Investigation of the relativistic antiferromagnetic resonance branches of CsMnI₃, an easy-axis one-dimensional antiferromagnet

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Experimental and theoretical investigations of the antiferromagnetic resonance spectrum of CsMnI₃, a quasi-one-dimensional hexagonal antiferromagnet with noncollinear spin ordering, are described. We demonstrate here that the three relativistic resonance branches we observed are all well described by spin-wave theory. We construct a phenomenological theory for magnetic resonance in a hexagonal antiferromagnet with a strong easy-axis anisotropy, and discuss how to determine the constants in the microscopic Hamiltonian from the available experimental data.

1. INTRODUCTION

The problem of how to adequately describe the spin dynamics of quasi-one-dimensional antiferromagnets with exchange-mediated noncollinear spin ordering using the standard theory of spin waves has a history which, although recent, is quite fascinating.

In 1983, Haldane[1] put forward a hypothesis about an unusual quantum effect: the existence of a gap in the spectrum of quantum excitations of a one-dimensional isotropic antiferromagnetic chain with integer-valued spin. Immediately after the publication of Ref. 1, an intense experimental search was undertaken to find real physical systems that might confirm this theory. Nowadays, the consensus is that the Haldane gap has been observed with some degree of confidence only in the compound Ni(C₂H₈N₂)NO₂ClO₄, abbreviated NENP. Neutron inelastic scattering and electron spin resonance data, measurements of the magnetization in strong magnetic fields, and other experiments, all attest to the validity of this statement. Apparently, NENP is an almost ideal material for investigating the one-dimensional spin chain, as its interchain exchange interactions are so small that three-dimensional magnetic ordering is not observed down to the lowest temperatures.

Other materials in which Haldane's theory could be verified are CsNiCl₃ and RbNiCl₃, which are hexagonal antiferromagnets with the so-called triangular structure. In contrast to NENP, rather strong interchain interactions in these antiferromagnets lead to long-range magnetic order as the temperature is lowered (T_N=4.4 K for CsNiCl₃ and T_N=11.1 K for RbNiCl₃). In both of these compounds the Ni ion has unit spin. One of the most productive methods for investigating the excitation spectra of a spin system is inelastic neutron scattering; for this reason, it is not surprising that a large number of neutron-scattering studies of these antiferromagnets have appeared recently.[2] The definite assertions that are characteristic of articles with titles such as "Direct Observation of the Haldane Gap" have gradually been replaced by cautious discussions of the possibility of interpreting data obtained as indirect confirmation of the existence of such a gap. In any case, it has become clear that the standard theory of spin waves, which is based on the Hamiltonian

$$\hat{H} = 2J \sum_{\langle i,j \rangle}{}' S_i S_j + 2J' \sum_{\langle i,j \rangle}{}'' S_i S_j + D \sum_i (S_i^z)^2$$

$$- H \sum_i S_i, \qquad (1)$$

(the sign ′ next to the summation sign denotes summation over nearest neighbors along a chain, while the sign ″ denotes summation in the basal plane) does not describe the dispersion of magnetic excitations in the ordered phases in CsNiCl₃ and RbNiCl₃. The disagreement with spin-wave theory is interpreted either in terms of Haldane's hypothesis, as Affleck[3] has stated, or in terms of geometric frustration of the triangular spin lattice, as Plumer and Caille have claimed.[4]

Experiments with CsMnI₃, which has the same magnetic structure as CsNiCl₃ but involves half-integral spins S=5/2, could clarify this situation and answer the question of what is causing the disagreement with spin-wave theory—geometric peculiarities of the structure or quantum effects. The half-integral spin excludes any possibility that the phenomena observed in this system are connected with a Haldane gap. Based on their neutron-diffraction study of CsMnI₃, Harrison et al.[5] concluded that the spectrum of magnetic excitations in this compound is rather well-described by the linear spin-wave theory for a certain choice of constants in the Hamiltonian J, J', and D. However, there are two problems with this: first, some important features of the spectrum could not be explained by this theory; and secondly, the values of J, J', and D obtained give incorrect values for certain measured physical quantities, i.e., the spin-flop field and the angle of deviation of the spins from the hexagonal axis. As the authors themselves acknowledge, their work requires continuation. We

have saved a detailed discussion of their results to the section labeled "Discussion."

Despite these problems, it has been established that the magnetic field dependence of the resonance frequencies of $CsNiCl_3$ and $RbNiCl_3$ is very well described by spin-wave theory for the low-lying relativistic branches of the spectrum.[6] The values of J, J', and D obtained by comparing the theory with data from resonance measurements have been used to calculate the frequency of the exchange branches of the spectrum. The fact that the values obtained in this way for $\omega(k=0)$ deviate significantly from the experimental results can be interpreted as a consequence of Haldane-like behavior of the system.

