Magnons in the Linear-Chain Antiferromagnet $CsMnCl_3 \cdot 2D_2O$†

J. SKALYO, JR., AND G. SHIRANE
Brookhaven National Laboratory, Upton, New York 11973
AND
S. A. FRIEDBERG AND H. KOBAYASHI*
Carnegie-Mellon University, Pittsburgh, Pennsylvania 15213
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This paper reports the first neutron scattering measurements on spin waves in a linear-chain antiferromagnet. Measurements were made on $CsMnCl_3 \cdot 2D_2O$ and clearly indicate a large directional anisotropy of the spin coupling. The dominant exchange occurs along chains extending in the a direction, $J_1 = -0.304 \pm 0.003$ meV. The exchange parameters in the b and c directions were measured in the combinative form $J_2 + J_3 = -0.0021 \pm 0.0004$ meV. Short-wavelength excitations along the chain direction persist even at $2T_N$.

The class of substances to which $CsMnCl_3 \cdot 2H_2O$ belongs may be described as linear-chain antiferromagnets. In these materials, for structural reasons, strong superexchange coupling of paramagnetic ions occurs only in one direction. The crystal structure of $CsMnCl_3 \cdot 2H_2O$ has been determined by Jensen and Andersen.[1] It belongs to the orthorhombic space group *Pcca* with four molecules in the chemical unit cell. The cell dimensions are $a = 9.06$ Å, $b = 7.285$ Å, and $c = 11.455$ Å. A projection on the (001) plane is shown in Fig. 1. Dominant superexchange occurs in $-Mn^{++}-Cl^{-}-Mn^{++}-Cl^{-}-$ chains which extend in the a direction. Interchain superexchange and dipolar interactions are expected to be rather weak, because Mn^{++} spins are well separated in the b and c directions by at least two intermediate atoms.

The first evidence of linear-chain behavior in $CsMnCl_3 \cdot 2H_2O$ was given by the susceptibility measurements of Smith and Friedberg.[2] Above ≈ 9°K these data could be accurately described by a model consisting of independent linear chains of Mn^{++} ions ($S = \frac{5}{2}$, $g = 2.00$) coupled by antiferromagnetic isotropic exchange with $J_1 = -0.27$ meV. Marzzacco and McClure[3] find that the electronic absorption spectra of $CsMnCl_3 \cdot 2H_2O$ are amenable to an analysis based on this model. At lower temperatures, antiferromagnetic long-range order is established through the action of the weak interchain coupling. Forstat *et al.*[4] have measured the heat capacity and found that $\approx 80\%$ of the spin entropy reduction associated with magnetic ordering takes place above $T_N = 4.89$°K. This is consistent with the expectation based on the linear-chain model that substantial intrachain spin correlations develop well above T_N.

The intrachain correlations have been directly observed in our recent quasi-elastic neutron diffraction experiments.[5] It was found, for example, that independent chains of ≈ 5 correlated spins exist at $\approx 3T_N$. Interchain correlations become detectable only below $\approx 2T_N$. Below $T_N = 4.89$°K, long-range three-dimensional order was observed. The magnetic space group was found to be $P_{2b}c'ca'$, confirming the NMR results of Spence *et al.*[6] The lower half of the magnetic unit cell is shown in Fig. 1. The interchain coupling which permits this ordering to occur above 0°K was estimated to be ≈ -0.003 meV by substituting T_N and J_1 into Oguchi's formula.[7]

These results suggest that $CsMnCl_3 \cdot 2H_2O$ offers a hitherto unrealized opportunity for the direct observation of dynamical behavior closely approximating that of the antiferromagnetic Heisenberg linear chain. We wish now to report some findings of a study by inelastic neutron scattering of several aspects of spin dynamics in this system. This work confirms our expectation that the spin-wave or magnon spectrum of $CsMnCl_3 \cdot 2H_2O$ below T_N is highly anisotropic with little dispersion perpendicular to the a^* direction in reciprocal space. By fitting a model of weakly interacting chains to these spectra, we obtain quantitative values for inter- and intrachain coupling constants. Of particular interest are the observations made as the temperature is raised through T_N. The short-wavelength spin-wave modes in the linear chains are found to persist even at $\approx 2T_N$.

