Magnetic Structure of $MnSO_4$†

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The magnetic structure of $MnSO_4$ has been determined from a powder neutron-diffraction study. It consists of a cycloidal spiral arrangement related to the simple $CrVO_4$ type of magnetic structure, in which ferromagnetic (001) sheets are coupled antiparallel to adjacent sheets. The propagation vector of the spiral is directed along the a axis, with a periodicity of 30 Å (about $6a$), and the spiral spin components lie in the ab plane. The moment of each Mn^{2+} ion is $4.8\mu_B$, and the cone half-angle is about 78°.

INTRODUCTION

BECAUSE of their interesting magnetic properties the sulfates of the $3d$ transition elements have been the object of extensive studies from as early as 1911.[1,2] In $FeSO_4$, $CoSO_4$, $NiSO_4$, and $CuSO_4$, antiferromagnetic ordering has been indicated by magnetic measurements,[3] and confirmed by neutron diffraction[4] during the last few years. The spin configurations of $FeSO_4$ and $NiSO_4$ are of collinear type consisting of antiferromagnetic sheets with ferromagnetic coupling between the sheets. In both compounds the spin direction is parallel to the b axis. In the case of α-$CoSO_4$ a coplanar structure occurs, while in β-$CoSO_4$ a complicated arrangement is found in which there are spin components along all three axes.

Rather less is known about the remaining member of the series, $MnSO_4$. As far as is known, the most complete susceptibility measurements available date back to 1913,[2] and cover the temperature range between 20°K and room temperature. There are indications of the onset of an antiferromagnetic transition slightly below 20°K. More recent measurements over the temperature range 77–300°K are in essential agreement.[5] This paper describes the results of a neutron-diffraction investigation of polycrystalline $MnSO_4$.

EXPERIMENTAL

Powder $MnSO_4$ was prepared by dehydration of $MnSO_4 \cdot H_2O$ ("Baker Analyzed" grade) under vacuum at 190°C for several hours. The weight loss was within 0.2% of theoretical and a diffractometer trace showed only a single orthorhombic phase with the lattice parameters $a=5.260$ Å, $b=8.042$ Å, and $c=6.847$ Å in agreement with published values.[6,7] Neutron-diffraction patterns, shown in Fig. 1, were obtained at 77 and 4.2°K from a cylindrical sample containing about 40 g of material. The neutron wavelength was 1.03_3 Å.

CRYSTAL STRUCTURE

Previous work has shown that $MnSO_4$ is isostructural with $NiSO_4$ and $MgSO_4$ crystallizing in the orthorhombic space group $Cmcm$ (D_{2h}^{17}). The following positions are occupied:

$$\text{Mn in } 4(a) \text{ at } (0,0,0);$$
$$\text{S in } 4(c) \text{ at } (0,y_1,\tfrac{1}{4});$$
$$\text{O}_\text{I} \text{ in } 8(f) \text{ at } (0,y_2,z_2);$$
$$\text{O}_\text{II} \text{ in } 8(g) \text{ at } (x_3,y_3,\tfrac{1}{4}).$$

The parameter values resulting from a least-squares analysis of the neutron and x-ray powder diffraction data (given in more detail in a separate publication[7]) are as follows:

$$y_1=0.361;$$
$$y_2=0.255;\ z_2=0.071,$$
$$x_3=0.230;\ y_3=0.459.$$

They differ slightly from those of the isostructural compounds, the latter in some cases giving calculated neutron-diffraction intensities differing by as much as 50% from the observed values.

