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# Magnetic and crystallographic order in $\alpha$ -manganese

A. C. Lawson, Allen C. Larson, M. C. Aronson,<sup>a)</sup> S. Johnson,<sup>b)</sup> Z. Fisk, P. C. Canfield,<sup>c)</sup> J. D. Thompson, and R. B. Von Dreele  
Los Alamos National Laboratory, Los Alamos, New Mexico 87545

We have made time-of-flight neutron diffraction measurements on  $\alpha$ -manganese metal. Powder diffraction measurements were made at 14 temperatures between 15 and 305 K, and single crystal measurements were made at 15 and 300 K. We found that the crystal structure of  $\alpha$ -Mn is tetragonal below its Néel point of 100 K, with crystal symmetry  $I42m$  and magnetic (Shubnikov) symmetry  $P_{\bar{1}}42_1c$ . In agreement with the earlier results of Yamada *et al.*, there are six independent magnetic atoms, and we found that their moments are weakly temperature dependent. The onset of magnetic order causes slight changes in the atomic positions and in the average atomic elastic constant.

## I. INTRODUCTION

$\alpha$ -manganese has a surprisingly complex cubic crystal structure with 58 atoms per body-centered cell.<sup>1</sup> The complexity is surprising, because most elements have simple structures. In the case of Mn, the complexity is thought to arise from an instability of the  $3d$  electron shell that gives rise to the formation of "self-intermetallic" compounds. In other words, elemental Mn is actually an intermetallic compound between Mn atoms in different electronic configurations. This possibility was first pointed out by Bradley and Thewlis.<sup>1</sup>

$\alpha$ -Mn becomes antiferromagnetic at 95 K. Given the crystal structure, the magnetic structure is necessarily complex. The structure was solved by Yamada *et al.*,<sup>2</sup> who used single crystal neutron diffraction data and first principles magnetostructural analysis of heroic proportions.<sup>2-4</sup> We wished to examine the magnetic ordering in more detail by obtaining structural data at a large number of temperatures. The multitemperature requirement dictated the use of powder neutron diffraction. However, we found that information from single crystal data was essential to the complete solution of the problem.

## II. EXPERIMENTAL METHOD

$\alpha$ -Mn was prepared by heating Johnson-Matthey grade I electrolytic Mn in a turbomolecular pumped system in the  $\beta$ -phase region until outgassing was complete and then cooling slowly through the  $\alpha$ - $\beta$  transition. The material was cooled from 900 °C to 755 °C over 5 h, from 755 °C to 655 °C over 200 h, and finally furnace cooled to room temperature. Powder was prepared by grinding the resulting material. Small single crystals were cut from an arc-melted ingot that was prepared from this material and annealed for a long time below the  $\alpha$ - $\beta$  transition. Neutron powder diffraction data were taken on an  $\alpha$ -Mn sample at 14 temperatures between 15 and 305 K. We used the high intensity powder diffractometer (HIPD) and the Manuel Lujan, Jr. Neutron Scattering Center (LANSCE) at the Los Alamos National

Laboratory.<sup>5</sup> We also obtained single crystal diffraction data at 15 and 300 K on the single crystal diffractometer (SCD) at LANSCE. Powder data were analyzed by Rietveld analysis using the general structure analysis system (GSAS).<sup>6</sup> This refinement package allows for the refinement of magnetic reflections arising from structures that can be described by Shubnikov groups. Powder data from six detector bands were corefined in the analysis. Allowance was made for 0.90% (vol) of MnO that was present in the powder and for some weak aluminum lines from the cryostat. Single crystal data were also refined using GSAS. In this case, magnetic multidomain effects were treated as a twinning problem.

## III. RESULTS AND DISCUSSION

Since there was no evidence for an incommensurate structure, our approach to the analysis of our data was guided by the use of Shubnikov groups.<sup>7,8</sup> These are magnetic space groups that are supergroups of the ordinary crystallographic space groups, with certain symmetry elements replaced by "anti"-elements. The antielements are the ordinary translations, mirror planes, etc., familiar from crystallography, except that the spatial symmetry operator is augmented by a time-reversal operator that reverses the microscopic current

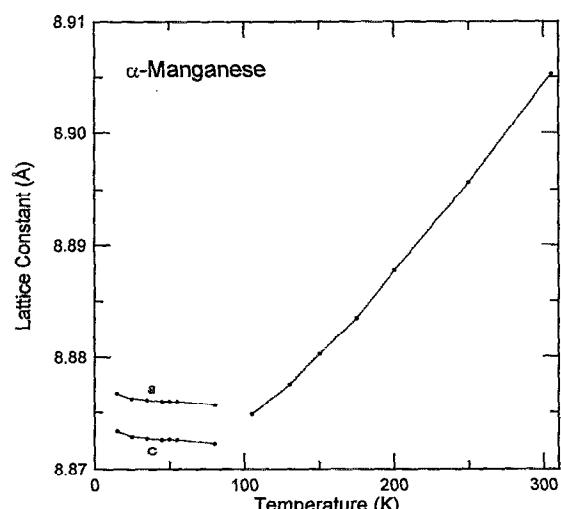


FIG. 1. Lattice constants vs temperature for  $\alpha$ -Mn. The error bars are smaller than the plotted points.

