JETP LETTERS VOLUME 69, NUMBER 1 10 JANUARY 1999

On the NMR spectrum in antiferromagnetic $CsMnI_3$

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(Submitted 1 December 1998)
Pis'ma Zh. Éksp. Teor. Fiz. **69**, No. 1, 41–45 (10 January 1999)

An explanation is proposed for the spin-reduction anisotropy observed in an investigation of NMR in the noncollinear six-sublattice antiferromagnet $CsMnI_3$. © *1999 American Institute of Physics.* [S0021-3640(99)00901-9]

PACS numbers: 75.50.Ee, 33.25.+k

In exchange-interaction magnets, relativistic effects lead to a definite orientation of the spin structure with respect to the crystal axes and to weak distortions of the relative orientation of the sublattices — weak ferromagnetism[1–3] or weak (additional) antiferromagnetism[2] (see the case of Cr_2O_3). In Ref. 4 relativistic distortions of a new type, which the authors termed spin-reduction anisotropy, were found in the noncollinear antiferromagnet $CsMnI_3$. In the present letter, a description of this phenomenon is given on the basis of the theory of exchange symmetry.[5]

The relative orientation of the sublattices in $CsMnI_3$ is shown in Fig. 1. Following Dzyaloshinskiĭ,[2] we introduce instead of the six sublattices their linear combinations

$$\begin{aligned}
\mathbf{M}&=\mathbf{M}_1+\mathbf{M}_2+\mathbf{M}_3+\mathbf{M}_4+\mathbf{M}_5+\mathbf{M}_6,\\
\mathbf{L}&=\mathbf{M}_1+\mathbf{M}_2+\mathbf{M}_3-\mathbf{M}_4-\mathbf{M}_5-\mathbf{M}_6,\\
\mathbf{L}_1&=\mathbf{M}_1-\frac{1}{2}(\mathbf{M}_2+\mathbf{M}_3)-\mathbf{M}_4+\frac{1}{2}(\mathbf{M}_5+\mathbf{M}_6),\\
\mathbf{L}_2&=\frac{\sqrt{3}}{2}(\mathbf{M}_2-\mathbf{M}_3)-\frac{\sqrt{3}}{2}(\mathbf{M}_5-\mathbf{M}_6),\\
\mathbf{L}_3&=\mathbf{M}_1-\frac{1}{2}(\mathbf{M}_2+\mathbf{M}_3)+\mathbf{M}_4-\frac{1}{2}(\mathbf{M}_5+\mathbf{M}_6),\\
\mathbf{L}_4&=\frac{\sqrt{3}}{2}(\mathbf{M}_2-\mathbf{M}_3)+\frac{\sqrt{3}}{2}(\mathbf{M}_5-\mathbf{M}_6),
\end{aligned}\tag{1}$$

which transform according to one-dimensional $\mathbf{M},\mathbf{L}$ and two-dimensional $(\mathbf{L}_1,\mathbf{L}_2),(\mathbf{L}_3,\mathbf{L}_4)$ representations of the group of permutations of the sublattices realized by the crystal transformations of the symmetry group D_{6h}^4 of the crystal. In the exchange approximation, in $CsMnI_3$ the antiferromagnetism vectors $(\mathbf{L}_1,\mathbf{L}_2)$ are nonzero; in addition, they are equal in modulus and perpendicular to each other, in agreement with the

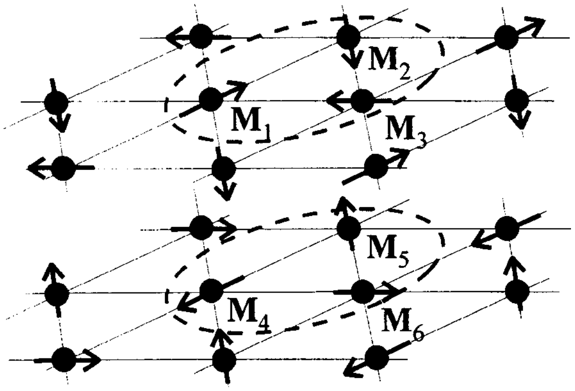

FIG. 1.

general requirements of exchange symmetry.[5] Analysis of the quadratic relativistic invariants shows that the remaining spin vectors do not arise in the structure as an effect due to weak ferromagnetism **M** or weak antiferromagnetism **L**, $(\mathbf{L}_3,\mathbf{L}_4)$. It is found that the distortions of the spin structure that were found in Ref. 4 reduce to breakdown of the exchange condition — the equality of the moduli of the vectors $(\mathbf{L}_1,\mathbf{L}_2)$. This effect arises for the following reasons.

