New phase transition in an easy-axis ''triangular'' antiferromagnet

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The NMR of ^{55}Mn in the quasi-one-dimensional noncollinear antiferromagnet $CsMnI_3$ is investigated at $T=1.3$ K in magnetic fields up to $\sim$80 kOe and angles between the field and C_6 axis $\varphi\approx 0.5°$ and $\varphi=7°$. A new reorientational magnetic phase transition is observed in a field $H_{c1}\approx 39.0$ kOe. The magnetic structure for $H>H_{c1}$ is determined. The average Mn^{2+} spins of the magnetic sublattices in the new phase are determined from an analysis of the NMR spectrum to be $\langle S_C\rangle=1.63$ and $\langle S_D\rangle=1.72$. © *1998 American Institute of Physics.* [S0021-3640(98)00712-9]

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In recent years a great deal of attention has been devoted to the investigation of easy-axis ''triangular'' antiferromagnets (AFs) ABX_3. Among the many unusual properties of these magnets, of greatest interest is the complicated $H-T$ phase diagram ($\mathbf{H}\|C_6$) of the paramagnetic and three antiferromagnetic phases which coexist at the multicritical point (T_m, H_m)[1,2] (for $CsMnI_3$ $T_m\approx 10$ K and $H_m\approx 60$ kOe). However, the number of phases is not exhausted by four. Thus, the possible existence of one other low-temperature antiferromagnetic structure ($T<T_{N2}$) in addition to the two structures which are already known, which we shall call 1 and 2, is being actively discussed. According to the simple theory, the boundary between the phases 1 and 2 (Refs. 3 and 4) is a first-order spin-flop transition (model I). However, the jumps characteristic for a first-order phase transition are absent in the longitudinal component of the magnetization, measured in a large series of easy-axis triangular AFs, and in the magnetostriction.[5] According to Refs. 6–8, there could be a new phase which separates phase 1 from phase 2. Instead of the spin-flop transition, there arise two second-order phase transitions (model II). This model describes satisfactorily the observed behavior of the magnetization.[8] However, additional experiments are required in order to obtain a detailed picture. Since the NMR spectrum in a magnetic field is sensitive to the structure of the magnet, the magnetic phase diagram of $CsMnI_3$ can be refined with its help.

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

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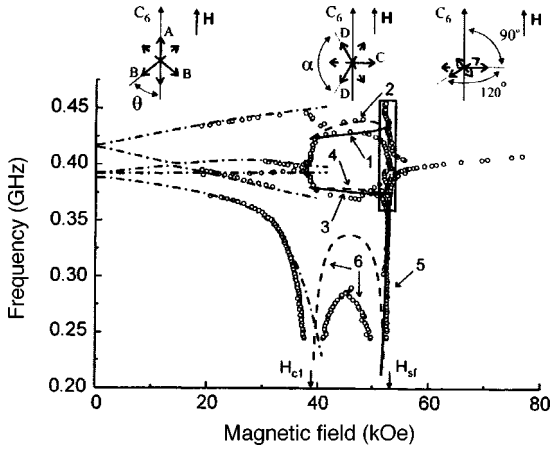

FIG. 1. The NMR spectrum of ^{55}Mn in $CsMnI_3$ for $\varphi \approx 0.5°$ and $T = 1.3$ K — open circles. Rectangle — expected region of absorption accompanying a spin-flop transition. The rest of the lines were computed (see text). Inset: Magnetic structures of $CsMnI_3$ with $\mathbf{H} \| C_6$.

the Mn^{2+} ions are crystallographically equivalent. The distance between the Mn^{2+} ions along the C_6 axis is approximately half that the basal plane. Correspondingly, the exchange constants are $J = 198$ GHz (Ref. 4) and $J' = 1$ GHz (Refs. 9 and 4). 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 the rest of the spins make an angle $\theta = 51° \pm 1°$ with it (B spins)[3,4] (see the inset in Fig. 1). All of the Mn^{2+} spins are coplanar to one plane, which we shall call the spin plane. There is no anisotropy in the hexagonal plane, so that in the presence of a magnetic field component perpendicular to the C_6 axis the normal to the spin plane is parallel to this component. If a field is applied in the hexagonal plane, then such a structure is stable. For $\mathbf{H} \| C_6$ in the field H_{sf} ($H_{sf} = 53$ kOe with $T = 1.7$ K), according to model I there occurs a spin-flop transition above which all spins turn into a position perpendicular to **H** and form an equilateral triangular structure oriented in the hexagonal plane. For an arbitrary direction of the external field relative to C_6 the spin plane rotates smoothly, so that[9]

