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MAGNETIC ORDERING OF THE LINEAR CHAIN ANTIFERROMAGNET $CsMnBr_3$

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ABSTRACT

Results of neutron diffraction, magnetic susceptibility and specific heat measurements on single crystal samples of the hexagonal linear chain compound $CsMnBr_3$ are reported. Three-dimensional magnetic ordering occurs at T_N=8.3°K. Above T_N neutron scattering maxima are observed at reciprocal lattice planes, indicative of one-dimensional correlations along the chain. Below T_N the Mn^{2+} magnetic moments are coupled antiferromagnetically along the chains but lie in the basal plane, where they form a triangular array. The magnitude of the Mn^{2+} moment extrapolated to 0°K is indicative of a substantial zero-point spin deviation. From about 90°K to 300°K the susceptibility data could be fit with Fisher's exact solution for the susceptibility of a classical, nearest-neighbor, one-dimensional Heisenberg antiferromagnet. We found J=9.6°K and χ_{max} at 90°K. Evidence of anisotropy was observed in the susceptibility data. The specific heat data below 13°K is dominated by a term linear in T. The coefficient of the linear term is 0.057 cal/mol-deg^2, which is about 42% higher than the coefficient computed for the isotropic Heisenberg linear antiferromagnet on the basis of our value for J.

INTRODUCTION

Recently, considerable experimental attention has been given to substances which exhibit one-dimensional magnetic ordering. Properties characteristic of one-dimensional magnetic behavior are to be expected in $CsMnBr_3$ from the nature of the crystal structure. In this hexagonal compound, space group $P6_3/mmc(D^4_{6h})$, there are chains of $MnBr_6$ octahedra along the c axis with an interchain separation (7.6 Å) more than double the intrachain separation (3.2 Å). Magnetic studies of isomorphous chloride compounds have revealed pronounced one-dimensional magnetic behavior.[2-5] We report here the results of neutron diffraction, magnetic susceptibility and specific heat measurements which were undertaken to clarify the nature of the magnetic ordering in $CsMnBr_3$.

EXPERIMENTAL

The compound was prepared by careful dehydration of a solution of Cs_2CO_3 and $MnCO_3$ in dilute hydrobromic acid, followed

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by melting under an atmosphere of anhydrous HBr.[6] Single crystals were grown by the Bridgman technique. The crystals have excellent (100) cleavage planes and are pink in color. Powder and single crystal neutron data were obtained using neutrons of wavelength 1.03 and 1.20 Å, respectively, at temperatures between 4.2 and 300°K. Magnetic susceptibility measurements between 1.5°K and 300°K were performed in a pendulum magnetometer. Specific heat measurements were carried out on a 0.923 gram single crystal of $CsMnBr_3$ between 1.8 and 30°K using a heat pulse technique.

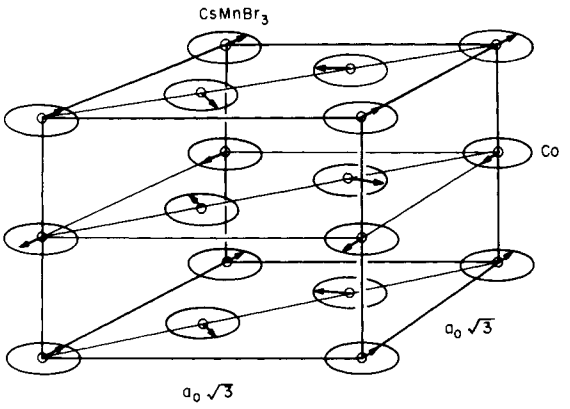

Fig. 1. Magnetic unit cell of $CsMnBr_3$ (not to scale).

