Spin, charge, and orbital order in Mn$_2$OBO$_3$

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The magnetic ordering in Mn$_2$OBO$_3$ has been determined from neutron diffraction and magnetization measurements. Long range antiferromagnetic order occurs below $T_N=26$ K, other apparent magnetic transitions are due to secondary phases. The magnetic order has a $(\frac{110}{2})$ propagation vector and the antiferromagnetic spin arrangement has been refined. The low ordering temperature and ordered moment (1.0 $\mu_B$) at the Mn$^{3+}$ sites evidence magnetic frustration arising from the charge and orbital ordered arrangement of Mn$^{2+}$ and Jahn-Teller Mn$^{3+}$ states. This is supported by a qualitative assessment of the Mn-O-Mn superexchange interactions.

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I. INTRODUCTION

The interplay of spin, charge and orbital degrees of freedom in solid transition metal compounds is of current interest. Semivalent materials are particularly useful as they display the simplest (1:1) charge ordered ground states which, when lattice disorder is minimal, are often sufficiently long range ordered to be observed in crystallographic studies. Any orbital order that breaks the degeneracy of localized-ion states can also be found from structure refinement, and neutron diffraction permits the spin order resulting from the superexchange between the localized moments to be determined. Examples of well-ordered, semivalent transition metal oxides that show long range spin, charge and orbital order are the perovskite types La$_{0.5}$Ca$_{0.5}$MnO$_3$,$^1$ YBaMn$_2$O$_5$,$^2$ YBaCo$_2$O$_5$,$^3$ TbBaFe$_2$O$_5$,$^4$ and TbBaMn$_2$O$_6$,$^5$ and the spinel magnetite (Fe$_3$O$_4$).$^6,7$ Semivalent behavior can also be found in more complex networks such as the homometallic warwickite structure.

Many mixed metal oxyborates MM’OBO$_3$ adopt the warwickite structure,$^8$ where M and M’ are, respectively, a divalent and a trivalent metal. Homometallic (M=M’) warwickites are known only for M=Fe (Refs. 9–11) or Mn.$^{12,13}$ The aristotype orthorhombic warwickite structure is based on hexagonal close packing of oxygen ions. The metal ions have octahedral coordination, these octahedra share edges to form ribbons of four infinite chains of octahedra linked by corner sharing and the trigonal planar BO$_3$ groups. The warwickite structure has two inequivalent sites for the metal ions (M(1) and M(2)), as can be seen in Fig. 1. The homometallic warwickites have been of previous interest because the iron and manganese compounds show different types of charge ordering. Mn$_2$OBO$_3$ has the divalent and trivalent ions on different crystallographic sites,$^{12}$ i.e., Mn(1)$^{3+}$Mn(2)$^{2+}$OBO$_3$ but Fe$_2$OBO$_3$ has equal numbers of divalent and trivalent ions on each site, i.e., Fe(1)$^{3+}$Fe(1)$^{3+}$Fe(2)$^{2+}$Fe(2)$^{2+}$Fe(2)$^{3+}$OBO$_3$.$^9,11$ The different charge orderings within these materials lead to different monoclinic distortions of the orthorhombic warwickite structure.

Fe$_2$OBO$_3$ undergoes a charge ordering transition at 317 K, at which the orthorhombic Pmcn to monoclinic $P2_1/c$ structural distortion is observed. Magnetic order occurs below $T_c=155$ K. The magnetic structure of Fe$_2$OBO$_3$ is L-type ferrimagnetic.$^9,11$ Magnetic moments on the Fe(1) and Fe(2) chains are antiparallel, so the magnetic structure is almost antiferromagnetic, but the symmetry inequivalence of the two sites leads to an inexact cancellation and a small ferrimagnetic moment of $\sim 0.06 \mu_B$ per formula unit results.

Mn$_2$OBO$_3$ was first prepared by Norrestam et al.$^{12}$ by annealing Mn(NO$_3$)$_2$·4H$_2$O and H$_2$BO$_3$ at 700° C for 3 days, and crystals were grown from a borax flux. The 300 K

![FIG. 1. The crystal and magnetic structures of Mn$_2$OBO$_3$ projected on the $ab$ plane showing the relative moment direction for Mn atoms at $z=1/4$ and $z=3/4$. The unit cell of the crystal lattice is shown.](image-url)
structure was found to crystallize in the $P11_2_1/n$ monoclinic subgroup of $Pmcn$. Full Mn$^{2+}$/Mn$^{3+}$ charge ordering was revealed by the difference in bond valence sums at the two sites. Orbital order was revealed by a pronounced axial elongation of the Mn$(1)O_6$ octahedra, this is a typical Jahn-Teller distortion for Mn$^{3+}$. Specific heat and magnetization studies on Mn$_2$OBO$_3$ were subsequently carried out,$^{13}$ a magnetic transition at 104 K to an antiferromagnetic state with weak ferromagnetism below 70 K was reported. In this paper we report the low temperature spin ordering in Mn$_2$OBO$_3$ based on a powder neutron diffraction and magnetization study.