$$\tan(2\psi) = \frac{H^2 \sin(2\varphi)}{H^2 \cos(2\varphi) - H_{sf}^2}, \tag{1}$$

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.

According to model II,[8] for $\mathbf{H} \| C_6$ there are two second-order phase transitions in the fields H_{c1} and H_{c2}. An intermediate magnetic phase, in which the spin plane rotates smoothly to the position $\psi = 0$ occurs, lies between them.

If the dynamic frequency shift (DFS) due to the interaction with low-lying AFMR modes is neglected, the spectrum ω_{ni} of the ith ^{55}Mn NMR branch[a)] is described by the simple formulas

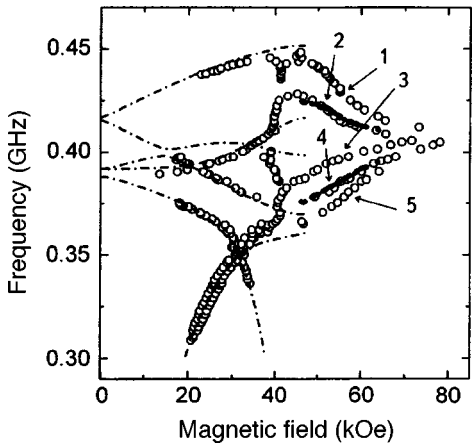

FIG. 2. The NMR spectrum of ^{55}Mn in $CsMnI_3$ for $\varphi \approx 7°$ and $T = 1.3$ K. Dot-and-dash line — calculation of the spectrum in the low-field phase,[10] filled circles— calculation of the branches *2* and *4* according to Eq. (6).

$$\frac{\omega_{ni}}{\gamma_n} = |\mathbf{H}_{ni} + \mathbf{H}|, \quad \mathbf{H}_{ni} = -\frac{A_0}{\gamma_n \hbar}\langle \mathbf{S}_i \rangle, \tag{2}$$

where $\gamma_n/2\pi = 1.06$ MHz/kOe is the gyromagnetic ratio for ^{55}Mn nuclei, H_{ni} is the hyperfine field, $\hbar$ is Planck's constant, and A_0 is the hyperfine interaction constant. The number of branches in the unshifted NMR spectrum is determined by the number of nonequivalent orientations of the ion spins in the magnetic structure with respect to the field. For $\mathbf{H} \| C_6$ the spectrum should consist of four branches which diverge as the field increases. If model I is correct, then at the spin-flop transition field the splitting of the spectrum should vanish abruptly, so that above it only one NMR branch with frequency $\omega \approx \gamma_n H_n$ should be observed. Conversely, if model II is realized, then the NMR branches will smoothly merge into a single branch in the range $H_{c1} < H < H_{c2}$.

The NMR of ^{55}Mn in $CsMnI_3$ in fields less than 40 kOe was investigated in Ref. 10, where it was shown that the DFS is strong and the NMR spectrum is described well by the solutions of equations of the form

$$(\omega_{ej}^2 - \omega^2) = \omega^2 \omega_T^2 \sum_i \frac{\rho_i}{\omega_{ni}^2 - \omega^2}, \tag{3}$$

where $\omega_{ej} = \omega_{e2}$, ω_{e3} are the AFMR modes measured in Ref. 9, the coupling frequency $\omega_T \sim T^{-1/2}$ is determined according to the temperature-dependent gap in the AFMR spectrum, the summation extends over the unshifted NMR branches ω_{ni} interacting with ω_{ej}, and ρ_i is the fraction of the nuclear spins in the ith unshifted NMR branch among the total number of nuclei involved in the interaction.

