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Magnetic structure of antiferromagnetic $MnCl_2 \cdot 4H_2O$ [†]

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The magnetic structure of monoclinic $MnCl_2 \cdot 4H_2O$ has been determined by analysis of neutron-diffraction data on single crystals. A collinear antiferromagnetic structure was found in which the magnetic and crystallographic unit cells were the same. The Mn^{++} spins were found to point neither along the *c* axis nor along the *c*′axis (perpendicular to the *ab* plane), but in a direction intermediate between the two.

I. INTRODUCTION

$MnCl_2 \cdot 4H_2O$ is a monoclinic antiferromagnet with four magnetic ions per unit cell.[1–7] In spite of its relatively complex crystallographic structure, it has been studied extensively as a good example of a simple uniaxial Heisenberg antiferromagnet. For example, it has a well-defined spin-flop phase, which separates the antiferromagnetic and paramagnetic phases at low temperatures.

Many magnetothermal,[8–27] magnetic resonance,[28–30] and spectroscopic[31] studies have been made on this compound without any real knowledge of the preferred spin direction. Indications were that the spins were collinear with the spin direction lying in the vicinity of the *c* axis or *c*′ direction (direction perpendicular to the *ab* plane–see Fig. 1). In a monoclinic system these two axes do not coincide, and, furthermore, there is no apparent reason for either to be the preferred axis. In this paper we shall report the results of neutron-diffraction experiments[32] on $MnCl_2 \cdot 4H_2O$ and shall discuss the implications of our results with respect to earlier studies. Deuteration was not attempted, since it is known to have a small effect on the ordering temperature,[33,34] and this in turn might affect the magnetic structure slightly. Moreover, the background due to incoherent scattering from the hydrogen was not large enough to interfere with the determination of the Mn^{2+} spin directions.

II. EXPERIMENTAL

Single crystals of $MnCl_2 \cdot 4H_2O$ were grown from aqueous solution at 22 °C, and two such crystals were shaped into cylinders having the cylindrical axis of rotation parallel to the crystal *a* and *b* axes, respectively. After being shaped, the crystals were coated with GE 7031 varnish to prevent deterioration via water loss. The samples were mounted on the end of a copper block which was in turn connected to the bottom of a small helium container. This entire assembly was suspended from the bottom of a larger helium bath held at 4.2 °K. The small helium vessel was connected (i) to the main helium reservoir by a needle valve and (ii) to a vacuum pump. With this arrangement, sample temperatures of 1.1 °K can be reached and maintained for 24 h or longer by pumping on the secondary container. A calibrated germanium thermometer was mounted in the sample holder and a Cryotronics ac resistance bridge was used to measure the resistance.

For each zone, a crystal was aligned in the Dewar and standard θ–2θ scans were taken of Bragg peaks both above and below the Néel temperature. The computer control[35] varied the counting time during a scan in proportion to the counting rate in a manner which optimized statistics. θ–2θ scans with the crystal sample rotated off the Bragg peak were taken to determine background not produced by the sample. Integrated intensities were obtained for 16 peaks in both the $(h, 0, l)$ and $(0, k, l)$ zones.

The analysis of the data was complicated by the large chlorine cross section for true absorption, by a large incoherent background from the 32 hydrogen atoms per unit cell, and by secondary extinction effects. In addition, the locations of the hydrogen atoms within the unit cell were not known with sufficient accuracy to allow useful nuclear-structure-factor calculations to be made. The formula for magnetic intensity which is extracted from a mixed magnetic and nuclear reflection and corrected empirically for extinction, can be written

$$\begin{aligned} &P^{\text{obs}}_{hkl}(\text{total})A^*\exp[-\beta P^{\text{calc}}_{hkl}(\text{total})] \\ &\quad - P^{\text{obs}}_{hkl}(\text{nuclear})A^*\exp[-\beta P^{\text{calc}}_{hkl}(\text{nuclear})] \\ &\quad\quad = KF^2_{hkl}(\text{magnetic})f^2(\sin\theta/\lambda)\sin^2(\alpha), \qquad (1) \end{aligned}$$

where $P^{\text{obs}}_{hkl}(\text{total})$ is the observed sum of the nuclear and magnetic integrated intensities, $P^{\text{obs}}_{hkl}(\text{nuclear})$ is the observed nuclear intensity, A^* is the attenuation correction factor, $\exp(-\beta P^{\text{calc}}_{hkl})$ is the ex-