The magnon measurements were performed on a triple-axis spectrometer at the Brookhaven high-flux beam reactor. Pyrolytic graphite was used for both the monochromator and analyzer. Measurements were made in the constant-**Q** mode with an initial neutron energy that varied between 5.2 and 20 meV, depending upon resolution requirements. The sample was a single crystal of $CsMnCl_3 \cdot 2D_2O$ with the approximate dimensions 2, 0.5, and 1 cm in the a, b, and c directions, respectively. The deuterated isomorph was used to obtain an improved signal by eliminating the large incoherent scattering of hydrogen. It should be noted that we have found the magnetic susceptibilities of $CsMnCl_3 \cdot 2D_2O$ and $CsMnCl_3 \cdot 2H_2O$ to be practically identical.

Measurements were made in the [ζ00] and [0 ζ 2ζ] directions using the Brillouin zone with magnetic Bragg peak at $(1, \frac{1}{2}, 1)$ as shown in Fig. 1. The spin-wave energy has been obtained using the expression given by Keffer[8] for a uniaxial two-sublattice antiferromagnet. This is an approximation for the present system in which there are eight Mn atoms in the primitive mag-

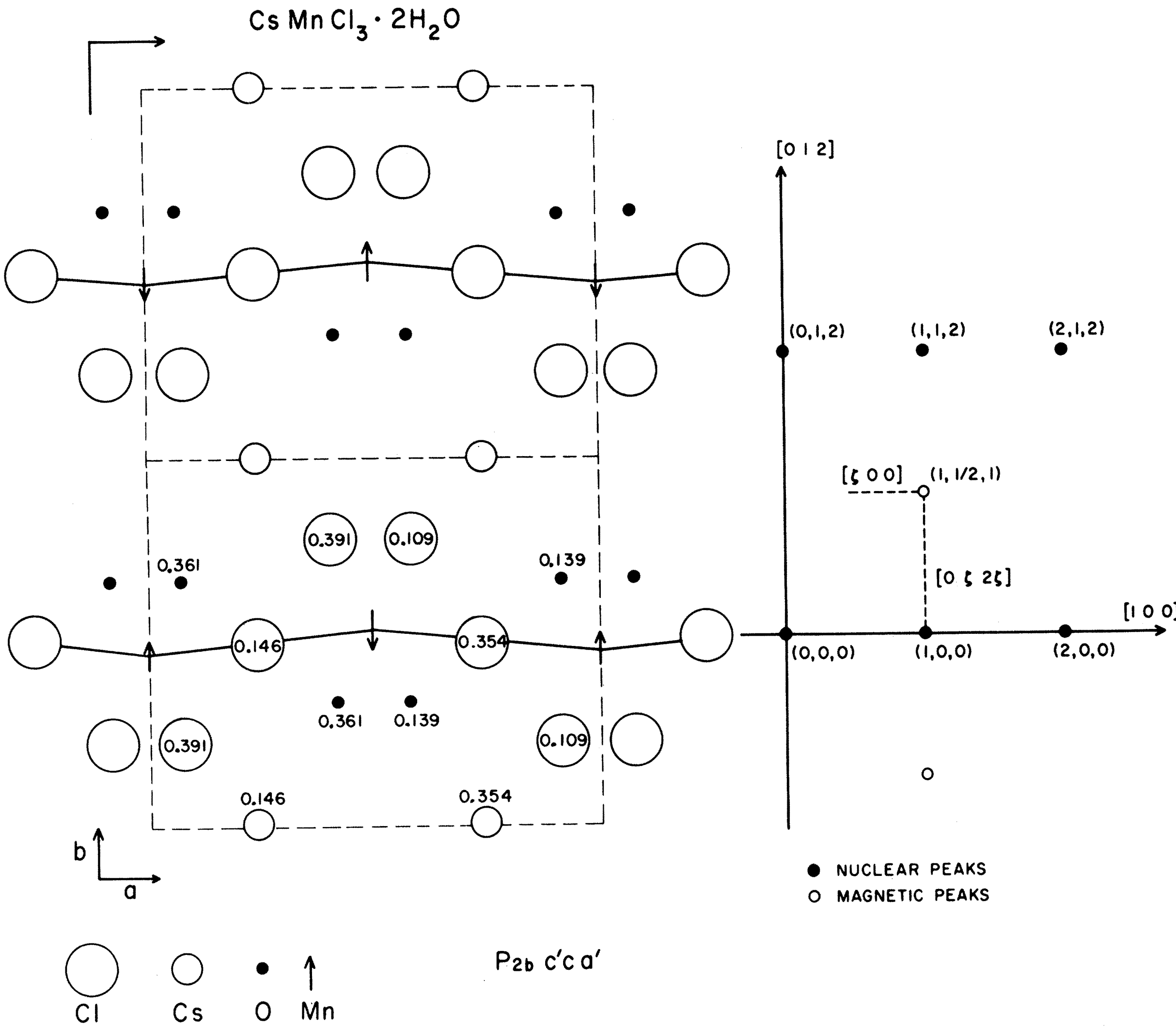

FIG. 1. A (001) projection of the lower half of the magnetic cell of $CsMnCl_3 \cdot 2H_2O$. The Mn^{++} ions are at the level $z=0.25$ and the upper half of the cell is related to the lower half by symmetry. Measurements were made in reciprocal space utilizing $(h\ k\ 2k)$ reflections. The location of the measurements is indicated by the dashed lines emanating from the $(1, \frac{1}{2}, 1)$ magnetic Bragg peak.