The exchange energy of a structure with arbitrary magnitudes and relative orientation of the spin vectors $\mathbf{L}_1,\mathbf{L}_2$ is a function of the form

$$E\{\mathbf{L}_1^2+\mathbf{L}_2^2,\quad 4(\mathbf{L}_1\cdot\mathbf{L}_2)^2+(\mathbf{L}_1^2-\mathbf{L}_2^2)^2\}. \tag{2}$$

We introduce as the variables characterizing the magnitudes and relative orientation of the vectors $\mathbf{L}_1,\mathbf{L}_2$ the parameters ξ, ζ, and ϕ, defined as

$$L_1=\xi\cos\zeta,\quad L_2=\xi\sin\zeta,\quad \mathbf{L}_1\cdot\mathbf{L}_2=L_1L_2\cos\phi. \tag{3}$$

The minimum of the exchange energy in $CsMnI_3$ corresponds to the value $\xi=\xi_0$ and

$$\zeta=\pi/4,\quad \phi=\pi/2. \tag{4}$$

Near this minimum the exchange energy is a positive-definite quadratic form with respect to small deviations:

$$\mathrm{const}+C_1[4(\delta\zeta)^2+(\delta\phi)^2]+C_2(\delta\xi)^2. \tag{5}$$

The anisotropy energy of first-order in $(v/c)^2$ reduces to the invariant

$$-B(L_{1z}^2+L_{2z}^2)/2. \tag{6}$$

As a result of this term, the vectors $\mathbf{L}_1,\mathbf{L}_2$ will differ from the values $\mathbf{L}_1^0,\mathbf{L}_2^0$ of the exchange approximation (3) and (4) by some amount $\delta\mathbf{L}_1,\delta\mathbf{L}_2$. The term in the anisotropy energy (6) that is linear in these deviations has the form

$$-B(L_{1z}^0\delta L_{1z}+L_{2z}^0\delta L_{2z}). \tag{7}$$

In $CsMnI_3$ in the ground state the spin plane is perpendicular to the basal plane of the crystal (the anisotropy constant B is positive). The orientation of the sublattices in the

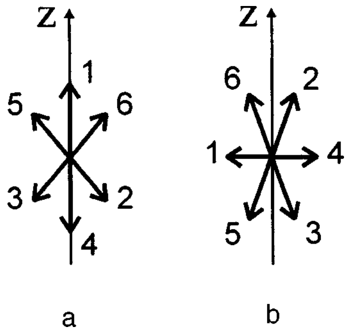

FIG. 2. Distortions of the exchange structure by anisotropy in $CsMnI_3$.

spin plane and the azimuthal orientation of the spin plane itself are fixed by the sixth-order anisotropy energy.[6] In the presence of a magnetic field directed along a symmetry axis of the crystal, the following three orientational states are observed:[7,8] In fields below $H_{c1}=39$ kOe — the phase I ($L_{1z}^0=L_1^0, L_{2z}^0=0$, Fig. 2a); in the interval $H_{c1}<H<H_c=52.5$ kOe — the phase II ($L_{1z}^0=0, L_{2z}^0=L_2^0$, Fig, 2b); and, for $H>H_c$ — the phase III ($L_{1z}^0=L_{2z}^0=0$, Fig. 1).

Minimizing the sum of expressions (5) and (7), we find that in each phase the vectors $(\mathbf{L}_1, \mathbf{L}_2)$ remain orthogonal ($\delta\phi=0$) and that

$$\begin{array}{lll} \text{phase I:} & \delta\zeta=-A_1, & \delta\xi=A_2\xi_0, \\ \text{phase II:} & \delta\zeta=A_1, & \delta\xi=A_2\xi_0, \\ \text{phase III:} & \delta\zeta=0, & \delta\xi=0, \end{array} \tag{8}$$

where the constants $A_1=B\xi_0^2/16C_1$ and $A_1=B/4C_2$ are positive.