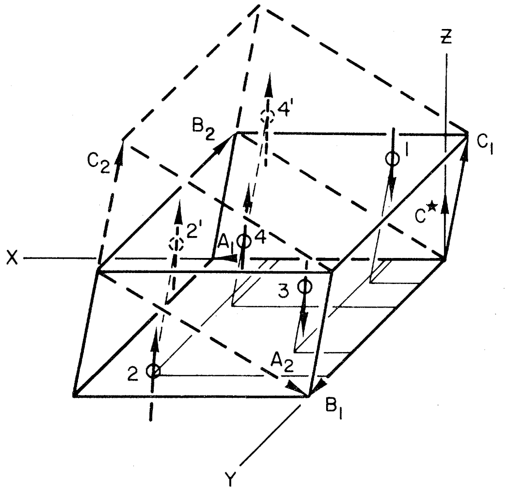

FIG. 1. Magnetic unit cell of $MnCl_2 \cdot 4H_2O$. Solid lines outline unit cell used in the present work and in Refs. 4 and 6. Dashed lines outline unit cell used by Spence and Nagarajan (see Ref. 29). Solid arrows represent the Mn^{2+} spin positions and directions as listed in Table II.

tinction correction factor, P_{hkl}^{calc} is the calculated integrated intensity, K is the instrumental constant, F_{hkl}^2 (magnetic) is the calculated magnetic structure factor, $f(\sin\theta/\lambda)$ is the magnetic-electron form factor taken from Watson and Freeman,[36] and α is the angle between the spin axis and the diffraction vector.

The simple form of the extinction correction[37] is justified on the basis that the range of 2θ values scanned was small, and the largest extinction correction was only about 3%. The absorption corrections for $\mu = 1.46\ \text{cm}^{-1}$ were taken from the International Tables for Crystallography. The large incoherent background from the hydrogen atoms produced a relatively large statistical error in integrated intensity. This problem necessitated taking a large number of reflections to get a significant determination of spin direction.

These difficulties led to a substantially different form of analysis in the two different zones. In the a^*-c^* plane, a fortuitous simplification occurs. Here the magnetic peaks occur at reciprocal lattice sites where the nuclear structure factor is zero. For this case, the intensity formula reduces to

$$P_{hkl}^{obs}(\text{magnetic}) = K \frac{F_{hkl}^2(\text{magnetic}) f^2(\sin\theta/\lambda)}{A^* \exp[-\beta P_{hkl}^{calc}(\text{magnetic})]} \sin^2\alpha. \qquad (2)$$

After the appropriate correction factors had been applied to the data, a two-parameter least-squares analysis was performed in order to determine K, the instrument constant, and α, the spin direction.

In the b^*-c^* plane the nuclear and magnetic reflections coincide. (The magnetic intensities along the c^* axis were all too small to be measured with significant precision.) However, in this plane reflections that are symmetrically placed about the c^* axis have the same nuclear intensities. The b^* and c^* axis are perpendicular to each other so that $(0, k, l)$ and $(0, \bar{k}, l)$ reflections form such pairs. The magnetic-intensity expressions are the same apart from the $\sin^2(\alpha)$ dependence. Taking ratios of such a pair gives the formula

$$\frac{\sin^2(\alpha_1)}{\sin^2(\alpha_2)} = \frac{P_{0kl}^{obs}(\text{total})/P_{0kl}^{obs}(\text{nuclear})e^{-\beta P_{0kl}^{cal}(\text{magnetic})} - 1}{P_{0\bar{k}l}^{obs}(\text{total})/P_{0\bar{k}l}^{obs}(\text{nuclear})e^{-\beta P_{0\bar{k}l}^{cal}(\text{magnetic})} - 1}. \qquad (3)$$

III. RESULTS

No noticeable change in nuclear structure occurred when the sample was cooled below the critical temperature ($T_N = 1.62\,^\circ\text{K}$). The magnetic ions are located in the four-fold general positions $\pm(x, y, z) \pm (\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z)$ (see Fig. 1 and Table I). A two-sublattice collinear model with the following spin assignments fits the data well:

(x, y, z)	$(-)$,
$(\bar{x}, \bar{y}, \bar{z})$	$(+)$,
$(\frac{1}{2}+x,\ \frac{1}{2}-y,\ \frac{1}{2}+z)$	$(+)$,
$(-\frac{1}{2}-x,\ -\frac{1}{2}+y,\ -\frac{1}{2}-z)$	$(-)$.