The goals of our work were the experimental investigation of the relativistic branches of the antiferromagnetic resonance spectrum in $CsMnI_3$, the construction of a theory that adequately describes all the observed resonance branches, and calculation of the frequencies of the exchange branches of the spectrum $\omega_{ex}(k=0)$. After carrying out this program, as will become clear, we have concluded that the spin dynamics of $CsMnI_3$ can be described by the Hamiltonian (1), possibly with some modification [see (1) and (22)].

2. THEORY

The theory of the low-lying branches of the magnetic resonance spectrum in easy-axis triangular antiferromagnets has been described previously in Refs. 7–9. For noncollinear structures formed by the exchange interaction, there exist three spin-wave branches in general, whose activated character is related to relativistic anisotropy or an external magnetic field. Zaliznyak et al.[7] have calculated the magnetic resonance frequencies for two of the so-called "acoustic" modes in terms of a macroscopic theory.[7]

Using the macroscopic theory of magnet dynamics[10], it is possible to obtain the spectrum of long-wavelength low-frequency oscillations in an arbitrary magnetic field very simply, starting only from general symmetry principles applied to the magnetic ordering, without making any special assumptions of the sort that are unavoidable in model calculations. However, to first order in v^2/c^2 the energy anisotropy used in Ref. 7 has a degenerate character. This implies that one of the resonance frequencies (ω_3) is always equal to zero.

Extending the range of frequencies under study beyond that investigated in Ref. 7 quickly leads to the observation of yet another spectral line, and with it the question of how to describe it theoretically.[8,9] Both the calculations given in Refs. 8 and 9 were carried out at $T=0$ in the mean-field approximation using the Hamiltonian (1), under the assumption that (1) can give a satisfactory description of quasi-one-dimensional antiferromagnets. Nevertheless, the expressions obtained in these papers for the frequency $\omega_3(H)$ are different (to show this, it is necessary to identify the smallest root after expanding all coefficients in the small parameter $D/3J'$ rather than solving the corresponding dispersion relation numerically as was done in Ref. 8).

In order to calculate the dependence of the resonance frequencies on the magnitude and direction of the magnetic field, we will apply the phenomenological theory of Ref. 10.

The exchange symmetry of the magnetic structure of $CsMnI_3$, like that of $CsNiCl_3$ and $RbNiCl_3$ and many other quasi-one-dimensional hexagonal antiferromagnets, is specified by introducing two orthogonal unit pseudovectors that transform according to a single irreducible representation:

$$S \sim A \exp(i\mathbf{k}\mathbf{r}) + A^* \exp(-i\mathbf{k}\mathbf{r}), \quad A = l_1 + il_2,$$

$$\mathbf{k} = \left(\frac{4\pi}{3a}, 0, \frac{\pi}{c}\right). \tag{2}$$

In the absence of a magnetic field, all the spins lie in a plane perpendicular to the vector $\vec{n} = (\vec{l}_1 \times \vec{l}_2)$. The dynamics of the antiferromagnet is determined by the Lagrange function:

$$L = \frac{\chi_\perp}{2\gamma^2}(\mathbf{\Omega} + \gamma\mathbf{H})^2 + \frac{\eta\chi_\perp}{2\gamma^2}(\mathbf{n}, \mathbf{\Omega} + \gamma\mathbf{H})^2 - U_a, \tag{3}$$

where $\eta = (\chi_\parallel - \chi_\perp)/\chi_\perp$; here γ is the gyromagnetic ratio, $\mathbf{\Omega}$ is the angular velocity of rotation in spin space, and U_a is the potential energy of magnetic anisotropy.

In order to derive equations of motion it is necessary to parametrize the group of spin rotations (see Ref. 10). It is simpler to proceed directly to linearized equations of motion, using the following expansion up to terms of second order in the small angle of rotation θ for the law of transformation of an arbitrary spin vector σ and the angular velocity $\mathbf{\Omega}$:

$$\sigma = \sigma_0 + (\theta\sigma_0) + \frac{1}{2}[\theta(\theta\sigma_0)], \quad \mathbf{\Omega} = \dot{\theta} + \frac{1}{2}(\theta\dot{\theta}). \tag{4}$$

Varying the Lagrange function L with respect to $\dot{\theta}$ and θ, we obtain equations for small vibrations around the equilibrium position.