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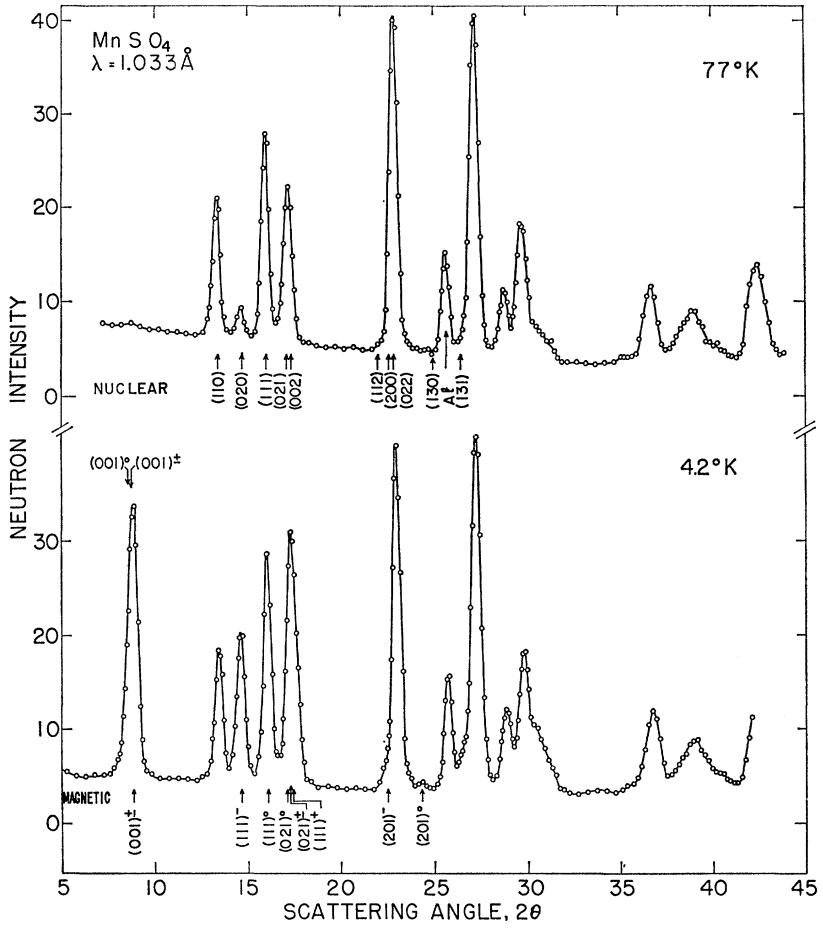

FIG. 1. Neutron-diffraction patterns of $MnSO_4$ at 77°K (top) and 4.2°K (bottom).

MAGNETIC STRUCTURE

A. Magnetic Models

A number of simple configurations possible in this type of orthorhombic structure have been considered in detail in a recent paper.[4] If the magnetic unit cell is the same as the crystallographic cell, there are four possible collinear structures, three antiferromagnetic and one ferromagnetic. With the previous notation, the reflection conditions are as follows:

$M_1(+-+-)$: $(h+k)$ even, l odd,
$M_2(++--)$: $(h+k)$ odd, l even,
$M_3(+--+)$: $(h+k)$ odd, l odd,
$M_4(++++)$: $(h+k)$ even, l even (ferromagnetic).

The positive and negative signs refer to the spin direction of ions at (0,0,0), $(0,0,\frac{1}{2})$, $(\frac{1}{2},\frac{1}{2},0)$, and $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$, respectively. Various combinations of these structures are also possible, of course, leading to the appearance of more than one set of diffraction peaks.

B. Structure Analysis

In the diffraction pattern obtained at 4.2°K, additional peaks are observed arising from magnetic ordering (Fig. 1). These can be seen more clearly in the difference pattern shown in Fig. 2. The observed scattering angles of these peaks (Table I) are close to or coincide with values calculated on the basis of the original cell. In particular, the peaks (001), (020), and (002) appear to contain large magnetic contributions, and there is a small contribution to (111), but no combination of the collinear models above will account for the intensity ratio of (001) and (111), say, or the presence of (020) and (002) and the absence of (110).

