sign at $|D|/J' \approx 1$. According to the data[15] on which this calculation was based one has $|D|/J' = 1.2$, while the AFMR data[7] imply a value $|D|/J' = 0.81 \pm 0.06$. Thus our experiment has demonstrated different spin reduction in magnetically nonequivalent Mn^{2+} chains in $CsMnI_3$, as predicted in Ref. 5; for a quantitative comparison it is necessary to improve the description of the anisotropy in substances belonging to this class.

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[a)]See Ref. 9 for a more detailed discussion of this phenomenon.
[b)]As follows from Ref. 7, these modes do not interact with one another.
[c)]In our range of fields $\omega_6/2\pi \ll 200$ MHz for $\varphi < 0.5°$.

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