To first order in v^2/c^2, the relativistic interaction terms reduce to a single invariant $A_x^* A_x \sim l_{1x}^2 + l_{2x}^2$, in equivalent form, $U_a = an_x^2/2$. The easy-axis nature of the structure implies $a > 0$. In this case, an external magnetic field H_c ($H_c^2 = a/\eta\chi_\perp$) applied along the symmetry axis z causes flipping of the sublattices, so that the spins lie in the basal plane of the crystal. For $H < H_c$ ($\mathbf{H} \parallel \hat{z}$) there is only one resonant branch with frequency[7]

$$\omega_1^2(H) = \gamma^2(\eta H_c^2 + H^2). \tag{5}$$

In fields that exceed the spin-flop field, or for $\mathbf{H}$ inclined to the $\hat{z}$-axis, a second resonant branch $\omega_2(H)$ appears that reduces to zero at $H=0$ (see Ref. 7 and below). Correcting the anisotropy energy to second order in v^2/c^2 in L does not change these results qualitatively: $\omega_3(H) \equiv 0$, $\omega_2(0) = 0$.

A preferred orientation for the vectors l_1 and l_2, and consequently for the spins with respect to the crystallographic axes, emerges only in terms of sixth order in the components of the vector $\mathbf{A}$:

$$(A_x + iA_y)^6 + (A_x - iA_y)^6 + (A_x^* + iA_y^*)^6 + (A_x^* - iA_y^*)^6, \tag{6}$$

$$A_z^6 + A_z^{*6} = 2(l_{1z}^6 - 15l_{1z}^4 l_{2x}^2 + 15l_{1z}^2 l_{2x}^4 - l_{2x}^6). \tag{7}$$

The first invariant that distinguishes a direction for the vector $\mathbf{n}$ in the basal plane of the crystal leads to a nonzero value of $\omega_2(0)$. Since the experimental value is $\omega_2(0) = 0$, we will neglect this anisotropy in what follows.

The invariant (7) orients the triangular spin structure in a plane passing through the axis of symmetry, and creates a gap at zero field for the third resonance branch. Such anisotropy energies arise as a result of spin-orbit interactions between the angular momentum density (2) and the electric crystal field. Such interactions are not included in model (1). However, the same sort of anisotropy (7) appears when we go from the Hamiltonian (1) to the macroscopic level, taking into account the deviation of the spins from the ideal 120° structure.

In addition to (7), the following invariants are also responsible for orienting the vectors $\mathbf{l}_1$ and $\mathbf{l}_2$ in a magnetic field:

$$A_z^4(\mathbf{AH})^2 + A_z^{*4}(\mathbf{A^*H})^2, \quad A_z^2(\mathbf{AH})^4 + A_z^{*2}(\mathbf{A^*H})^4,$$

$$(\mathbf{AH})^6 + (\mathbf{A^*H})^6. \tag{8}$$

Formally, they correspond to a lower order of expansion in the anisotropy energy in powers of the v^2/c^2. However, because the spin-flop field satisfies $H_c^2 \sim D \sim v^2/c^2$ for $H \ll H_c$, their energy is comparable to the energy (7).

Let us denote the phenomenological constants with which the invariants (7) and (8) enter into the Lagrangian by $g_i/12$. Then $g_1 > 0$ holds, i.e., according to neutron scattering data, one of the three pairs of sublattices is directed along the $\hat{z}$-axis when $H = 0$.

From the Lagrange equations, to first order in g_i we obtain the following expression for the frequency of the third resonant branch:

$$\omega_3^2(H) = \frac{\gamma^2}{\chi_\perp} \frac{6\eta}{1+\eta} \frac{H_c^2 - H^2}{\eta H_c^2 + H^2} (g_1 + g_2 H^2 + g_3 H^4 + g_4 H^6). \tag{9}$$

As is clear from (9), the behavior of $\omega_3(H)$ is in general quite arbitrary.

For a spin system described by the Hamiltonian (1), the phenomenological parameters predicted by the symmetry approach are connected with one another in a definite way. Thus, at $T = 0$ the form of (1) for a system of classical spins[8,9] requires $\chi_\perp = 1/16J$, $a = D$, and $\eta = 1$. In order to find the function $\omega_3(H)$ it is most important to establish relations between the parameters g_i.

The strongest interaction in (1) is exchange along the c_6 axis. Therefore, neglecting the contribution to the susceptibility from interchain exchange, let us introduce an individual antiferromagnetic vector for each chain. Then the energy of a chain in a magnetic field coincides with the corresponding expression for an ordinary two-sublattice antiferromagnet. Each elementary magnetic cell contains three chains; omitting terms of order J'^2/J, D^2/J, we find for these chains:

$$E = -2JS^2 + 2J'S^2[\cos(\alpha - \beta) + \cos(\alpha - \gamma)$$

$$+ \cos(\beta - \gamma)] - \frac{H^2}{48J}(\sin^2 \alpha + \sin^2 \beta + \sin^2 \gamma)$$