netic cell.[5,6] It is justified if we consider only the magnetic Mn^{++} ions and ignore the very slight zigzag of the chains which they form. The magnetic interaction is $H_{ij}=-2J_{ij}\mathbf{S}_i\cdot\mathbf{S}_j$, $S=\frac{5}{2}$, and the spin direction is fixed by a simple anisotropy energy $g\mu_B H_A$. The resulting formula is

$$E(\mathbf{q})=\{[g\mu_B H_A-4S(J_1+J_2+J_3)]^2-16S^2 \times(J_1\cos\tfrac{1}{2}q_xa+J_2\cos q_yb+J_3\cos\tfrac{1}{2}q_zc)^2\}^{1/2}, \quad (1)$$

where only the nearest neighbors in the a, b, and c directions are considered. For the two directions studied, in addition to J_1, only the combination J_2+J_3 can be determined. The data and the fit obtained are illustrated in Fig. 2. The resulting parameters are

$$g\mu H_A=0.003\pm0.001 \text{ meV},$$

$$J_1=-0.308\pm0.001 \text{ meV},$$

$$J_2+J_3=-0.0021\pm0.0001 \text{ meV}.$$

If, as is likely, $J_2\approx J_3$, each of these parameters is 300 times smaller than the intrachain exchange J_1, in reasonable agreement with our earlier estimate. The above parameters give an energy gap of 0.14±0.02 meV at 4.2°K. This can be compared with the antiferromagnetic resonance measurements of Nagata and Tazuki.[9] They obtain a value of 0.19 meV at 1.5°K, which agrees with the neutron value if one assumes an

