attempt to correlate any temperature dependence in D with that in μ_S, the temperature independence of the one implies a temperature independence in the other, as observed experimentally.

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Neutron Diffraction and Magnetic Structure of $CsMnCl_3$

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The room-temperature (paramagnetic) structure of $CsMnCl_3$ is verified by neutron powder diffraction studies. This compound is found to be a perovskite-related compound (the nine-layer structure) which belongs to the trigonal space group D_{3d}^5-$R\bar{3}m$. The compound is antiferromagnetic below 67 °K; its magnetic structure is deduced from its neutron diffraction pattern at liquid-helium temperature. This structure is of the G type with a $\vec{k}$ vector $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ related to the rhombohedral crystallographic lattice. The spin direction is perpendicular to the body diagonal of the rhombohedral unit cell. The magnetic symmetry is monoclinic, belonging to the space group $C_{2c}2/m$. A dipolar energy calculation confirms the spin direction found. A magnetic moment of $(5.5 \pm 0.5)\mu_B$ is calculated for the Mn^{+2} ions.

INTRODUCTION

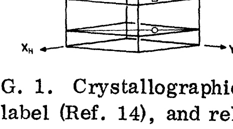
The compound $CsMnCl_3$ was prepared[1–5] and investigated by x rays,[2,5] nuclear magnetic resonance (NMR),[6] antiferromagnetic resonance (AFMR),[7,8] and ultraviolet fluorescence.[9] This compound was reported by Kestigian *et al.*[4] to have a hexagonal unit cell ($a_H = 7.288$, $c_H = 27.44$) with nine formula units. According to the same authors[10] this compound is not related to the perovskite structure. According to Seifert and Koknat[11] the arrangement of the ions in this unit cell (after Andersen[11,12]) is based on the AX_6 octahedra which build the perovskite-related compounds of formula ABX_3. This unit cell with the nine Mn^{+2} ions is shown in Fig. 1. McMurdie *et al.*[13] propose for $CsMnCl_3$ the space group D_{6h}^4-$P6_3/mmc$. This space group is inconsistent with Refs. 11 and 12. Rinneberg and Hartman[6] conclude from NMR measurements that this compound has trigonal symmetry with the space group D_{3d}^5-$R\bar{3}m$, which is consistent with Refs. 11 and 12.

Magnetic measurements were carried out on $CsMnCl_3$ by Asmussen[3] and by Kedzie *et al.*[7,8] Asmussen[3] reported an effective magnetic moment of $6.13\mu_B$ and a Curie-Weiss temperature of −145 °K. Kedzie *et al.*[7] reported the results of AFMR observations on $CsMnCl_3$; they reported it to be an antiferromagnet with a Néel temperature of (69 ± 3) °K. In another paper[8] they report that the spins of the Mn^{+2} ions lie in the plane normal to the hexagonal c axis.

We report here the results of a neutron diffraction study of powder sample of $CsMnCl_3$. Our results concerning the crystallographic and magnetic structures are in agreement with the results reported in Refs. 4–8, 11, and 12 but inconsistent with 10 and 13.

EXPERIMENTAL

The material $CsMnCl_3$ was prepared according to the following procedure: Stoichiometric amounts of anhydrous $MnCl_2$ and CsCl were mixed in a quartz ampoule. The ampoule, after being evacuated and sealed, was heated up to 700 °C and kept at this temperature for several hours, and then slowly cooled down to room temperature. The manganese ion content in the resulting red compound was determined by ethylene diamine-tetraacetic-acid (EDTA) complexometric titration. The chlorine ion content was determined by argentometric titration. Results of the chemical analysis were: Mn, 18.6; Cl, 36.2 (calculated: Mn, 18.67; Cl, 36.15). X-ray measurements were done on a powder sample and a single crystal of $CsMnCl_3$ and showed it to possess rhombohedral symmetry.[5]



COORDINATES	SITE	SPIN
(2/3, 1/3, 17/18)	6c	+
(2/3, 1/3, 15/18)	3b	-
(2/3, 1/3, 13/18)	6c	+
(0, 0, 11/18)	6c	-
(0, 0, 9/18)	3b	+
(0, 0, 7/18)	6c	-
(1/3, 2/3, 5/18)	6c	+
(1/3, 2/3, 3/18)	3b	-
(1/3, 2/3, 1/18)	6c	+

FIG. 1. Crystallographic unit cell with the coordinates, site label (Ref. 14), and relative spin direction of the magnetic ions in $CsMnCl_3$. (The ideal close-packing parameter is assumed here for the magnetic ions.)