$$- \frac{DS^2}{3}(\cos^2 \alpha + \cos^2 \beta + \cos^2 \gamma), \tag{10}$$

where α, β, γ are angles formed by the antiferromagnetic vectors of the chain and the $\hat{z}$-axis. For $H = 0$ and $D = 0$ the angles between the magnetizations of neighboring ions along the basal plane (i.e., $\alpha - \beta$, $\alpha - \gamma$, and $\beta - \gamma$) equal 120°. It is clear from (10) that the deviation of the spins from an ideal structure, and the anisotropy energy with them, depend only on the parameter

$$\lambda = \frac{DS^2}{3} - \frac{H^2}{48J}. \tag{11}$$

In the spin-flop field H_c, which in the model (1) equals $H_c^2 = 16DJS^2$, we find that $\lambda = 0$ and the anisotropy of the form $(7) + (8)$ drops out of the energy (10). Minimizing (10) with respect to β and γ, we obtain in third-order perturbation theory with respect to λ:

$$E^{(3)} = -\frac{D^3 S^2}{216J'^2} \left(1 - \frac{H^2}{H_c^2}\right)^3 \cos 6\alpha. \tag{12}$$

Comparing (7) and (8) with our expressions, we find that

$$g_1 = \frac{D^3 S^2}{36J'^2}, \quad g_2 = -\frac{3g_1}{H_c^2}, \quad g_3 = \frac{3g_1}{H_c^4}, \quad g_4 = -\frac{g_1}{H_c^6}, \tag{13}$$

while Eq. (9) for $\omega_3(H)$ acquires the form:

$$\omega_3^2(H) = \gamma^2 \frac{6\eta g^2}{1+\eta} \frac{H_c^2 - H^2}{\eta H_c^2 + H^2} \left(1 - \frac{H^2}{H_c^2}\right)^3,$$

$$g = \frac{2DS}{3J'}\sqrt{DJ},$$

$$\frac{\omega_3(0)}{\omega_1(0)} = \frac{g}{H_c}\sqrt{\frac{6}{\eta(1+\eta)}} = \frac{D}{J'\sqrt{6\eta(1+\eta)}}. \tag{14}$$

The function $\omega_3(H)$ we have obtained coincides with the results of Ref. 8 for $\eta = 1$ (if the expansion mentioned above is carried out). The equation for the frequency of the lower relativistic resonance branch found in Ref. 9 is incorrect.

We should emphasize one more time that the detailed form of the dependence of ω_3 on magnetic field is not universal, and, e.g., should be different for the case $J' \sim J$.

Let us find the resonance frequencies when the magnetic field is directed at an angle φ to the $\hat{z}$-axis. The equilibrium direction of the vector $\mathbf{n}$, which is given by the angle ψ in the plane $(\mathbf{H}, \hat{z})$, is determined by minimizing the magnetic energy and anisotropy energy. When finding the spectrum it is necessary to avoid too much accuracy. Thus, the kinetic energy of rotation of the spins must be left in the exchange approximation (3); correction terms in

the equations of motion that follow from the invariants (7) and (8) are retained only in those quantities that equal zero for $g=0$ [see matrix (16) below], and the angle ψ is

defined without taking into account this additional anisotropy:

$$\operatorname{tg} 2\psi = \frac{H^2 \sin 2\varphi}{H^2 \cos 2\varphi - H_c^2}.$$ (15)

This results in the following cubic equation:

$$\det \begin{vmatrix} \omega^2 - \eta P(H,\varphi) & -i\omega H(1-\eta)\cos(\psi-\varphi) & -B(H,\varphi) \\ i\omega H(1-\eta)\cos(\psi-\varphi) & \omega^2 - \eta Q(H,\varphi) & i\omega H(1+\eta)\sin(\psi-\varphi) \\ -B(H,\varphi) & -i\omega H(1+\eta)\sin(\psi-\varphi) & \omega^2(1+\eta) - A(H,\varphi) \end{vmatrix} = 0,$$ (16)

where

$$Q(H,\varphi) = \sqrt{H^4 + H_c^4 - 2H^2 H_c^2 \cos 2\varphi},$$

$$P(H,\varphi) = \tfrac{1}{2}(Q(H,\varphi) - H_c^2 + H^2),$$

$$A(H,\varphi) = 6g^2 \left(\sin^2 \psi - \frac{H^2}{H_c^2} \sin^2(\psi-\varphi) \right)^3,$$

$$B(H,\varphi) = 6g^2 \left[\sin^5 \psi \cos \psi - \frac{H^2}{H_c^2} [2 \sin^3 \psi \cos \psi \sin^2 \right.$$