The projection of the spin on the a^*-c^* plane was found to be 2.8° ± 1.4° from the c^* axis toward the c axis, as shown in Fig. 2. The projection of the spin on the b^*-c^* plane was 0.5° ± 0.5°. The χ^2 value for the a^*-c^*-plane least-squares analysis was 0.90 and for the b^*-c^* plane was 1.08. The comparison between the observed Bragg-peak intensities and those calculated assuming the above spin model is shown in Table II.

IV. DISCUSSION

The magnetic structure of the antiferromagnetic phase of $MnCl_2 \cdot H_2O$ was examined by Spence and

TABLE I. Coordinates of manganese spins in unit cell.

Unit-cell coordinates		Cartesian coordinates (Å)		
$x,\ y,\ z$	(1)[a]	1.571	1.627	6.178
$\bar{x},\ \bar{y},\ \bar{z}$	(2)	8.565	7.886	0.085
$\frac{1}{2}+x,\ \frac{1}{2}-y,\ \frac{1}{2}+z$	(3)	7.688	3.130	2.969
$-\frac{1}{2}-x,\ -\frac{1}{2}+y,\ -\frac{1}{2}-z$	(4)	2.448	6.383	3.134
unit cell parameters[b]		$a_0 = 11.186$ (6), $c_0 = 6.186$ (2),	$b_0 = 9.513$ (5), $\beta = 99.74$ (4)	
structural parameters[c]		$x = 0.23292$ (10), $z = 0.98658$ (19)	$y = 0.17129$ (13),	

[a] Numbers (indices) used in Fig. 1.

[b] See Ref. 4.

[c] See Ref. 6.

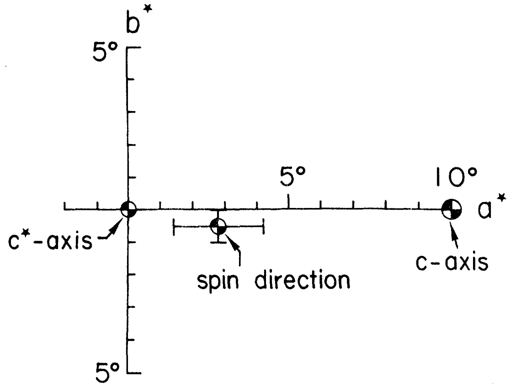

FIG. 2. Projection of spin direction relative to projection of crystallographic axes.

Nagarajan^{29} using proton and chlorine NMR. Three different space groups were found to be consistent with the stereogram of the internal magnetic fields at the proton sites, but only one of these, the $P2_1'/a$, produced a reasonable agreement between the magnitudes of the observed and calculated fields.

The present neutron measurements confirmed this space-group assignment. The magnetic structure is outlined in Fig. 1, which gives the location and orientation of the manganese spins within a unit cell. The unit cell used by Spence and Nagarajan is also shown in Fig. 1.

In addition to the determination of the magnetic structure, the orientation of the moments relative to the crystallographic axes was also measured. As indicated in Sec. III, this preferred direction for spin alignment is closer to the c' direction (perpendicular to the ab plane) than to the crystallographic c axis. In $\mathrm{MnCl_2 \cdot 4H_2O}$ the c axis and the c' direction differ by 9.74°; so the preferred spin direction is almost 7° from the c axis.

Many of the experimental studies on this compound have been performed in the presence of an external magnetic field and have been used to observe the various field induced phase transitions which occur. Below about 1.25 K, with the external field along the preferred direction, there is a transition from the antiferromagnetic (AF) state to the spin-flop (SF) state at a field of about 7.5 kOe, followed by a transition from the SF state to the paramagnetic (P) state at a higher field.