II. EXPERIMENT

An 8 g sample of polycrystalline Mn$_2$OBO$_3$ was prepared by heating MnO and H$_3$BO$_3$ in air at 800°C for three days, and then reheating for three periods of three days under argon at 800°C. The sample was reground between these periods of heating. The powder x-ray diffraction pattern of the sample agreed with that obtained by Norrestam et al.$^{12}$ Rietveld analysis showed that the sample also contained 1 wt% of Mn$_3$O$_4$. This impurity could not be eliminated by varying the preparation conditions, samples heated for longer times also contained Mn$_2$O$_3$. Magnetizations were measured on a superconducting quantum interference device magnetometer. Data were recorded in a 500 Oe field while warming the sample from 5 to 300 K in 1 K steps, following zero field cooling (ZFC), and field cooling (FC).

Neutron diffraction patterns were obtained in the range 10 to 60 K in 10 K intervals on OSIRIS, ISIS facility, Rutherford Appleton Laboratory, UK. OSIRIS is optimized for measurements at long $d$-spacings with a high resolution and a high counting rate,$^{14}$ six out of the eight possible detector modules were deployed in these measurements. The high flux of neutrons on OSIRIS allowed the sample of Mn$_2$OBO$_3$ containing natural B to be used. The sample of around 8 g was held in a flat plate aluminum can to minimize the effect of neutron absorption by boron-10. Data were collected in the range $d=1.4$ to 6.3 Å. The 10 K data were collected for 12 h, other patterns were recorded in 6 h.

III. RESULTS

A. Crystal structure

Powder neutron diffraction patterns of Mn$_2$OBO$_3$ for $d=3.5$–5.5 Å are shown in Fig. 2. The crystal structure was fitted to the 60 K data, with the $P2_1/n$ symmetry structure determined by Norrestam et al.$^{12}$ as a starting model. The GSAS software package$^{15}$ was used to carry out all structural and magnetic refinements. The refined 60 K lattice parameters in the $b$-unique monoclinic setting were $a=9.2919(7)$ Å, $b=9.5311(7)$ Å, $c=3.2438(3)$ Å and $\beta=90.733(2)^\circ$. The atomic coordinates obtained were in agreement with those obtained by Norrestam et al. but with large experimental uncertainties. These result from poor intensity statistics due to neutron absorption by boron and the presence of several diffraction peaks from a secondary phase of Mn$_3$O$_4$. The peaks due to the Mn$_3$O$_4$ and the aluminum sample can were excluded from the refinement.

B. Magnetic structure

Figure 2 shows that on cooling, a prominent magnetic diffraction peak (marked with an asterisk) appears at $d=4.9$ Å in the 40 K profile. This magnetic Bragg peak is not indexed on the Mn$_2$OBO$_3$ cell but can be indexed as the Mn$_3$O$_4$ (101) reflection. This peak is more intense than might be expected from 1% of an impurity because of microabsorption—the minority phase does not contain boron whereas the principal phase does. A further set of magnetic Bragg peaks appears between 30 and 20 K—these arise from the magnetic ordering in the principal Mn$_2$OBO$_3$ phase. The magnetic structure of Mn$_2$OBO$_3$ was determined from a (10 K–30 K) difference profile (Fig. 3), obtained by subtracting the 30 K neutron scattering from the 10 K pattern with appropriate scaling to allow for the different counting times. This removes the Mn$_2$OBO$_3$ nuclear scattering and the nuclear and magnetic scattering from Mn$_3$O$_4$ from the 10 K data, leaving only the Mn$_2$OBO$_3$ magnetic scattering.

The magnetic Bragg peaks of Mn$_2$OBO$_3$ were all indexed by the $(\frac{1}{2},0,\frac{1}{2})$ propagation vector. To fit the magnetic structure, a magnetic supercell ($m$ subscripts) related to the structural cell by the following transformation was used.
TABLE I. The positions and refined magnetic moment components (μₐ, μₕ, and μ₉) are parallel to aₐ, bₖ, and aₕbₖ, respectively) of the unique Mn sites in the P₂₁/c magnetic supercell. The Shubnikov (magnetic) group symmetry is also P₂₁/c.