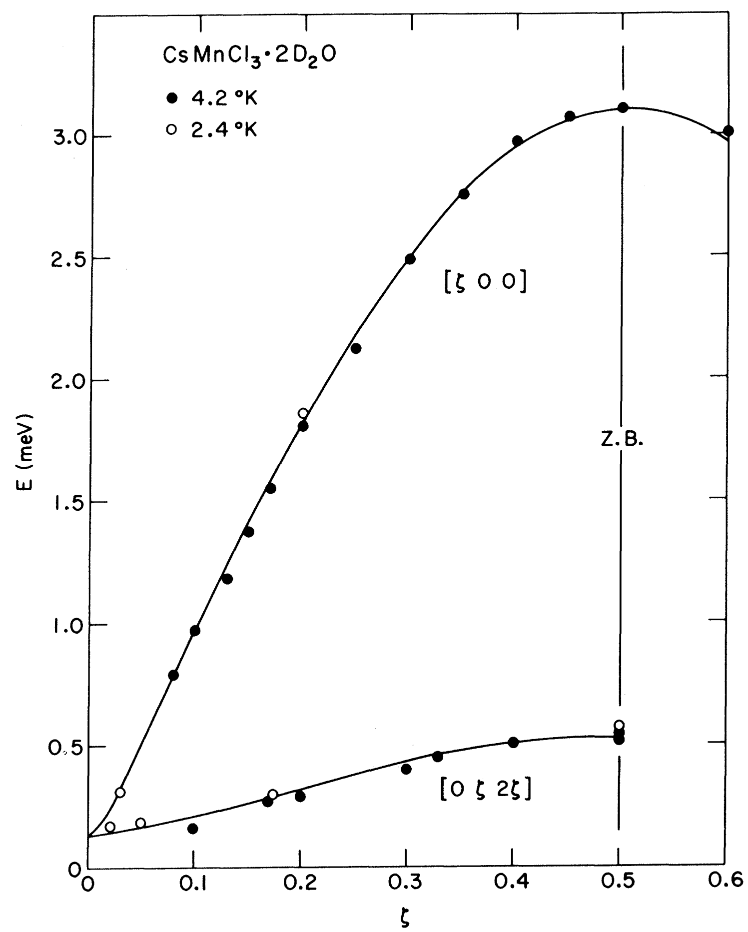

FIG. 2. Magnon dispersion in $CsMnCl_3 \cdot 2D_2O$. The solid line is the fit to the data assuming exchange coupling to nearest neighbors in the a, b, and c directions. The estimated errors are approximately ±0.05 meV for points below 1 meV, increasing to ±0.10 meV for points above 1 meV.

energy renormalization proportional to the magnetization.[5]

A precise measure of the second-neighbor exchange along the chain J_4 was not possible because of its extremely high statistical correlation with J_1 when $J_4 \ll J_1$. An equally good fit of the data could be obtained for all values $|J_4| < 0.035$ meV. For small values of $g\mu_B H_A$ and J_2+J_3 the relevant expression for the energy in the [ζ00] direction can be written as

$$E \cong 4S\,|J_1|\,\sin\tfrac{1}{2}q_x a\left[1-4\frac{J_4}{J_1}+\left(\frac{2J_4}{J_1}\sin\tfrac{1}{2}q_x a\right)^2\right]^{1/2}. \quad (2)$$

For $J_4 \ll J_1$ this may be considered the dispersion relation of a chain with an effective intrachain nearest-neighbor exchange $J_1'=J_1(1-4J_4/J_1)^{1/2}$. The data, when analyzed for the allowable extremes of J_4, yield a value of J_1' of -0.304 ± 0.003 meV and the value -0.0021 ± 0.0004 meV for J_2+J_3.

Measurement of magnons in three-dimensional antiferromagnets has indicated that considerable renormalization and shortening of lifetimes occur as T_N is approached.[10] A recent study of the two-dimensional antiferromagnet K_2NiF_4 has shown that long-wavelength spin waves ($\lambda \approx 110$ Å) exhibit little renormalization or lifetime reduction up to $\approx 1.1T_N$.[11] It is of considerable interest, therefore, to examine the corresponding behavior of magnons in an approximately one-dimensional case.

Depicted in Fig. 3 are a few examples of energy scans of magnons taken at various temperatures and $\mathbf{q}$ values. It is expected that as T_N is approached, the $\mathbf{q}=0$ mode energy must go to zero. The mode [0 ζ 2ζ], $\zeta=0.02$, clearly is affected by the change of temperature from 2.4 to 4.2°K. It broadens so that the peak cannot be separated from the incoherent background, which is centered at $E=0$ and extends to ≈ 0.1 meV. The zone-boundary magnon [0 ζ 2ζ], $\zeta=0.5$, with an energy of 0.56 meV at 2.4°K has broadened and has renormalized $\approx 10\%$ at 4.2°K.