The AF-to-SF transition is expected, by thermodynamic arguments, to be of first order, since there is a finite discontinuity in the magnetization at the critical field. It has been shown recently,^{38,39} however, that the first-order nature of the transition will exist only within a very restricted range of angles between the external field and the preferred direction. Outside a certain maximum angle the spins will rotate more gradually to their new equilibrium positions as the field is increased.

For the case of a simple two-sublattice model with uniaxial anisotropy Rohrer and Thomas^{38} showed that the maximum angle at $T = 0$ is approximately given by $\psi = H_a/2H_e$, where H_a and H_e are the effective anisotropy and exchange fields, respectively. A more exact relation for ψ given by Rohrer and Thomas^{38} and by Blazey *et al.*,^{39} which has more general validity, predicts that for $\mathrm{MnCl_2 \cdot 4H_2O}$ $\psi = 6.5°$. The angle ψ decreases with increasing temperature, becoming zero near the complex critical point where all the phase boundaries merge.

Most of the reports of experimental work in an external field quote the c axis as the preferred direction (see, for instance, Refs. 16, 17, 19, 23, 27, 31, and 33). In the adiabatic studies of Giauque *et al.*^{21} and McElearney *et al.*^{20} with $\vec{H} \parallel \vec{c}$ no abrupt first-order transition was observed. This is a perfectly predictable result consistent with the theory of Rohrer and Thomas,^{38} since the c axis differs from the preferred direction by 7°, and the maximum critical angle for observing the first-order transition is only 6.5° at $T = 0$.

These experimental studies,^{20,21} along with the present neutron diffraction results, make it clear

TABLE II. Observed and calculated intensities.[a]

Reflection	Observed intensity	Observed intensity corrected for extinction	Standard deviation in observed intensity	Calculated intensity
[$(h0l)$ reflections used to assess moment direction in $a^* - c^*$ plane]				
(300)	153584	167406	2447	168358
(102)	12762	12889	2075	9659
$(\bar{1}02)$	8624	8796	1721	6871
$(\bar{3}02)$	39497	40681	2801	38318
$(\bar{5}02)$	24972	25471	1907	27172
(500)	49090	50562	3725	46399
$(\bar{4}01)$	10651	10757	2575	10567
(302)	18140	18502	3508	18381
$(\bar{7}02)$	9084	9174	1540	10630
(700)	10406	10510	1603	11282
$(\bar{6}01)$	10461	10565	1751	9845
(502)	8805	8893	1525	8679
$(\bar{5}04)$	3763	3763	1611	3413
(401)	17184	17537	2644	14111
$(\bar{3}04)$	2203	2203	1471	2089
(900)	1698	1698	1435	2090
$(\bar{2}01)$	4752	4752	1908	2574
[$(0kl)$ reflection used to assess moment direction in $b^* - c^*$ plane]				
(053)	10842	10855	1033	11124
$(0\bar{5}3)$	9421	9432	961	10766
(042)	51269	51545	1171	51021
$(0\bar{4}2)$	50496	50768	1164	49650
(013)	7147	7177	1293	4080
$(0\bar{1}3)$	11830	11835	1286	3465
(071)	27919	27991	1205	24340
$(0\bar{7}1)$	23537	23598	1267	24151
(011)	149655	152057	2239	153496
$(0\bar{1}1)$	142146	144427	2007	145361
(022)	48596	48821	3237	44591
$(0\bar{2}2)$	39116	39297	3026	42228
(051)	44529	44766	2444	49988
$(0\bar{5}1)$	47249	47500	2541	49447

[a] Integrated neutron counts.

that in a number of low symmetry magnetic systems similar to $MnCl_2 \cdot 4H_2O$ it is very important to have the preferred spin direction precisely determined before making extensive studies of the magnetic properties of the system. Serious errors can occur, eg., the loss of the first-order nature of the AF-to-SF transition, if the external field is aligned along a direction substantially different from the preferred direction.

After the neutron diffraction measurements determined the precise preferred direction, Benedict and Rives[15] made very careful magnetic susceptibility measurements in the neighborhood of the AF-to-SF transition, with the external field aligned within ± 2° of the preferred direction as determined by the neutron diffraction. These measurements clearly proved the AF-to-SF transition to be of first order for $T < 0.4$ K. Subsequent susceptibility measurements performed at several angles relative to the preferred direction verified that the first-order behavior disappeared outside a certain critical angle, as discussed in the text.

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