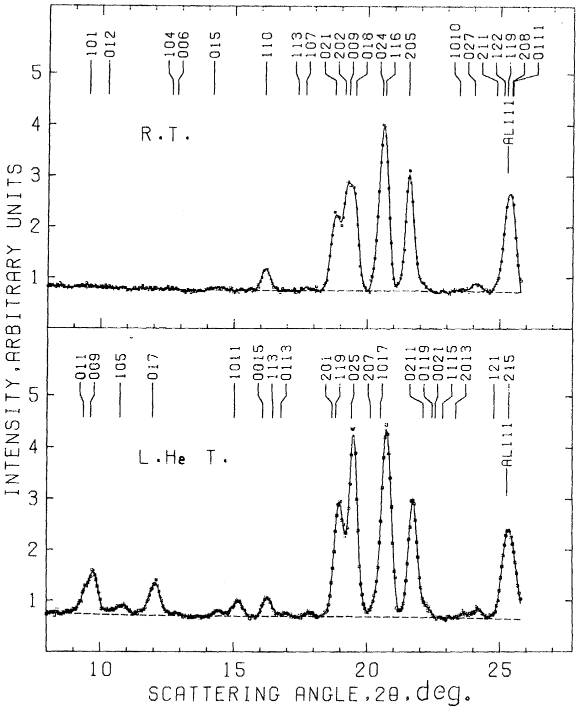


FIG. 2. Neutron (λ = 1.023) diffraction patterns of $CsMnCl_3$ at room temperature (R. T.) and liquid-helium temperature (L. He T.). The R. T. pattern is indexed according to the hexagonal cell $a_H = 7.288$, $c_H = 27.44$ and only allowed reflections $(-h_H + k_H + l_H = 3n)$ are shown. The L. He. T. pattern is indexed according to the hexagonal cell with $a_H' = a_H$ and $c_H' = 2c_H$ and only the allowed magnetic reflections ($h_H - k_H + l_H = 3n$, l_H odd) are shown. The indices *hkl* labeling the reflections stand for the set $\{hkl\}$.

Neutron diffraction patterns of a powder sample of $CsMnCl_3$ were taken at room- and liquid-helium temperature (R. T. and L. He T. in Fig. 2). The room-temperature pattern is indexed according to the hexagonal unit cell proposed by Kestigian *et al.*[4] ($a_H = 7.288$, $c_H = 27.44$). Reflections which do not satisfy the relations $-h_H + k_H + l_H = 3n$ are absent in this pattern. This pattern can also be indexed according to a rhombohedral unit cell with three formula units ($a_R = 10.07$, $\alpha = 42°26'$) having one-third the volume of the hexagonal cell (Fig. 3). The rhombohedral (h_R, k_R, l_R) and the hexagonal (h_H, k_H, l_H) indices are related by $h_R = (2h_H + k_H + l_H)/3$, $k_R = (-h_H + k_H + l_H)/3$, $l_R = (-h_H - 2k_H + l_H)/3$ using the obverse rhombohedral setting.[14]

A least-square analysis of the room-temperature pattern using 11 experimental lines including zero-intensity lines (Table I) yielded a residual[15] $R = 0.067$. The analysis resulted in the ion positions (in the trigonal space group D_{3d}^5-$R\bar{3}m$, hexagonal setting) given in Table II and a Debye-Waller factor[16] $B = 2.2$ Å^2. The pattern taken at L. He T. (Fig. 2) exhibits superlattice lines; these lines can be indexed with unit-cell translations $a_H' = a_H$, $c_H' = 2c_H$ as shown in Fig. 2. The indices $\{hkl\}$ with l even in this unit cell were omitted since they correspond to $\{hk\frac{1}{2}l\}$ (with $\frac{1}{2}l$ being an integer) in the crystallographic unit cell (which are given with the R. T. pattern). The alternative unit cell in the rhombohedral setting is eight times the crystallographic unit cell ($a_R' = 2a_R$, $\alpha' = \alpha$). The magnetic lattice has therefore $\vec{k} = (0, 0, \frac{1}{2})$ in the hexagonal setting, and $\vec{k} = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ in the rhombohedral setting.

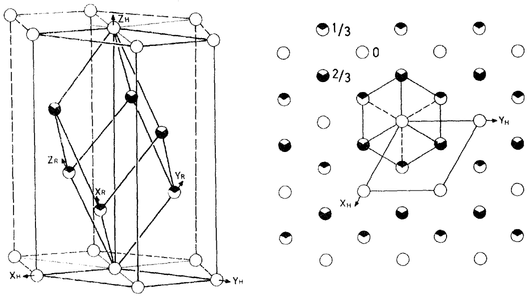


FIG. 3. Connection between the primitive rhombohedral and the hexagonal lattices in trigonal symmetry. The projection is on the hexagonal (001) plane.