However, a careful examination of the observed peak positions reveals in particular that the magnetic peak

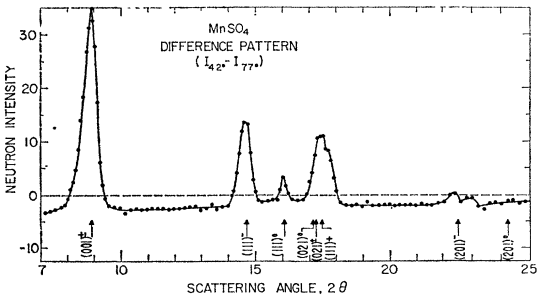

FIG. 2. Temperature difference pattern of $MnSO_4$ showing magnetic contributions at 4.2°K.

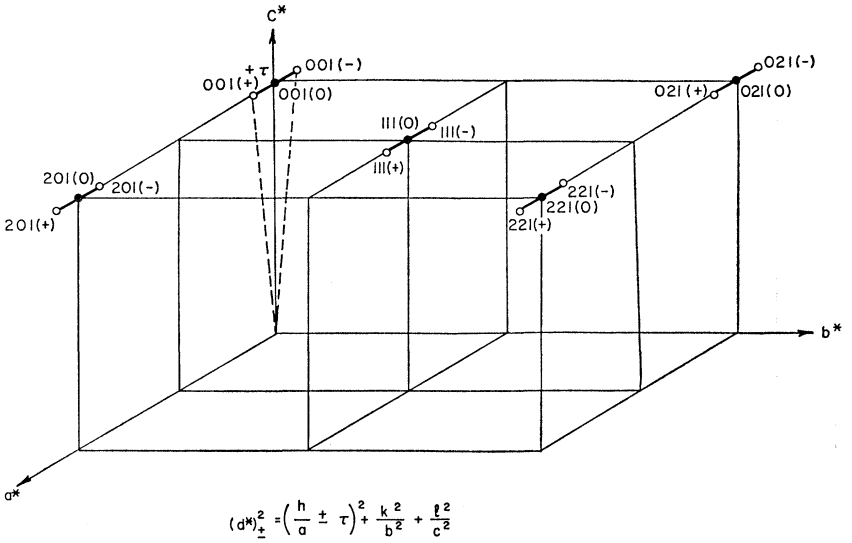

FIG. 3. Reciprocal lattice of $MnSO_4$. The filled circles represent reciprocal lattice points in fundamental positions. The open circles are the satellite points produced by a propagation vector τ along [100].

"(001)" is in fact shifted about 0.25° from its calculated position, a difference well outside the experimental error limits, which are ±0.1°. Analysis was therefore attempted on the basis of a helical spin configuration. Such a situation gives rise to satellite peaks associated in general with reciprocal lattice vectors

$$(\mathbf{d}^*)_{\pm}=\mathbf{d}^*\pm\boldsymbol{\tau}, \tag{1}$$

where τ is the propagation vector. The first reflection can then be indexed as $(001)^{\pm}$ (in conventional notation) arising from a split of (001) into two overlapping satellites. The observation of only one satellite peak (the half-width is unaltered) requires $d^*(001)^+ = d^*(001)^-$, which is satisfied only by a propagation vector lying within the (001) plane. Moreover, the (021) peak, also characteristic of the M_1 type of magnetic structure, is not split either, indicating that the propagation vector lies along [100]. Figure 3 depicts the reciprocal lattice associated with M_1 with τ directed along [100] in which case Eq. (1) reduces (in standard crystallographic notation) to

$$(d^*)^2_{\pm}=\left(\frac{h}{a}\pm\tau\right)^2+\frac{k^2}{b^2}+\frac{l^2}{c^2}. \tag{2}$$

Figure 4 shows $(d^*)_{\pm}$ for a number of peaks as a function of the magnitude of τ along [100]. Good agreement between observed and calculated peak positions is found for $(\boldsymbol{\tau}\cdot\mathbf{a})=\frac{1}{6}$, about 30 Å. The markers represent the experimental uncertainties. A few other propagation directions, such as [010] and [110], were also checked, but no agreement could be found.