$$\times (\psi-\varphi) + \sin^4 \psi \sin(\psi-\varphi)\cos(\psi-\varphi)]$$

$$+ \frac{H^4}{H_c^4} (2 \sin^3(\psi-\varphi)\sin^2 \psi \cos(\psi-\varphi)$$

$$+ \sin^4(\psi-\varphi)\sin \psi \cos \psi) - \frac{H^6}{H_c^6} \sin^5$$

$$\left. \times (\psi-\varphi)\cos(\psi-\varphi) \right].$$

For an arbitrary direction of the field, there are no remaining symmetries that permit the various resonant frequencies to intersect, and all three branches of the spectrum should repel each other. However, for the parameters g_i entering into the model (1), the nondiagonal element $B(H,\varphi)$ is small compared to g^2 over the entire range of variation of the parameters H and φ. Therefore the gap between the two lower relativistic branches should be undetectable (if, e.g., we have $g_1 \neq 0$ and $g_2 = g_3 = g_4 = 0$, then this will no longer be so). The angular dependence of the frequency of the third relativistic mode of the spectrum is given by the expression

$$\omega_3^2(H) = \frac{6g^2\gamma^2}{1+\eta} \frac{\eta Q(H,\varphi)}{\eta Q(H,\varphi) + (1+\eta)H^2 \sin^2(\psi-\phi)}$$

$$\times \left(\sin^2 \psi - \frac{H^2}{H_c^2} \sin^2(\psi-\varphi) \right)^3.$$ (17)

For the remaining relativistic branches, when $\omega_1 \gg \omega_2$,

$$\omega_1^2(H) = \gamma^2 [\eta Q(H,\varphi) + (1+\eta)H^2 \sin^2(\psi-\phi)],$$ (18)

$$\omega_2^2(H) = \gamma^2 \eta P(H,\varphi).$$ (19)

If, however, the condition $\omega_1 \gg \omega_2$ does not hold, then the expressions from Ref. 7 must be used for $\omega_1(H)$ and $\omega_2(H)$. Those expressions can also be obtained from Eq. 16.

3. EXPERIMENT

The antiferromagnetic resonance spectrum in $CsMnI_3$ was measured using a direct-amplification spectrometer in the frequency range 9 to 178 GHz and temperature interval 1.4 to 20 K according to the usual method: resonant power absorption was detected by observing the change in the amplitude of a micro-wave signal P at fixed frequency ω passing through a cell containing the sample, while sweeping the static magnetic field H. We used a truncated 4-mm waveguide or 8-mm rectangular resonant cavity as an absorption cell for the spectrometer. When the resonant cavity was used, we were able to change the orientation of the sample with respect to the magnetic field. Fields up to 60 kOe were created by a superconducting solenoid. The temperature was measured with a semiconductor thermometer.

In preparing the $CsMnI_3$ we used the following method. Metallic manganese was heated in an evacuated quartz ampule in iodine vapor up to 1000 °C. The resulting brown product was freed of excess iodine by heating in a vacuum, and then was sublimated under continuous pumping at 1000 °C. The rose sublimate of MnI_2 was melted in vacuum with an equivalent amount of CsI to form $CsMnI_3$, which is dark red in color. This was then lowered into a cylindrical oven in a sealed ampule (the oven was heated to 430 °C; the melting temperature of $CsMnI_3$ is 413 °C). The single crystals of $CsMnI_3$ obtained in this way were annealed in the same ampule at 300 °C over a period of 200 hours. After a variety of trials it was established that the best way to protect $CsMnI_3$ from hydration was to use a resin glue.

The fact that the crystal structure of the compound obtained was indeed that of $CsMnI_3$ was established by x-ray phase analysis. All the crystals used were easily cleaved along the (110) plane and had clearly distinguishable veins along the C_6 axis, allowing us to orient them visually.

FIG. 2. Dependence of the resonance field on the angle between the field and the C_6 axis for a frequency of 29.9 GHz, $T = 1.3$ K. The solid curves were plotted using Eqs. (17) and (19) with the same parameters $\eta = 0.894$, $H_c = 52$ kOe, and $g = 7$ kOe.
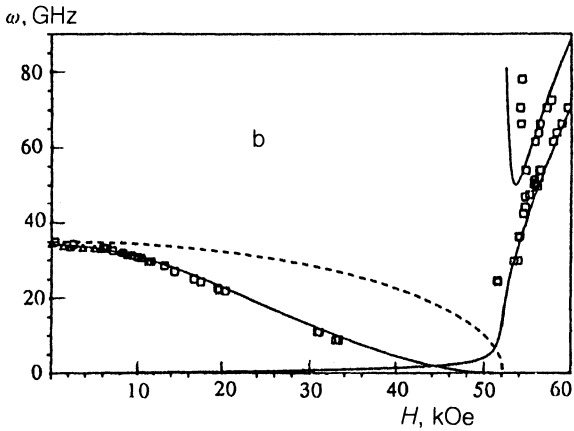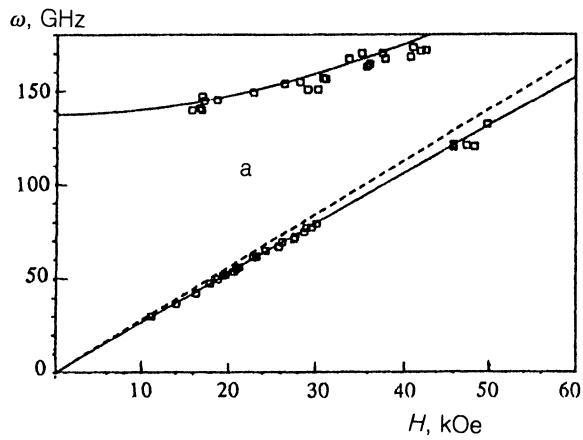
FIG. 1. Magnetic field dependence of the resonance frequency for $H \parallel C_6$ (a) and $H \perp C_6$ (b), $T = 1.4$ K. The squares display the results of our measurements, the triangles the date of Ref. 8. The solid curves were drawn using expressions from Ref. 7 for $\varphi = 0.5°$ with parameters $\eta = 0.894$, $H_c = 52$ kOe, using Eq. (14) with the parameter $g = 7$ kOe. The dashed curve was plotted by using Eq. (5) of Ref. 9.