Measurements of the line peak intensity as a function of temperature were taken for the lines at $2\theta = 9°45'$ (Fig. 4) and at $2\theta = 12°6'$. The first line revealed a transition point at (67 ± 2) °K. The reduced magnetization was calculated from this curve and is compared with the results of molecular field

TABLE I. Comparison of calculated and observed integrated intensities for the R. T. pattern of $CsMnCl_3$. The calculated intensities were obtained using the parameter values given in Table II and a Debye-Waller factor (Ref. 16) of 2.2 Å^2.

$\{hkl\}$	Observed	Calculated
1 0 1	11 ± 6	3
0 1 2	···	···
1 0 4 0 0 6	···	3
0 1 5	10 ± 6	···
1 1 0	92 ± 10	42
1 1 3 1 0 7	12 ± 8	15
0 2 1 2 0 2 0 0 9 0 1 8	1000 ± 16	1000
0 2 4 1 1 6	771 ± 13	789
2 0 5	511 ± 13	577
1 0 10	···	5
0 2 7	36 ± 8	30

model in Fig. 5. The same results were obtained from measurements on the second line.

DETERMINATION OF CRYSTALLOGRAPHIC AND MAGNETIC STRUCTURES

Our first step in the search for the magnetic structure of $CsMnCl_3$ is to confirm its crystallographic structure. The hexagonal unit cell proposed by Kestigian[4] is consistent with our R. T. neutron diffraction pattern. The same author found from density measurements that this unit cell contains nine formula units. The space group $P6_3/mmc$ proposed by McMurdie[13] is inconsistent with the latter result because it does not have any site with an odd number of positions and therefore cannot accommodate nine ions in a unit cell. The absence rule found in our R. T. pattern, namely, only lines for which $-h_H+k_H+l_H=3n$ are allowed, rules out this space group. The rule on the other hand is consistent with some trigonal space groups. The highest symmetry trigonal space group which can also accommodate the nine ions is $R\bar{3}m$. This space group was taken as the most probable for $CsMnCl_3$ in agreement with x-ray measurements.[5] A least-square analysis of the intensities (Table I) resulted in the ion positions given in Table II, a Debye-Waller factor[16] $B=2.2$ Å^2 and a residual[15] $R=0.067$. The same space group is proposed by Andersen[12] for $CsMnCl_3$ (with ideal close packing parameters). The ionic positions proposed by Andersen differ from those given in Table II by one-half a unit-cell translation in the c direction, the point symmetry being the same in the two cases. The space group $R\bar{3}m$ is also reported for $BaRuO_3$,[17] which is a nine-layer (9L) perovskite-related compound and is isomorphic to Seifert's structure. The parameter values obtained here for the ion positions are very similar to those obtained for $BaRuO_3$.[17] The 9L structure is also reported for $CsCoF_3$,[18,19] and as the high-pressure form of $CsMgF_3$, $CsNiF_3$, and $BaMnO_3$.[19] This is a close-packed hexagonal structure symbolized by the sequence *hhc*.[20] It is built up of $MnCl_6$ octahedra[17,19] which are the typical perovskite motifs. The Goldschmidt tolerance factor[21] for $CsMnCl_3$ is 0.94, which conforms with a perovskitelike structure with hexagonal unit cell in $ABCl_3$ compounds.[13] The rhombohedral cell already mentioned is the primitive unit cell for this structure. This completes the first step.

TABLE II. Ionic positions in $CsMnCl_3$. Space group $R\bar{3}m$, hexagonal setting.

		$(0\ 0\ 0;\ \frac{1}{3}\ \frac{2}{3}\ \frac{2}{3};\ \frac{2}{3}\ \frac{1}{3}\ \frac{1}{3})+$	
3 Cs_I	in (a)	$0\ 0\ 0$	
6 Cs_{II}	in (c)	$\pm(0\ 0\ z)$	$z=0.215\pm0.005$
3 Mn_I	in (b)	$0\ 0\ \frac{1}{2}$	
6 Mn_{II}	in (c)	$\pm(0\ 0\ z)$	$z=0.385\pm0.005$
9 Cl_I	in (e)	$\frac{1}{2}\ 0\ 0;\ 0\ \frac{1}{2}\ 0;\ \frac{1}{2}\ \frac{1}{2}\ 0$	
18 Cl_{II}	in (h)	$\pm(x\ \bar{x}\ z;\ x\ 2x\ z;\ 2\bar{x}\ \bar{x}\ z)$	$x=0.150\pm0.005$ $z=0.560\pm0.005$