<table>
<thead>
<tr>
<th>Site</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>μₐ (μₙ)</th>
<th>μₕ (μₙ)</th>
<th>μ₉ (μₙ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn(1)</td>
<td>-0.3860</td>
<td>0.3836</td>
<td>0.1713</td>
<td>-0.41(9)</td>
<td>-0.84(3)</td>
<td>-0.19(7)</td>
</tr>
<tr>
<td>Mn(1′)</td>
<td>-0.8860</td>
<td>0.3836</td>
<td>0.6713</td>
<td>0.41(9)</td>
<td>0.84(3)</td>
<td>0.19(7)</td>
</tr>
<tr>
<td>Mn(2)</td>
<td>-0.1953</td>
<td>0.4028</td>
<td>-0.0252</td>
<td>0</td>
<td>4.40(7)</td>
<td>0</td>
</tr>
<tr>
<td>Mn(2′)</td>
<td>-0.6953</td>
<td>0.4028</td>
<td>-0.5252</td>
<td>0</td>
<td>-4.40(7)</td>
<td>0</td>
</tr>
</tbody>
</table>

This cell has twice the volume of the structural cell and has P₂₁/c space group symmetry. The magnetic basis consists of two spins at (x,y,z) and (x+½,y,z+½) for each of the independent Mn(1) and Mn(2) sites (Table I) and their equivalent sites under the P₂₁/c symmetry group operations. Good fits to the data were obtained only with a time reversal (spin inversion) operation between (x,y,z) and (x+½,y,z+½) site spins, but with no time reversal operations accompanying the P₂₁/c group operations, so the Shubnikov (magnetic symmetry) group is also P₂₁/c. The Mn(1) moments were found have significant components in the aₐcₖm plane and parallel to bₖm, but the Mn(2) moments are parallel to bₖm. The resultant Mn(1) (Mn³⁺) and Mn(2) (Mn²⁺) moments are 0.95(6) and 4.40(7) μₙ respectively. The fit of this antiferromagnetic structure to the (10 K–30 K) difference gave R_p=3.40%, wR_p=3.77% and χ²=3.35 and the observed, calculated and difference plots are shown in Fig. 3. Views of the spin arrangement are shown in Figs. 1 and 4.

FIG. 4. Magnetic order within the ribbons of four MnO₆ octahedral chains viewed in the bc plane. The ordered d₄₋₂₋₂ type orbitals containing the cₜ holes on Mn³⁺ are shown as broken lines, and the inequivalent superexchange interactions J₁ to J₆ are labeled.

C. Magnetization

The low temperature ZFC and FC magnetic susceptibilities of the Mn₂OBO₃ sample are shown in Fig. 5. Only two magnetic transitions are evident and these are assigned by comparison with the evolution of the neutron scattering in Fig. 2. Mn₃O₄ has a ferrimagnetic ordering transition at 42 K, which dominates the FC magnetization. The second transition, observed at 26 K through the change in slope of the ZFC data, is coincident with the onset of antiferromagnetic ordering seen in the neutron patterns of Mn₂OBO₃. Hence, Mn₂OBO₃ has only one intrinsic magnetic transition down to 4 K, a three-dimensional antiferromagnetic ordering at T_N=26 K.

IV. DISCUSSION

The variable temperature neutron diffraction experiments reveal the intrinsic magnetic ordering in Mn₂OBO₃. A previous study¹³ reported an antiferromagnetic transition at 104 K and weak ferromagnetism below 70 K for this phase, and our magnetization data taken alone would suggest a ferromagnetic or ferrimagnetic ordering at 42 K. However, neutron diffraction demonstrates that only a Neel transition to a three-dimensional spin ordering at 26 K is intrinsic to Mn₂OBO₃, and all the other transitions are due to impurity phases such as Mn₁O₄ which has T_c=42 K. This reflects the difficulty in preparing phase-pure samples of complex oxyborates.

The previously reported structure shows that Mn₂OBO₃ is a charge and orbitally ordered insulator at 300 K, and no changes are found down to 10 K in our study. The spin or-

FIG. 5. Magnetization/field measurements of the Mn₂OBO₃ sample in ZFC and FC conditions.
ordering at 26 K is dictated by the structural and orbital topology of the structure, as shown in Figs. 1 and 4. The structure results in considerable frustration of the magnetic exchange interactions. The order within the chains of edge-sharing octahedra (repeat period b) is antiferromagnetic, so exchange interactions with neighbouring chains are frustrated by the b/2 offset between neighboring chains within the ribbons of four chains (Fig. 1). Triangular connections through the BO₃ groups (Fig. 1) create further magnetic frustration. Reduction in the ordered moment commonly results from topological frustration. A striking feature of the magnetic structure of Mn₂OBO₃ is that the Mn(2) moment of 4.4 μ_B is as expected for S =½ Mn³⁺, allowing for typical covalent and zero-point reductions from the ideal value of 5 μ_B, but the Mn(1) site moment of 1.0 μ_B is greatly reduced from the ideal value of 4 μ_B for S =2 Mn³⁺.