<sup>a)</sup>Present address: Department of Physics, University of Michigan, Ann Arbor, Michigan.

<sup>b)</sup>Deceased.

<sup>c)</sup>Present address: Ames Laboratory, Iowa State University, Ames, Iowa 50011.

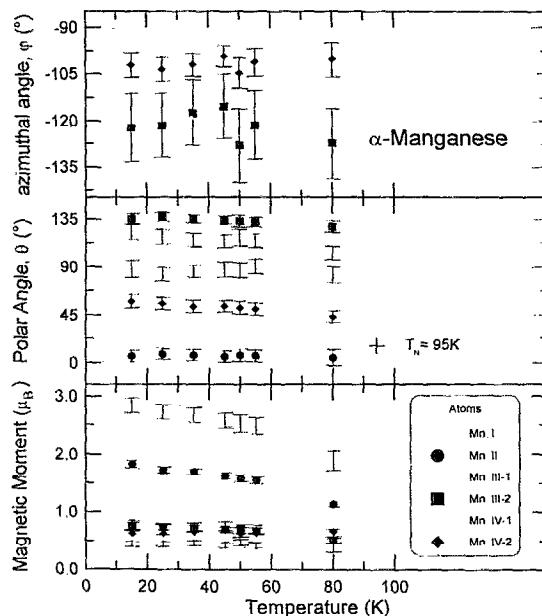


FIG. 2. Magnetic moments vs temperature for  $\alpha$ -Mn.

driving the magnetic moment of the atom to which it is applied. In this way, 1651 magnetic space groups can be obtained from the original 230 ordinary space groups. Only commensurate magnetic structures are described by the Shubnikov groups.

The space group of  $\alpha$ -Mn is  $I\bar{4}3m$ . The neutron diffraction data indicate a body-anti-centered lattice, so that the Shubnikov group  $P_1\bar{4}3m$ , or one of its subgroups, is indicated. The cubic and rhombohedral subgroups did not work, and we found that the best fit was obtained with the tetragonal Shubnikov group  $P_1\bar{4}2'm' \equiv P_1\bar{4}2c$ , which is a subgroup of the tetragonal space group  $I\bar{4}2m$ . This is equivalent to the magnetic model of Yamada *et al.*<sup>2</sup> The meaning of the symbol  $P_1\bar{4}2'm'$  is the same as the ordinary space group symbol  $I\bar{4}2m$ , except that (1) the ordinary body-centering operator is replaced by an operator that flips the spin (reverses the current) as the body centering is applied; (2) the mirror planes are replaced by operators that reverse the current as a magnetic atom is reflected; and (3) the twofold axes are replaced by operators that flip the spin (reverse the current) as the dyad operation is applied to a magnetic atom. (The distinction between spin flipping and reversing the current is important only for improper symmetry operators, such as mirror planes.)

TABLE I. Atomic coordinates for  $\alpha$ -Mn at 305 K.

|   | I | II          | III         | IV          |
|---|---|-------------|-------------|-------------|
| x | 0 | 0.318 36(5) | 0.357 76(3) | 0.090 81(4) |
| y | " | "           | "           | "           |
| z | " | "           | 0.035 43(4) | 0.282 76(5) |

In addition to the group  $P_1\bar{4}2'm'$ , we also tried fits with  $P_1\bar{4}2m$ ,  $P_1\bar{4}'2m'$ , and  $P_1\bar{4}'2'm$ . (Of these four, only the first does not exclude a magnetic moment on site I by symmetry.) The models with  $P_1\bar{4}2m$  and  $P_1\bar{4}'2m'$  can be excluded by the single crystal data, which clearly show the presence of (300), (500), etc. magnetic reflections, in agreement with Yamada *et al.*<sup>2</sup> This is indicative of the presence of the two-fold antiaxis 2'. These reflections are not directly observable in the powder data because of overlapping allowed reflections, so that powder data cannot distinguish between 2 and 2'.

The quality of the powder fits for  $P_1\bar{4}2'm'$  and  $P_1\bar{4}'2m'$  is very similar, so that single crystal data was essential for making this distinction. However, the use of powder data is the only practical way of making observations at a large number of temperatures in a reasonable amount of time. The combination of both types of experiment was necessary in this case.

Since the magnetic structure of  $\alpha$ -Mn is tetragonal, a tetragonal nuclear (or chemical) structure is implied. This structure was found by Rietveld refinement. The space group is  $I\bar{4}2m$ , and there are six unique atoms in the tetragonal unit cell. Above the Néel point, the structure is cubic with four unique atoms in the cell. There are 58 atoms per unit cell in each case.