In addition to the satellite peaks, there is a small but significant contribution to the fundamental reflection (111) (see Fig. 2), which may be attributed to the presence of a collinear component of M_1 type. The magnetic structure is therefore a cone spiral. The intensity of the fundamental peaks is given by the usual expression

$$(I^0_{hkl})^2=K\langle q^2\rangle p^2|F_{hkl}|^2, \tag{3}$$

where K contains the proportionality constant, temperature and geometrical factors, and multiplicity, $\langle q^2\rangle$ is given by $\langle\sin^2\alpha\rangle$, and

$$p=\mu f\cos\theta, \tag{4}$$

where μ is the moment of the Mn^{2+} ion, f the form factor, and θ the cone half-angle. In the case of the satellite peaks, $\langle q^2\rangle$ may be conveniently expressed as[8]

$$\langle q^2\rangle=\frac{1}{2}\left(\frac{1+\langle\cos^2 k\rangle}{2}\right), \tag{5}$$

where k is the angle between the scattering vector $\mathbf{e}$, and the normal $\mathbf{n}$ to the plane containing the spiral component of spin, and

$$p=\mu f\sin\theta. \tag{6}$$

Systematic variation of the parameters μ and θ led to very satisfactory agreement of the observed and calculated intensities when $\mu=4.8\mu_B$ and $\theta=78°$ for the

TABLE I. Observed and calculated magnetic peak positions in $MnSO_4$ at 4.2°K. Model I is based upon conventional indexing and model II upon the helical structure. M_1 and M_4 are defined in the text.

Model I			Model II		
hkl	Type	2θ (Calc)	*hkl*	2θ (Calc)	2θ (Obs)
001	M_1	8.65	$001^{\pm}$	8.85	8.88
020	M_4	14.76	111^-	14.76	14.65
111	M_1	16.04	111^0	16.04	16.05
021	M_1	17.13	$021^{\pm}$	17.24	17.35
002	M_4	17.35	111^+	17.42	

[8] J. M. Hastings and L. M. Corliss, Phys. Rev. **126**, 556 (1962).