Therefore the easy-axis anisotropy can lead to $L_1^2\neq L_2^2$ and to an increase in the squared order parameter $L_1^2+L_2^2$. In the general case, evidently, relativistic effects can also destroy the orthogonality of the antiferromagnetism vectors. In $CsMnI_3$ the exchange interaction between the nearest neighbors along the z axis is much greater than exchange in the basal plane.[9] It is easy to show that this leads to $C_2\gg C_1/\xi_0^2$, so that when comparing with experiment we neglect the contribution of A_2.

Inverting the system (1) with respect to the magnetizations of the sublattices with allowance for the uniform magnetization in the external magnetic field, we obtain

$$\mathbf{M}_j=\frac{1}{6}\mathbf{M}+\frac{1}{3}\{\mathbf{L}_1\cos(\mathbf{Q}\cdot\mathbf{r}_j)+\mathbf{L}_2\sin(\mathbf{Q}\cdot\mathbf{r}_j)\}, \quad \mathbf{Q}=\left(\frac{4\pi}{3a}, 0, \frac{\pi}{c}\right), \tag{9}$$

where a and c are the periods of the crystal lattice. Up to terms linear in the magnetic field, we obtain in the phase I

$$M_1=M_0\left(1+A_1+\frac{H}{H_E'}\right), \quad \cos\alpha_1=1,$$

$$\begin{aligned} &M_{2,3}=M_0\left(1-\frac{1}{2}A_1-\frac{1}{2}\frac{H}{H_E'}\right), \quad \cos\alpha_{2,3}=-\frac{1}{2}-\frac{3}{4}A_1+\frac{3}{4}\frac{H}{H_E'},\\ &M_4=M_0\left(1+A_1-\frac{H}{H_E'}\right), \quad \cos\alpha_4=-1,\\ &M_{5,6}=M_0\left(1-\frac{1}{2}A_1+\frac{1}{2}\frac{H}{H_E'}\right), \quad \alpha_{5,6}=\frac{1}{2}+\frac{3}{4}A_1+\frac{3}{4}\frac{H}{H_E'}, \end{aligned} \tag{10}$$

where $H_E'=M_0(N_A/\chi_\perp)\approx 4\times 10^3$ kOe, N_A is Avogadro's number, $\chi_\perp$ is the magnetic susceptibility in the spin plane; we used the value $\chi_\perp=0.75\times 10^{-2}$ cgs units/mole from Ref. 9; α_j is the angle between the magnetization of the jth sublattice and the z axis. In the phase II

$$\begin{aligned} &M_{1,4}=M_0(1-A_1), \qquad \cos\alpha_{1,4}=\frac{H}{H_E'}\\ &M_{2,6}=M_0\left(1+\frac{1}{2}A_1+\frac{\sqrt{3}}{2}\frac{H}{H_E'}\right), \quad \cos\alpha_{2,6}=\frac{\sqrt{3}}{2}+\frac{\sqrt{3}}{4}A_1+\frac{1}{4}\frac{H}{H_E'},\\ &M_{3,5}=M_0\left(1+\frac{1}{2}A_1-\frac{\sqrt{3}}{2}\frac{H}{H_E'}\right), \quad \cos\alpha_{3,5}=-\frac{\sqrt{3}}{2}-\frac{\sqrt{3}}{4}A_1+\frac{1}{4}\frac{H}{H_E'}. \end{aligned} \tag{11}$$

The structural distortions under discussion are shown schematically in Fig. 2. In phase III the magnetizations of all sublattices are M_0, and $\cos\alpha_j = H/H_E$, where $H_E = M_0(N_A/\chi_\parallel)^2 \approx 2\times 10^3$ kOe and $\chi_\parallel$ is the electronic magnetic susceptibility along the normal $\mathbf{n}$ to the spin plane.