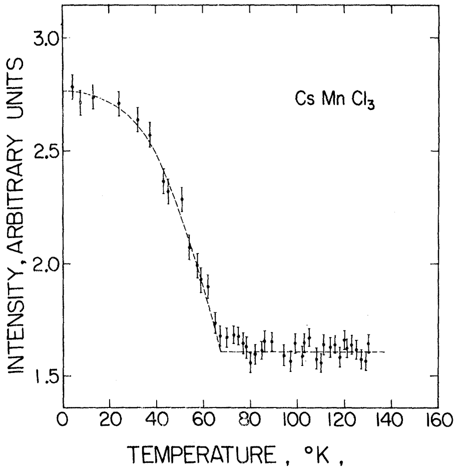


FIG. 4. Temperature dependence of the peak intensity of the {011}+{009} magnetic line of $CsMnCl_3$.

In the second step we determine the magnetic lattice. Since there is an odd number of magnetic ions in a crystallographic cell (nine) and the compound was reported[7] to be an antiferromagnet, it follows that the magnetic unit cell is an even multiple of the crystallographic cell. The magnetic reflections (Fig. 2) can be indexed on $\{h_H k_H \frac{1}{2} l_H\}$ with l_H odd (or $\{\frac{1}{2}h_R \frac{1}{2}k_R \frac{1}{2}l_R\}$ with h_R, k_R, l_R odd) with respect to the crystallographic hexagonal (or rhombohedral) unit cell. It is therefore concluded that the magnetic lattice is connected to the crystallographic lattice with $\vec{k}=(0,0,\frac{1}{2})$ [or $\vec{k}=(\frac{1}{2},\frac{1}{2},\frac{1}{2})$]. This corresponds to a P_{2c} hexagonal lattice (or R_R rhombohedral lattice) in the notation of Opechowski and Guccione,[22] leading to a magnetic unit cell with $a'_H=a_H$ and $c'_H=2c_H$ (or $a'_R=2a_R$).

In the third step we determine the spin structure. Since there is no doubling of the hexagonal cell in the hexagonal plane, we conclude that the antiferromagnetic structure consists of ferromagnetic planes stacked along the hexagonal c axis. Taking into account only collinear structures we have $2^8=256$ possible sequences of antiferromagnetic ordering which are consistent with $\vec{k}=(0,0,\frac{1}{2})$ for a given spin direction. A computer program was used to compute the intensities of all spin sequences for two magnetization directions: along the hexagonal c axis and perpendicular to it. Comparison between the observed magnetic and the calculated[23] integrated intensities shows that only one of the sequences is in agreement with the experimental data (Table III). This sequence is the ordinary antiferromagnetic one and consists of ferromagnetic planes with neighbor planes having antiparallel spins (Fig. 1), with the spin axis lying in the hexagonal plane (normal to the

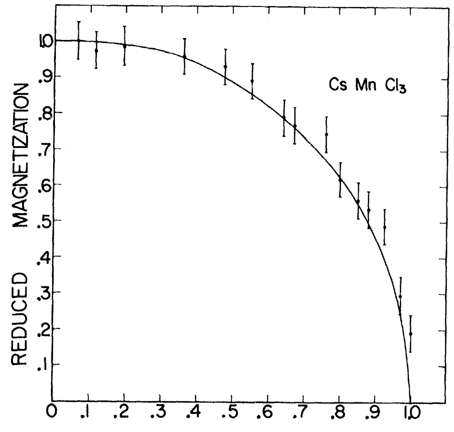


FIG. 5. Reduced temperature dependence of the sublattice magnetization of $CsMnCl_3$ derived from the magnetic line $\{011\}+\{009\}$, compared with the result of molecular field model for Mn^{+2} ($S=\frac{5}{2}$).

c axis). This spin direction is in agreement with the AFMR result of Kedzie *et al.*[8] The direction of the spins in the hexagonal plane cannot be determined from powder data. This completes the determination of the magnetic structure.

DISCUSSION

A calculation shows that the anisotropic part of the dipolar energy is minimal when the spins are perpendicular to the hexagonal c axis, in agreement with the experimental results. The corresponding anisotropy dipolar field perpendicular to c is about 3 kG (all directions in the hexagonal plane being equivalent).