Consider, however, the two high-energy magnons belonging to the [ζ00] branch and shown in the upper part of Fig. 3. These are chainlike excitations. The longer-wavelength $\zeta=0.2$ mode ($\lambda=45$ Å) shows little change between 2.4°K and T_N. At 8.4°K ($=1.7T_N$) it has broadened, without, however, significant energy

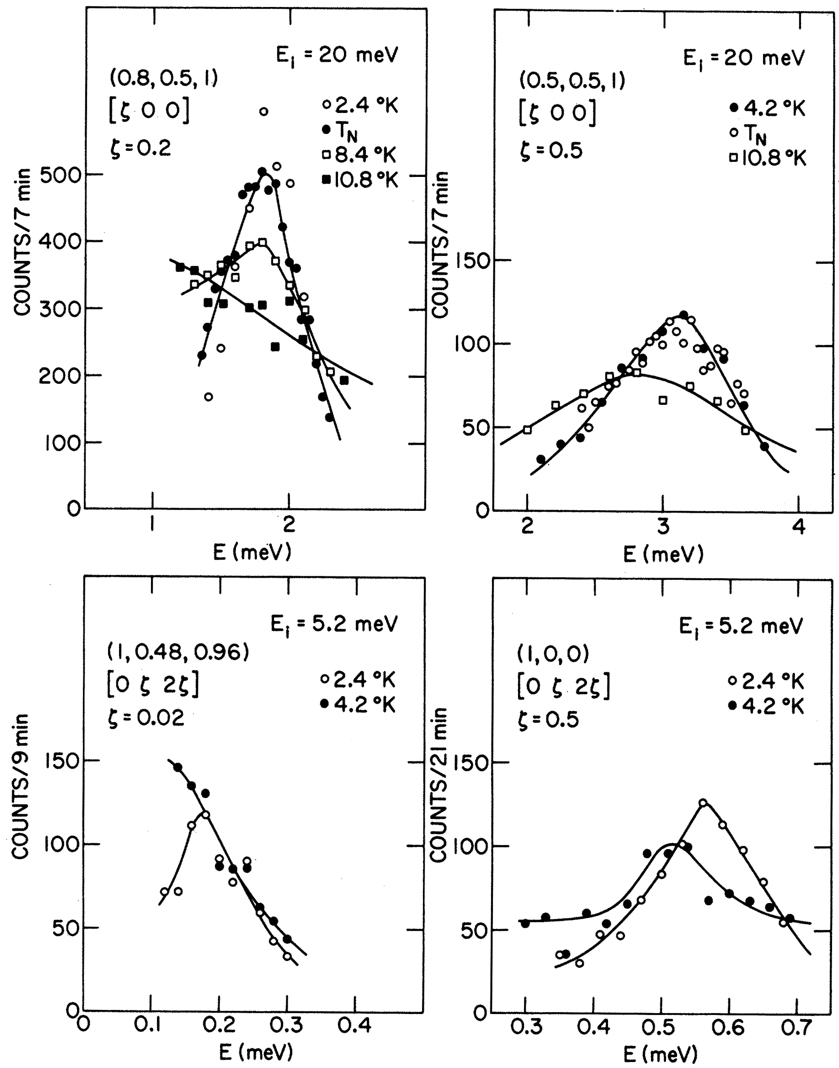

FIG. 3. Temperature dependence of magnons in the [ζ 0 0] and [0 ζ 2ζ] directions. In some of the scans, the counts were doubled to scale with the other scans of a particular mode. The position in reciprocal space where the measurement was made is indicated.

renormalization. By 10.8°K ($=2.2T_N$), it has also shifted in energy. The zone-boundary mode $\zeta=0.5$, on the other hand, is of short wavelength ($\lambda=18$ Å) and, while also unaffected as T is raised to T_N, is much more persistent at higher temperature. At $2.2T_N$, it has become renormalized by only 10% and broadened. These observations are consistent with the results of our quasi-elastic measurements which established the existence well above T_N of rather long correlated regions within the linear chain of spins.

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