Neglecting relaxation, the dynamics of the nuclear sublattice reduces[10,11] to the dynamics of a ferromagnet in an effective field. Therefore the Lagrangian of the low-frequency spin dynamics of the antiferromagnet $CsMnI_3$ will be the sum of the Lagrangian of a noncollinear antiferromagnet[5] and six Lagrangians of the nuclear sublattices coupled by the hyperfine interaction:

$$\frac{\chi_\perp}{2\gamma^2}(\mathbf{\Omega}+\gamma\mathbf{H})^2+\frac{\chi_\parallel-\chi_\perp}{2\gamma^2}(\mathbf{n}\cdot(\mathbf{\Omega}+\gamma\mathbf{H}))^2-\mathcal{U}_a+\frac{1}{6}\sum_{j=1}^{6}\mathbf{m}_j\cdot\left(\frac{\mathbf{\Omega}_{nj}}{\gamma_n}-A\mathbf{M}_j+\mathbf{H}\right), \tag{12}$$

where $\mathbf{\Omega}$ is the angular velocity of the electronic spin rotations; $\mathbf{\Omega}_{nj}$ is the angular velocity of the spin rotations of the nuclei in the jth sublattice; χ_n is the susceptibility of the nuclei; γ and γ_n are the electronic and nuclear gyromagnetic ratios; A is the hyperfine interaction constant; $\mathbf{m}_j$ is the magnetization of the jth nuclear sublattice, and its equilibrium value is $\chi_n(-A\mathbf{M}_j+\mathbf{H})$.

When the spin plane is normal to the basal plane of the crystal, the energy $\mathcal{U}_a$ reduces to the expression $f(H)\cos 6\varphi$, $f(H)=b_1+b_3H^2+b_4H^4+b_5H^6$, where φ is the angle between the vector $\mathbf{L}_1$ and the z axis. Since the function $f(H)$ changes sign in the field H_{c1},[8] it is convenient to introduce a different representation

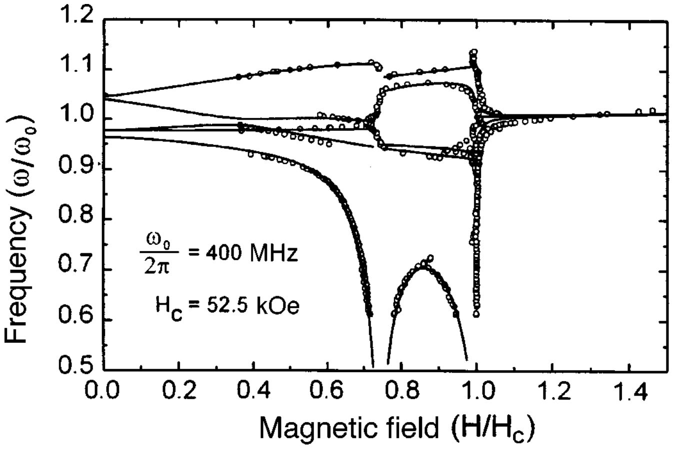

FIG. 3. NMR spectrum in CsMnI$_3$. The experimental data are taken from Ref. 7 at temperature 1.3 K.

$$f(H)=b_1\left[1-\left(\frac{H}{H_{c1}}\right)^2\right]\left[1+k_1\left(\frac{H}{H_c}\right)^2+k_2\left(\frac{H}{H_c}\right)^4\right]. \tag{13}$$

This function determines the field dependence of the AFMR frequency associated with oscillations of the angle φ. The constants b_1 (associated with the zero-field frequency) and $k_1=-1.7$ can be determined from the experimental data of Ref. 6; the contribution of the term $\propto k_2$ is small in the frequency range investigated in Ref. 6. The constant A_1 determines the zero-field splitting of the NMR frequencies:

$$\frac{\omega_1-\omega_2}{\omega_1}=\frac{M_1-M_2}{M_1}\approx\frac{3}{2}A_1. \tag{14}$$

According to the experimental data of Ref. 4, $\omega_1/2\pi=417$ MHz and $\omega_2/2\pi=390$ MHz, whence $A_1=0.045$.

The magnetic resonance spectrum described by the Lagrangian (12) consists of three AFMR branches (see Refs. 6 and 10) and six NMR branches. Five NMR branches for the values taken above for the parameters of the theory and for the two remaining adjustable parameters $\gamma_n A M_0/2\pi=\omega_0/2\pi=400$ MHz and $k_2=0.71$ are presented in Fig. 3. The frequency of the sixth branch neglecting in-plane anisotropy is zero.

We note that the function $f(H)$ for the indicated values of the parameters k_1 and k_2 vanishes in a field slightly above H_c, i.e., the system is accidentally close to a spin-flop transition from the phase II to the phase I as H_c is approached.

This work was partially supported by Grant No. 98-02-16572 from the Russian Fund for Fundamental Research.

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Translated by M. E. Alferieff