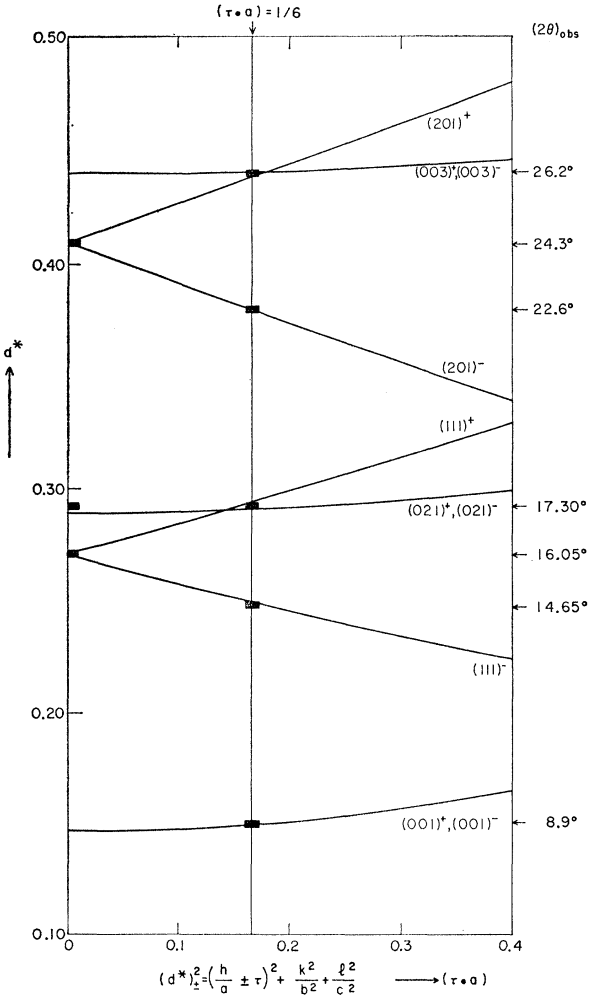

FIG. 4. Dependence of the splitting of the fundamentals on the wavelength of the [100] propagation vector. The vertical line at $(\boldsymbol{\tau}\cdot\mathbf{a})=\frac{1}{6}$ is the value adopted for the model. The thickness of the markers is an approximate measure of the uncertainty in the observed peak position.

reflections listed in Table II. The intensities of higher angle peaks are consistent with these values. Owing to the limited amount of information that can be obtained from powder data in this case, these values must be considered to have an accuracy no better than $\pm 10\%$.

A somewhat artistic impression of the final model is depicted in Fig. 5. It consists of a very open cone spiral derived from a simple antiferromagnetic structure of $CrVO_4$ type, in which ferromagnetic (001) layers are coupled antiparallel to adjacent layers. The cone axis is directed along [001] but the propagation vector lies along [100], and we are therefore observing a cycloidal spiral. The periodicity of the spiral component is very close to $6a$, about 30 Å, corresponding to an interlayer turn angle of 30°.

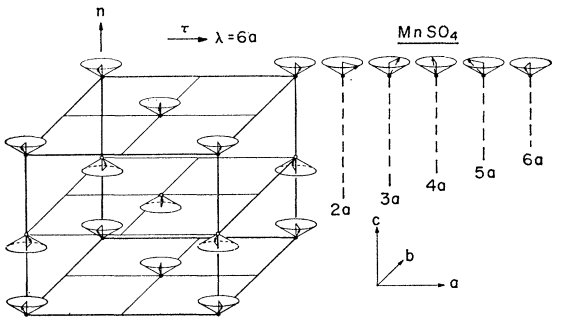

FIG. 5. An impression of the cycloidal cone spiral in $MnSO_4$ propagating along [100] with a wavelength of $6a$.

DISCUSSION

$MnSO_4$ is believed to be the first orthorhombic compound to have a spiral structure, and the fact that the spiral is cycloidal is particularly interesting. The interaction scheme is almost certainly complex; apart from the adjacent Mn^{2+} ions along [001], which are antiferromagnetically coupled, other interactions seem to require at least two intermediary oxygen ions or a sulphate group. Anisotropy is also expected to play an important role.

TABLE II. Observed and calculated intensities for fundamental and satellite reflections of magnetic origin in $MnSO_4$ at 4.2°K. $\mu=4.8\mu_B$, $\theta=78°$, and form factor for Mn^{2+} taken from Corliss *et al.*[a]

hkl	$j\|F\|^2_{\text{calc}}$	$j\|F\|^2_{\text{obs}}$
$(001)^0$	0	40
$(001)^{\pm}$	38	
$(111)^-$	41	40
$(111)^0$	11	11
$(021)^0$	5	61
$(021)^{\pm}$	34	
$(111)^+$	34	
$(201)^-$	11	5
$(201)^0$	4	5

[a] L. Corliss, N. Elliott, and J. Hastings, Phys. Rev. 104, 924 (1956).

If the interlayer turn angle is exactly 30°, the magnetic unit cell would be commensurate with a crystallographic cell six times larger than the original unit cell in the [100] direction, and the structure would be a rather special case of the spiral, and might be regarded as a kind of complicated canted arrangement. Whether this is significant is not known.

There is also the possibility of an additional phase difference between certain of the sublattices, for example, corner and c axis-centered Mn^{2+} ions. In view of the limited amount of data and the satisfactory agreement given by the simpler model, this possibility has not been explored. A detailed study must await the preparation of suitable single crystals.