In the disordered phase we observed a paramagnetic resonance line $\omega = \gamma H$ with $\gamma = 2.8$ GHz/kOe for $T > 12$ K. Figures 1(a) and 1(b) show the results of measuring the antiferromagnetic resonance spectrum in $CsMnI_3$ at $T = 1.3$ K for $H \perp C_6$ and $H \parallel C_6$ respectively. It is clear from the figure that we were able to detect the upper branch of the resonance, which has a gap of about 138 GHz, when the field was directed in the basal plane, while for the case $H \parallel C_6$ we were able to observe it only in magnetic fields above the phase transition field $H_c = 52$ kOe. Recall that in $CsNiCl_3$ and $RbNiCl_3$ this resonance branch was observed for any direction of magnetic field. In our view, the explanation for this phenomenon is that for crystals with large anisotropy we cannot describe the frequency ω_1 using Eq. (5), since the latter was obtained only to first order in D (see Ref. 8). For large D the function $\omega_1(H)$ is more gently sloping for $H \parallel C_6$ than Eq. (5) would indicate. The method used for these measurements does not allow us to detect a resonance whose frequency depends weakly on magnetic field.

If the magnetic field is directed in the basal plane of the crystal, then the field dependences of both resonance fre-
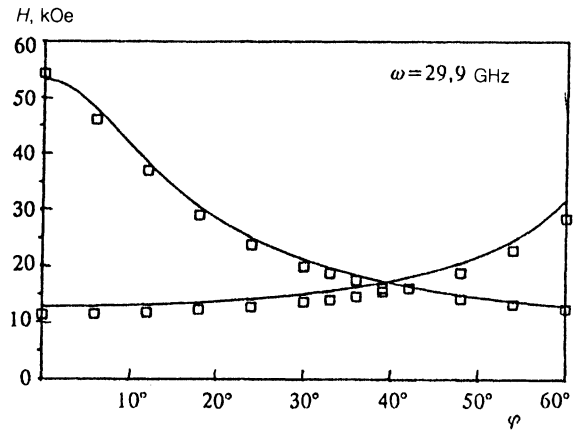
quencies coincide to within the accuracy of the constants with those of $CsNiCl_3$ and $RbNiCl_3$, and are well described by the expressions given in Ref. 7 with parameters $\eta = 0.894$, $H_c = 52$ kOe, at a temperature $T = 1.3$ K. The expression from Ref. 7 used to describe the resonance is just as useful for the case $H \parallel C_6$, $H > H_c$. The value of H_c agrees with data from static measurements[11] which predict a value of 54 kOe for the spin-flop transitions at $T = 2.0$ K.

In the range of fields below the spin-flop field, still another resonant branch is observed when $H \parallel C_6$ with a gap of 35 GHz that decreases as H increases. From the figure it is clear that the dotted curve plotted using the expressions from Ref. 9 is a much worse description of the experimental points than Eq. (14) which we have obtained (the solid curve) when the parameter $g = 7$ kOe is used to determine the value of the gap.

Figure 2 shows how the resonance field depends on the angle between H and the C_6 axis for a frequency of 29.9 GHz. As we should expect, the "gap" from repulsion of the two lowest resonance branches was so small that we were unable to observe it experimentally. The angular dependence of the spectrum is well described by the theoretical expressions (17) and (19) (solid curves) with the same parameters η, H_c, g.

As the temperature decreases the widths of the resonance lines abruptly increase, the intensity of the signal decreases, and, unfortunately, we were unable to track the functions $\eta(T)$ and $H_c(T)$ as was done for $RbNiCl_3$. For this reason, we are unable to say anything definite about the resonant properties of the intermediate phase between the paramagnetic state and the three-dimensional ordered state for $T_{N2} < T < T_{N1}$ ($T_{N1} = 11.4$ K, $T_{N2} = 8.2$ K).