RESULTS AND DISCUSSION

At 100°K powder and single crystal neutron data revealed no peaks of magnetic origin. All the reflections could be indexed on the basis of the chemical cell (a=7.56$_1$ Å, c=6.45$_1$ Å and Br(x) =0.1625). At 4.5°K a number of additional magnetic peaks of the type (h/3, k/3, ℓ) with h and k ≠ 3n, and ℓ=2n+1 were observed (all the indices in the paper are based on the chemical cell.) This is a characteristic feature of the triangular structure observed in other compounds of this type.[3-4]

Table I. Observed and calculated intensities for single crystal of $CsMnBr_3$ at 4.5°K. I_{calc} is based on Mn^{2+} moment of 3 μ_B. Scattering amplitudes taken as 0.55, -0.36 and 0.67×10^{-12}cm for Cs, Mn and Br (Ref. 7), respectively.

hkℓ	I_{obs}	I_{calc}
1/3 1/3 1	71.4	74.9
2/3 2/3 1	42.9	41.7
1 1 0	48.7	48.5
4/3 4/3 1	14.2	12.2
2 2 0	370.6	525.3
3 3 0	17.1	17.6

A least-squares refinement of the single crystal data gave a good fit (Table I) for the magnetic structure depicted in Fig. 1. The volume of the magnetic unit cell is three

times larger than that of the chemical cell. The Mn^{2+} magnetic moments are coupled antiferromagnetically along the chains and lie in the basal plane. Adjacent moments in the plane are directed 120° apart to form an antiferromagnetic array.

The magnitude of the Mn^{2+} moment at 4.5°K is only 3.0±0.3 μ_B. The uncertainty is due to the limited amount of nuclear data collected and the difficulty of making proper correction for extinction effects. However, a check of this result is provided by the value derived from the (1/3,1/3,1) powder peak: 3.5±0.3 μ_B at 4.5°K. This low value for the magnitude of the magnetic moment of Mn^{2+} (which averages to about 3.3 μ_B extrapolated to 0°K) can be explained by the existence of a substantial zero point spin deviation, amounting to some 40%, which reflects the basically one-dimensional nature of the magnetic order.[8]

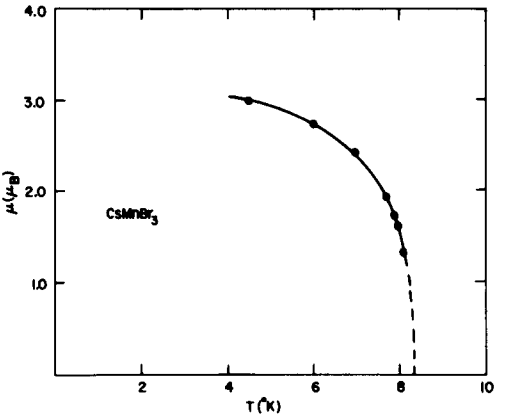

Fig. 2. Temperature dependence of the magnetic moment.

The temperature dependence of the magnetic moment was determined by following the intensity of the single crystal (1/3,1/3,1) peak and is plotted in Fig. 2. The intensity of the critical scattering close to this Bragg reflection had a maximum at 8.3°K, which was taken to be the three-dimensional magnetic ordering temperature T_N.

Above T_N neutron scattering maxima are observed at reciprocal lattice planes indicative of one-dimensional correlations along the chain. The correlation length at 30°K is approximately 15°A, about the same value found in $(CD_3)_4NMCl_3$(TMMC).[9]

The magnetic susceptibility curves vs. temperature of $CsMnBr_3$ in a field of 15,300 Oe are shown in Fig. 3. The broad maxima near 90°K are characteristic of a linear chain antiferromagnet and represent the influence of magnetic coupling along individual chains of manganese ions upon the bulk susceptibilities. From about 90 to 300°K the χ data could be fit with Fisher's[10] exact solution for the susceptibility of a classical nearest-neighbor one-dimensional Heisenberg antiferromagnet. For g=2 and S=5/2 we found J=9.6°K gives a good fit to the experimental data. Below 90°K the χ curves are in qualitative agreement with recent theoretical curves calculated by Walker et al.[11] which have shown that in a linear chain antiferromagnet with isotropic nearest-neighbor exchange anisotropic interactions are significant. The anisotropy of χ is evident in Fig. 3. The transition to true long-range order between the chains around 8.3°K is marked by small bumps on the χ curves. The χ data for $CsMnBr_3$ suggest that below