All measurements were performed in a continuous-wave wide-band NMR spectrometer, described in detail in Ref. 11, with a re-entrant resonator and frequency modulation. The spectra were obtained on single-crystal samples by passing through resonance with respect to the magnetic field at $T = 1.3$ K.

The measured NMR spectra with $\phi \approx 0.5°$ and $\phi = 7°$ are presented in Figs. 1 and 2

(open circles). In fields less than 39 kOe, five branches are observed, which, when the DFS is taken into account, correspond to the well-known low-field magnetic structure for $CsMnI_3$. The dot-and-dash line shows the calculation from Ref. 10. The splitting of the NMR spectrum in zero magnetic field, due to the fact that $\langle S_A\rangle \neq \langle S_B\rangle$, is also explained there.

In high fields two regions of rearrangement of the NMR spectrum are observed at $H_{c1} \approx 39$ kOe and $H_{sf} = 52.5$ kOe. The position of the upper feature coincides with the transition, determined according to the maximum of $d\mathcal{M}/dH$, in the high-field phase[3,2] and manifests the characteristic features of a spin-flop transition — sharp restructuring into one branch, the presence of absorption of width ~ 0.2 kOe at H_{sf} in a wide frequency range (the almost vertical branch in Fig. 1), and the existence of a feature only for small angles $\varphi \approx 0.5°$ (compare with Fig. 2). This means that for small angles φ the rotation of the spin plane to a position perpendicular to the external field occurs abruptly, i.e., model I is realized.

A sharp restructuring of the NMR spectrum occurs near 39 kOe, indicating a change in the angles between the Mn^{2+} spins and the external field. Above the transition the top three branches in Fig. 1 continue to diverge from one another, i.e., rotation of the spin plane does not occur. For this reason, it is natural to suppose that the feature observed at H_{c1} is due to reorientation within the spin plane. The behavior of the lowest NMR branch, which as $H \to H_{c1}$ becomes softer more rapidly than follows from the calculation (the dot-and-dash curve in Fig. 1), serves as an additional argument in favor of this conjecture. This means that the AFMR mode associated with it has the behavior $\omega_{e3} \to 0$ as $H \to H_{c1}$. This is the mode that determines the oscillations in the spin plane.

In the presence of a triangular spin structure in the spin plane, there are only two possible configurations that are symmetric with respect to **H**: The spins in one of the three AF chains are either parallel to the C_6 axis (the phase 1 structure) or perpendicular to it (see Fig. 1). We assumed that the latter configuration is realized for $H > H_{c1}$, and we checked its compatibility with the observed NMR spectrum. In this case, the unshifted NMR spectrum should consist of three twofold degenerate branches, whose frequencies in an approximation linear in H/H_n (the designations C and D correspond to the inset in Fig. 1) are given by

$$\frac{\omega_{n1,2}}{\gamma_n} = H_{nD}\left[1 \pm \frac{H}{H_{nD}}\sin(\alpha/2)\sin(\psi-\varphi)\right], \quad \frac{\omega_{n3}}{\gamma_n} = H_{nC}, \tag{4}$$

where α is the angle between the directions of the neighboring AF chains D. The interaction with low-lying AFMR modes ω_{e2} and ω_{e3} lifts the degeneracy present in the unshifted spectrum, and when the DFS is taken into account, the NMR frequencies are roots of the two independent equations

$$(\omega_{e2,3}^2 - \omega^2) = \frac{\omega_T^2}{3}\sum_{i=1}^{3}\frac{\omega^2}{\omega_{ni}^2 - \omega^2}, \tag{5}$$

Let us analyze first the NMR spectrum at $\varphi \approx 7°$. For this angle $\omega_{e2}^2 \gg \omega_T^2$ in fields greater than 40 kOe,[9] and the DFS is negligibly small for the NMR branches interacting with this mode. They can be easily indentified, since the interaction always decreases the NMR frequency by an amount less than the distance to the neighbors of the unshifted branch.