Figure 1 shows the lattice constants of  $\alpha$ -Mn plotted versus temperature. We emphasize that no tetragonal splitting of the diffraction lines was observed directly; rather, the metric tetragonality was found by testing the powder data with Rietveld refinement. Simultaneous refinements of the strain broadening were well behaved, and sensible atomic positions were found, so we have some confidence in this result. The average of the tetragonal lattice constants agree with previous diffraction measurements for which the low-temperature structure was taken to be cubic.<sup>9,10</sup>

The magnetic moments are plotted versus temperature in Fig. 2. These were obtained from the powder refinements using the form factors for the  $3d^54s^2$  state of neutral Mn determined by Freeman and Watson.<sup>11</sup> Thus, we did not allow for a variation of the form factor among the atoms, as

TABLE II. Atomic coordinates and magnetic moments ( $\mu_B$ ) for  $\alpha$ -Mn at 15 K.

|       | I        | II        | III-1     | III-2     | IV-1      | IV-2      |
|-------|----------|-----------|-----------|-----------|-----------|-----------|
| x     | 0        | 0.3192(2) | 0.3621(1) | 0.3533(2) | 0.0921(2) | 0.0895(2) |
| y     | "        | "         | "         | 0.0333(1) | "         | 0.2850(1) |
| z     | "        | 0.3173(3) | 0.0408(2) | 0.3559(2) | 0.2790(3) | 0.0894(2) |
| $m_x$ | 0        | 0.14(12)  | 0.43(8)   | -0.25(10) | 0.27(8)   | -0.08(4)  |
| $m_y$ | "        | "         | "         | -0.25(10) | "         | -0.45(8)  |
| $m_z$ | 2.83(13) | 1.82(06)  | 0.43(8)   | -0.32(4)  | -0.45(8)  | 0.48(5)   |

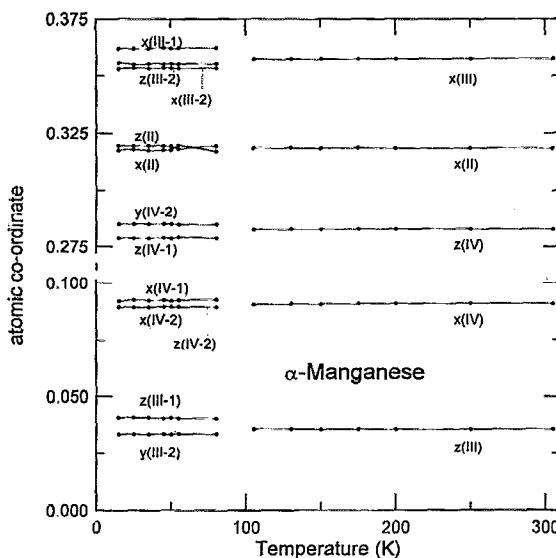


FIG. 3. Positional parameters for  $\alpha$ -Mn. The error bars are smaller than the plotted points.

did Yamada *et al.*<sup>2</sup> The moments we found are somewhat different from theirs, but the significant qualitative feature of groups of large and small moments is retained. The large moments on atoms I and II are somewhat temperature dependent, and the smaller moments on the remaining atoms are not.

The atomic positions also show the effects of magnetic ordering. Below the Néel temperature, the original four crystallographic sites of the cubic structure (Table I) split into the six sites of the tetragonal structure (Table II). The atomic positions obtained from the powder refinements are plotted versus temperature in Fig. 3. A diagram of the magnetic structure is given in the compilation by Wijn.<sup>12</sup> The Cartesian components of the magnetic moments at 15 K are given in Table II.

Magnetic ordering in  $\alpha$ -Mn causes a stiffening of the lattice. Figure 4 shows the average mean-square thermal displacement,  $\langle u^2 \rangle$ , plotted versus temperature. The  $\langle u^2 \rangle$  is obtained from the Debye-Waller factors from the Rietveld analysis of the powder data; it is averaged over atomic sites and direction.<sup>13,14</sup> We have made separate fits above and below the Néel temperature to the  $\langle u^2 \rangle$  versus temperature data with a simple Debye model. The increase in  $\Theta_{DW}$  observed at the Néel point (from 438 to 536 K) is quite large.

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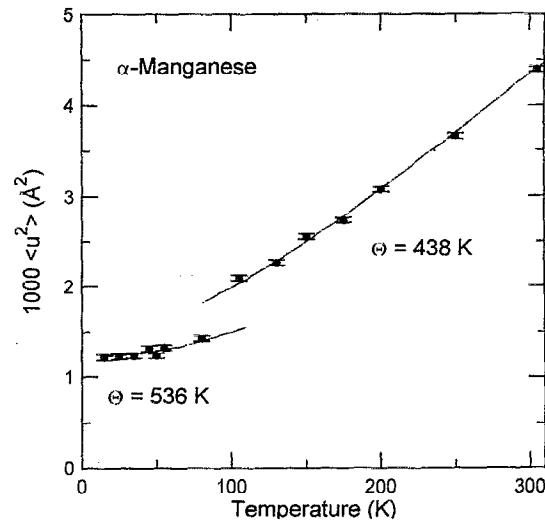


FIG. 4. Average mean square thermal displacement,  $\langle u^2 \rangle$ , vs temperature for  $\alpha$ -Mn. The lines through the points are fits to a simple Debye-Waller formula. The fitted Debye-Waller temperatures are different above and below the Néel temperature.

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