4. DISCUSSION

The experimental results we have obtained in the course of our investigation of the antiferromagnetic spectrum of $CsMnI_3$ unequivocally indicate that the magnetic

field dependence of the resonant frequencies is well described by the usual spin-wave theory, as is the case for $CsNiCl_3$ and $RbNiCl_3$.

In constructing a theory of magnetic resonance in antiferromagnets with exchange noncollinear spin structure, we can either start with the microscopic Hamiltonian (1) and make use of mean-field theory[8,9] or use a phenomenological approach like the one employed in Ref. 7 and developed in this paper. Of course, the results obtained agree with one another and give practically the same field dependence for the resonance frequencies; however, there are a number of distinctive features as well. The method of Ref. 10 predicts the existence of two different resonance branches for the case $H \parallel C_6$, $H > H_c$, which is observed experimentally. These branches differ from one another to the extent that the parameter η differs from unity, which also destroys the relation between the value of the gap for the upper relativistic resonant branch and the spin-flop field transition implied by mean field theory: for the model approach we have $\omega_1 = \gamma H_c$, while for the phenomenological approach we have $\omega_1 = \gamma \sqrt{\eta H_c^2}$.

Let us discuss the determination of the constants J, J', and D of the model Hamiltonian (1). The parameter J can be found with good accuracy from inelastic neutron scattering data: $J = 198$ GHz.[5] However, it is not entirely correct to determine J' and D from the dispersion of the exchange spin-wave branches, since, first of all, we do not yet have a satisfactory theory for the exchange branches of the spectrum, and secondly, the neutron measurements are not accurate enough in the range of frequencies smaller than 500 GHz, within which the dispersion curves depend significantly on J' and D. The anisotropy constant D can reliably be found from the spin-flop field: $H_c = \sqrt{16JDS^2} = 52$ kOe; therefore, $D = 1.07$ GHz.

The ratio of the anisotropy D to the exchange J' can be determined from the angle the spins make with the hexagonal axis $\vartheta = (51 \pm 1)°$, which is well-known from neutron scattering:[5,11]

$$\frac{D}{J'} = 6 - \frac{3}{\cos \vartheta} = 1.23 \pm 0.1. \qquad (20)$$

Knowing the constants of the spin Hamiltonian (1), we can find the resonant frequency of the exchange branches at $k = 0$, making use of the expressions derived in Ref. 8. Taking the values $J = 198$ GHz, $D = 1.07$ GHz, and $J' = 0.87$ GHz, we obtain

$$\omega_4 = 240 \text{ GHz}, \quad \omega_5 = 340 \text{ GHz}, \quad \omega_6 = 416 \text{ GHz}.$$

In the paper by Harrison et al.[5] on inelastic neutron scattering only one experimental point was given at zero wave vector; its frequency $\omega = 424$ GHz agrees with the value of ω_6. As we will see, when the considerable anisotropy is taken into account, the two lowest exchange resonance branches are split so that the ratio $\omega_6/\omega_{4,5} = \sqrt{2}$, which holds for $D \ll J'$, does not hold. Experimentally, the lowest exchange branches are not observed, and finding them requires further investigation. However, the frequencies corresponding to them are not at all comparable to $\omega_6/\sqrt{2}$, as was found for $CsNiCl_3$ and $RbNiCl_3$.[2]

The ratio of the anisotropy D to the interchain exchange J' can also be determined without going beyond the limits of this paper from the ratio of the resonance frequencies in zero field:

$$\frac{D}{J'} = \frac{\omega_3(0)}{\omega_1(0)} \sqrt{6\eta(1+\eta)} = 0.81 \pm 0.06. \qquad (21)$$

The accuracy of $\pm 1°$ which the authors of Ref. 5 claimed in their determination of angles implies an error of 10% for the ratio D/J'. The values of D/J' found from resonance and neutron-scattering experiments differ by more than 30%, which can in no way be explained by inadequate accuracy of our measurements. If the angle of deviation of the spins is determined to this kind of accuracy, then in our view the reason for the disagreement must be sought in the incompleteness of the Hamiltonian (1). It is known that the spin-orbit interaction is small for the Mn^{2+} ion; consequently, describing the relativistic effects by adding a single-ion anisotropy to the Hamiltonian (1) cannot be fully correct. [The absence of single-ion anisotropy in $CsMnI_3$ is also confirmed by the fact that $\omega_2(0) = 0$, since the existence of an anisotropy of the form (6) would be obligatory if the electronic shells of the Mn^{2+} were distorted by the crystal environment]. Apparently it is more correct to introduce a different-ion anisotropy between nearest neighbors (this is often called an exchange interaction anisotropy) and to replace the Hamiltonian (1) with a Hamiltonian

$$\hat{H} = 2 \sum_{\langle i,j \rangle}{}' (J S_i S_j + D_1 S_i^z S_j^z) + 2 \sum_{\langle i,j \rangle}{}'' (J' S_i S_j$$
$$+ D_2 S_i^z S_j^z) - H \sum_i S_i. \qquad (22)$$