To gain insight into the ordered spin arrangement and the moment reduction of the Mn³⁺ sites in Mn₂OBO₃, estimates of the superexchange interactions are needed. Many inequivalent superexchange pathways are present in this complex network, but the dominant interactions are mediated through the MnO₂Mn bridges between edge-sharing MnO₆ octahedra, as shown in Fig. 4. The ferro- or antiferromagnetic nature of each Mn-O-Mn connection depends primarily on the e_g electron density in the Mn-O bonds, i.e., upon the orbital ordering. For charge ordered Mn³⁺/Mn⁴⁺ arrangements such as (La₉₋ₓCeₓ)MnO₃, the sign of the superexchange interactions predicted from the orbital ordering is consistent with the complex CE-type magnetic arrangement. Orbitally non-degenerate Mn⁴⁺ states (d⁴) have no e_g electrons, whereas Mn⁵⁺ states (d⁵) have one e_g electron, so the presence of one e_g electron per Mn³⁺+Mn⁴⁺ pair is key; the density of this electron is associated with the Mn³⁺ d₁² orbital identified with a pair of elongated MnO₆ bonds. In a charge ordered Mn⁵⁺/Mn³⁺ arrangement as found in Mn₀₂OBO₃, orbitally non-degenerate Mn⁵⁺ has both e_g orbitals singly occupied, whereas Mn⁵⁺ states have only one e_g electron, so each Mn³⁺+Mn⁴⁺ pair has one e_g hole. This e_g hole density is in the Mn⁺⁺ d₁²,2 type orbital associated with four short, coplanar MnO₆ bonds.

The orbital ordering of the e_g holes within the ribbons of four octahedral chains is shown in Fig. 4, together with the six distinct MnO₂Mn superexchange bridges J₁ to J₆. The ferromagnetic (F) or antiferromagnetic (AF) nature of the two Mn-O-Mn contributions to each bridge are listed in Table II. The Mn-O-Mn angles are distorted from 90° (with values from 78° to 91°) so it is assumed, following the Goodenough-Kanomouri rules that e_g⁻¹⁻O:2p−e_g¹⁻ contributions (to J₁ and J₆) are AF, whereas e_g⁻¹⁻O:2p−e_g⁰⁻ overlaps (in J₁, J₂, J₃, J₄) are F. In the case of e_g⁰⁻O:2p−e_g⁰⁻ orbital combinations (J₁), t₂g¹⁻O:2p−t₂g¹⁻ overlap will lead to weaker π-type AF interactions. This simple approach gives an unambiguous prediction of the sign for all of the interactions except J₅. The observed spin alignments (Table II) agree with four of the five predicted interactions (J₁, J₂, J₄, J₅), but the remaining J₃ interaction is frustrated. J₅ favors a ferromagnetic alignment of moments within the Mn(1) chains (Fig. 4) but this is evidently outweighed by the J₂ + J₄ and J₁+J₃ interactions through neighboring chains that lead to an antiparallel alignment of spins in the Mn(1) chains. This frustration of the intrachain exchange by the interchain interactions provides an explanation for why the ordered moments in the Mn(1) (Mn³⁺) chains are considerably reduced by frustration, whereas the Mn(2) (Mn⁵⁺) site moments are unaffected.

Frustration of the magnetic interactions that result from the charge and orbital ordering also accounts for the difference in spin ordering between Mn₂OBO₃ and Fe₂OBO₃. Fe₂OBO₃ is an L-type ferrimagnet with a Curie temperature of 155 K, whereas the Neel temperature of Mn₂OBO₃ is only 26 K. In Fe₂OBO₃, which is not orbitally ordered, the spin chains are ferromagnetic and the antiferromagnetic interchain interactions are satisfied so the magnetic arrangement is relatively unfrustrated. Mn₀₂OBO₃ has a strong orbital ordering in the Mn(1) chains occupied by Mn³⁺. The orbital ordering results in a complex pattern of ferro- and antiferro-magnetic superexchange interactions that frustrates long range magnetic order, so that spin ordering takes place only at the relatively low temperature of 26 K.

### ACKNOWLEDGMENTS

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