It is interesting to look at the rhombohedral magnetic lattice. In the primitive crystallographic unit cell there are three Mn^{+2} ions, one at $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ and the other two at $\pm(xxx)$. Hence the three ions are located on the body diagonal of the rhombohedral cell (which coincides with the hexagonal c axis; compare Figs. 1 and 3) with the first ion at an inversion point. We found the spins of the last two ions to be parallel to each other and antiparallel to the spin of the first ion. We can represent this motif of three spins by one lattice point at $\frac{1}{2}\frac{1}{2}\frac{1}{2}$. The whole magnetic lattice is rhombohedral with three primitive translations of the crystallographic lattice being antitranslations in this case. If we disregard color, the magnetic lattice will coincide with the crystallographic lattice. We therefore obtain a magnetic unit cell which is doubled with respect to the crystallographic cell along the three primitive translations [i.e., $\vec{k}=(\frac{1}{2},\frac{1}{2},\frac{1}{2})$]. This cell contains eight lattice points. We can choose a primitive magnetic unit cell with only four lattice points by choosing the (1, 1, 0), (1, $\bar{1}$, 0), and (0, 0, 2) vectors (related to the axes of the crystallographic rhombohedral unit cell) as the new unit-cell translations.

We can see now that the magnetic structure is the G type[24]; namely, a given spin has the spins of all its first neighbors reversed with respect to itself. Notice that this rule holds for each single ion as well as for every lattice point. This magnetic structure is analogous to that found for many other pseudocubic perovskites (e.g., the orthoferrites); in this analogy the motif of three spins in $CsMnCl_3$ corresponds to a single spin in the cubic perovskite. The magnetic unit-cell translations of these perovskites are also given by the vectors (1, 1, 0), (1, $\bar{1}$, 0), and (0, 0, 2) (related to the axes of the cubic perovskite cell), and their magnetic structure is also of the G type.

The magnetic structure of $CsMnCl_3$ has a monoclinic symmetry, since the only special axis in the paramagnetic state—the threefold rotation axis—is inconsistent with the spin direction determined above. The magnetic space group is $C_{2c}2/m$ (for notation see Ref. 22) if the spins are perpendicular to the crystallographic mirror plane in $R\bar{3}m$, or, $C_{2c}2/m'$ if they are parallel to this plane (the space-group symmetry will be still lower if the spins are parallel to any other direction in the hexagonal plane). According to Opechowski and Guccione[22] weak ferromagnetism is not allowed in either of these two symmetries (a trivial consequence of the doubling of the unit cell). In both cases there are six possible domains, which are the directions

TABLE III. Comparison of the observed and calculated magnetic integrated intensities for $CsMnCl_3$. The observed magnetic integrated intensities are equal to the difference between the observed integrated intensities at R. T. and L. He`T., corrected for the Debye-Waller factor.

{*hkl*}	Observed	Calculated
0 1 1 0 0 9	100 ± 7	100
1 0 5	27 ± 4	29
0 1 7	77 ± 5	84
1 0 11	30 ± 4	45
0 1 13	8 ± 2	7
2 0 1 1 1 9 0 2 5	57 ± 13	64
2 0 7 1 0 17	21 ± 10	19
0 2 11 0 1 19 0 0 21 1 1 15 2 0 13	1 ± 7	15

equivalent under the threefold axis with their time conjugates. This is in agreement with the phase rule,[25] since the order[26] of the paramagnetic space group ($1'R\bar{3}m$) is 2×12, and the order[26] of the magnetic group ($C_{2c}2/m$) is 16; taking into account that the magnetic unit cell is four times the paramagnetic cell, the order of the factor group is $24/(16/4) = 6$, which is the number of the domains for each of the two symmetries mentioned above.

The sublattice magnetization was calculated from the temperature dependence of the peak intensities of the magnetic line $\{011\}+\{009\}$ (Fig. 4). The results are compared in Fig. 5 with the magnetization M/M_0 calculated in the molecular field model from the equation

$$\frac{M}{M_0}=B_{5/2}\left(\frac{T_N}{T}\,\frac{M}{M_0}\right),$$

where $B_{5/2}$ is the Brillouin function for $S=\frac{5}{2}$.

From the ratio of the integrated intensity of the $\{011\}+\{009\}$ magnetic line to that of the nuclear reflection $\{205\}$, a magnetic moment of $(5.5\pm 0.5)\mu_B$ was deduced for the Mn^{+2} ions.[23] The same result was obtained for the magnetic line $\{017\}$.

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[26] By "order of space group" we mean the order of its quotient group with respect to its translation group.