Mean-field calculations based on (22) analogous to those carried out in Ref. 8 give

$$H_c^2 = 16(D_1 + D_2)JS^2, \qquad (23)$$

$$\cos \vartheta = \frac{1 + D_2/3J'}{2 - (D_1 - D_2)/3J'}, \qquad (24)$$

$$\frac{\omega_3(0)}{\omega_1(0)} = \frac{\sqrt{D_1(D_1 + D_2)}}{2\sqrt{3}J'}. \qquad (25)$$

By introducing the two parameters D_1 and D_2 to describe the anisotropy, we can reconcile the experiments on inelastic neutron scattering with the resonance measurements. In principle, these data are enough to determine the three quantities J', D_1, and D_2. Substituting the results of these measurements into Eqs. [(24) and (25)], we obtain for them the following estimates:

$$J' = 1 \text{ GHz}, \quad D_1 = 0.4 \text{ GHz}, \quad D_2 = 0.7 \text{ GHz}.$$

The relativistic effects to first order in v^2/c^2 (i.e., the spin-flop field, the gap $\omega_1(0)$, the angle of deviation of the spins, and the splitting of the exchange frequencies) are deter-

mined by averaging the spin-orbit in (22) over the unperturbed 120° structure. Hence we may describe them by using an effective single-ion anisotropy with $D = D_1 + D_2$. However, in studying higher-order phenomena in v^2/c^2 [the branch $\omega_3(H)$], for whose existence it is necessary to have a somewhat small distortion of the exchange spin structure, the specific form of the spin-orbit interaction becomes important. We note that the accuracy of this procedure for determining these constants is not high, since the ratio D_2/D_1 is very sensitive to even rather small changes in the angle of inclination of the spins to the hexagonal axis.

To sum up, we can say that by using a natural modification of Eq. (1), which consists of introducing two anisotropy constants instead of one, we can describe all the experimental data known today regarding the spin structure and energy spectrum of $CsMnI_3$.

[1] Haldane, F. D. M., Phys. Rev. Lett. **50**, 1153 (1983).

[2] R. M. Morra, W. J. L. Buyers, R. L. Armstrong, et al., Phys. Rev. B **38**, 543 (1988); Z. Tun et al., Phys. Rev. B **42**, 4677 (1990); M. Steiner, J. Appl. Phys. **67**, 5593 (1990); Z. Tun, W. J. L. Buyers, A. Harrison, et al., Phys. Rev. B **43**, 13331 (1991).

[3] I. K. Affleck, Phys. Rev. Lett. **62**, 474 (1989); I. K. Affleck, Phys. Rev. Lett. **65**, 2447 (1990); I. K. Affleck, Phys. Rev. Lett. **65**, 2836 (1990).

[4] M. L. Plumer and A. Caille, Phys. Rev. Lett. **68**, 1042 (1992).

[5] A. Harrison, M. F. Collins, J. Abu-Dayyeh, and C. V. Stager, Phys. Rev. B **43**, 679 (1991).

[6] I. A. Zaliznyak, L. A. Prozorova, and S. V. Petrov, Zh. Eksp. Teor. Fiz. **97**, 359 (1990) [Sov. Phys. JETP **70**, 203 (1990)]; O. A. Petrenko, S. V. Petrov, and L. A. Prozorova, Zh. Eksp. Teor. Fiz. **98**, 727 (1990) [Sov. Phys. JETP **71**, 406 (1990)].

[7] I. A. Zaliznyak, V. I. Marchenko, S. V. Petrov, L. A. Prozorova, and A. V. Chubukov, Pis'ma Zh. Eksp. Teor. Fiz. **47**, 172 (1988) [JETP Lett. **47**, 211 (1988)].

[8] H. Tanaka, S. Teraoka, E. Kakekashi, K. Iio, and K. Nagata, J. Phys. Soc. Jpn. **57**, 3979 (1988).

[9] I. A. Zaliznyak, L. A. Prozorova, and A. V. Chubukov, J. Phys.: Cond. Matter **1**, 4743 (1989).

[10] A. F. Andreev and V. I. Marchenko, Usp. Fiz. Nauk **130**, 39 (1980) [Sov. Phys. Usp. **23**, 21 (1980)].

[11] H. W. Zandberger, J. Sol. State Chem, **35**, 367 (1980).

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