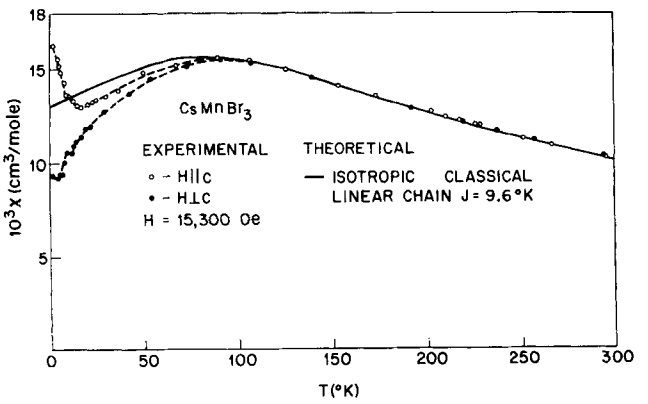

Fig. 3. Single crystal magnetic susceptibility data for $CsMnBr_3$. The solid curve is calculated using the isotropic classical linear chain from Fisher.[10]

T_N the compound is antiferromagnetic and that the main interaction is the intrachain interaction. The ratio between $\chi_{\parallel}$ ($H \parallel c$) and $\chi_{\perp}$ ($H \perp c$) extrapolated to 0°K is 2, in perfect agreement with the theoretical calculation for an anisotropic linear antiferromagnetic classical chain.[11]

A more precise measurement of the temperature of the onset of three dimensional ordering in $CsMnBr_3$ was obtained from heat capacity measurements, the results of which are shown in Fig. 4. A λ-type maximum in Cp is seen at 8.30±0.03°K. The lattice contribution to the specific heat was evaluated from measurements on isomorphic $CsMgBr_3$. Assuming that both compounds have the same Debye temperature and subtracting the two curves in Fig. 4, we obtained the magnetic specific heat. The resulting magnetic entropy below 8.5°K amounts to only 7% of the full entropy of ordering of spin 5/2, $Nk\ell n(2S+1)$ = 3.56 cal/mole deg. This indicates that almost all the magnetic entropy is found in the short range magnetic ordering region.

The magnetic specific heat data below 13°K is dominated by a linear term in T. The coefficient of the linear term is 0.057 cal/mole deg^2. This linear term we associate with the spin wave contribution to the specific heat.[12] Assuming the spin waves are bosons and using the neutron scattering dispersion relation[9] for a linear chain antiferromagnet we found in the limit $T \to 0$ that the coefficient of the linear term in the molar specific heat is $\alpha = 2\pi R/3K$, with K=10.85 J.[9] Using our value for J we obtained α=0.04 cal/mole deg^2, which is about 70% of the value measured.

In summary, the correlations along the chains above T_N, the low value of the Mn^{2+} magnetic moment, the broad maxima in the susceptibility curves, the low value of the long-range magnetic ordering entropy and the linear term in the specific heat are characteristic of a linear-chain Heisenberg antiferromagnet.

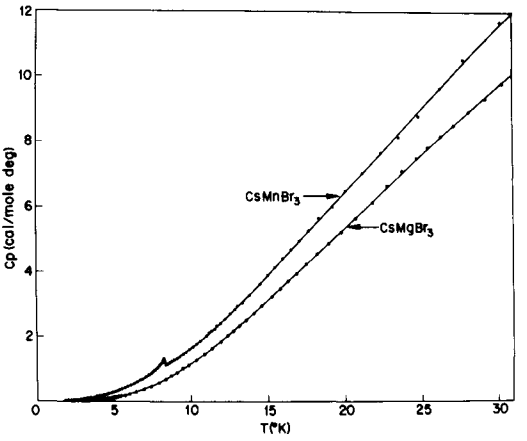

Fig. 4. The specific heat of $CsMnBr_3$ and $CsMgBr_3$.

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