For this reason, branches *1*, *3*, and *5* (see Fig. 2) should be described quite accurately by formulas (4), while the rest of the branches can be found from the solutions of Eq. (5) with ω_{e3}. The result of Ref. 9 can be used to estimate ω_{e3} for $H>H_{sf}$: $\omega_{e3}^2 \sim \omega_{e3}^2(0)\varphi^6 \ll \omega_T^2$. Under this condition one of the solutions of Eq. (5) is small, $\omega_6^2 \ll \omega_n^2$, and the equation for the two remaining nuclear modes assumes the form

$$\sum_{i=1}^{3} \frac{1}{\omega_{ni}^2 - \omega^2} \approx 0. \tag{6}$$

Knowing the field dependences of ω_{ni} from experiment (branches *1*, *3*, *5*), one can check whether this relation is satisfied for branches *2* and *4* without using any additional constants. The result of such a recalculation is shown by in Fig. 2 (filled dots). One can see that there is good agreement with the experimental data, which attests to the validity of the model we have chosen for the magnetic structure.[b)] Likewise, we can determine from our experimental data $H_{nC}=\omega_3/\gamma_n \approx 365$ kOe and $H_{nD}=(\omega_1+\omega_5)/2\gamma_n \approx 385$ kOe. The angle α can be estimated from the maximum absorption frequency at H_{sf} from the formula $\omega_{\max,\min}=\gamma_n|H_n \pm H \sin \alpha/2|$. We obtain $\alpha \approx 120°$, i.e., the spin structure is close to an equilateral triangular structure. Knowing α and φ, we determined the field dependence of the rotation angle ψ of the spin plane. It turned out that it is described well by formula (1), i.e., the character of the rotation of the spin plane for $\varphi \approx 7°$ corresponds to model I. From the values we determined for the hyperfine fields, and with the value of the hyperfine constant $A_0=(-1.49\pm 0.04)\times 10^{-18}$ ergs,[12]) known from data on the ESR of Mn^{2+} in $CsMnI_3$, we obtain $\langle S_C \rangle = 1.63$ and $\langle S_D \rangle = 1.72$.

Let us now return to the NMR spectrum for $\phi \approx 0.5°$. The calculation of the spectrum taking into account the interaction with the AFMR mode ω_{e2}, using the values which we obtained for H_{nC}, H_{nD}, and α and with $\psi(H)$ calculated according to Eq. (1), is presented in Fig. 1 (solid lines). One can see that it describes branches *1*, *3*, and *5* quite well. To calculate the rest of the branches it is necessary to know ω_{e3}. Unfortunately, there are no low-frequency experimental data for this mode in $CsMnI_3$. However, it is evident from the behavior of ω_6 that the frequency ω_{e3} is close to zero at both phase transition points. We took the very simple field dependence satisfying this condition,

$$\omega_{e3}^2 = \omega_{e3}^2(0)\left|\left(1-\frac{H^2}{H_{c1}^2}\right)\left(1-\frac{H^2}{H_{sf}^2}\right)\right|. \tag{7}$$

Using Eq. (7), we obtained qualitative agreement with the frequencies of the rest of the NMR branches without introducing new constants (dashed line in Fig. 1).

Thus, it follows from our results that in $CsMnI_3$ with $\mathbf{H} \| C_6$ there exists an intermediate magnetic structure between the two known low-temperature phases. In this phase the normal to the spin plane is perpendicular to the hexagonal axis, while the spins form a close to 120-degree triangular structure, so that one-third of the spins are directed perpendicular to C_6. This reorientational transition also exists when the vector $\mathbf{H}$ tilts substantially away from C_6 ($\varphi \approx 7°$). The transition from the new phase into the high-field phase 2 exhibits the characteristic features of a spin-flop transition.

The nature of the phase transition at H_{c1} remains unclear (we do not rule out the possibility of a double transition). The phase which we have discovered does not correspond to the magnetic structures calculated in Refs. 6–8. We believe that in order to

explain it, it will be necessary to take into account the reduction of the Mn^{2+} spins. There also arises the question of a possible increase in the order of the multicritical point in the $H-T$ phase diagram of $CsMnI_3$.

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[a)]This will be referred to below as the unshifted frequency.
[b)]We were unable to describe the NMR spectrum under the condition that the low-field phase *1* is preserved in the region $H_{c1}<H<H_{sf}$.

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