

LETTER TO THE EDITOR

X-Ray Absorption Spectroscopic Evidence for the Absence of Mn³⁺/Mn⁴⁺ Double Exchange in the CMR Pyrochlore Tl₂Mn₂O₇

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The X-ray absorption near edge spectra (Mn *K* edge) for Tl₂Mn₂O₇ pyrochlore exhibiting colossal magnetoresistance (CMR) has been studied at room temperature. The observed Mn *K* absorption edge coincides with the edges observed for MnO₂ and Er₂Mn₂O₇, both containing only Mn⁴⁺. In addition, the observed edge for Tl₂Mn₂O₇ is markedly shifted from the Mn *K* edge observed in CMR perovskite La_{0.7}Sr_{0.3}MnO₃, with an average Mn valence of +3.3, as well as Mn₂O₃ (containing only Mn³⁺). The above results further substantiate our earlier conclusion, drawn from the crystal structure study, which indicated that the Mn³⁺/Mn⁴⁺ double-exchange mechanism responsible for the CMR effect in perovskite is not operative in Tl₂Mn₂O₇. © 1996 Academic Press, Inc.

Manganese oxide perovskites with the general formula Ln_{1-x}M_xMnO₃ (Ln³⁺ = rare earth or Y; M²⁺ = Ca, Sr, Ba, or Pb) have recently been the subject of intense study due to their large change in the electrical resistance under applied magnetic field (1) and possible use of this effect in magnetic storage applications (2). This so-called colossal magnetoresistance (CMR) effect occurs near the ferromagnetic (FM) Curie temperature (*T*_c). The parent stoichiometric perovskite phase LnMnO₃ is an antiferromagnetic insulator, with all the Mn in the +3 oxidation state. Substitution of divalent *M* for trivalent *Ln* creates Mn⁴⁺ (holes) in the perovskite lattice and the material becomes a ferromagnetic conductor. In fact, for values of *x* close to 0.30, the high-temperature paramagnetic state is electrically insulating, whereas the low-temperature FM state is metallic (1). The *T*_c can be raised upon application of an external magnetic field, thereby producing the CMR effect. Qualitatively, the CMR in perovskites arises from double-exchange interactions (DE) (3), a process whereby a carrier can easily hop between Mn sites with aligned spins, but encounters a large barrier between anti-aligned neigh-

boring spins, due to the high energy involved in flipping the carrier spin (4). This explains the observed high conductivity in ferromagnetic state where the spins are aligned. Other more quantitative theories have included the importance of the Jahn–Teller distortions due to the presence of Mn³⁺ (a Jahn–Teller cation, high spin 3*d*⁴ ion) (5).

For some time, we have been studying the structure and electrical and magnetic properties of manganese oxides of the type A₂Mn₂O₇ (*A* = Dy–Lu, Y, Sc, In, and Tl) crystallizing in the pyrochlore-related structure (6–10). All the above phases crystallize in the face-centered cubic symmetry (space group: *Fd*3*m*; *a*_{cubic} ~ 10 Å). The pyrochlore structure of A₂Mn₂O₇ (or more appropriately, A₂Mn₂O₆O') is based on a network of corner-sharing MO₆ octahedra, just as in the perovskite CaMnO₃ (Fig. 1). The *A* atoms are located in the center of the hexagonal rings formed by oxygens (O, located at the 48*f* positions) with two more oxygens (O', at the 8*b* positions) located above and below the ring. Hence, the *A* atom environment can be considered as a distorted cube. The pyrochlore structure can also be viewed as two interpenetrating networks: one with the formula MnO₃ and the other with the formula A₂O'. Because the MnO₃ network forms the backbone of the structure, vacancies can occur only on the *A* and O' sites (12). However, unlike in the perovskite structure, the Mn atoms (as well as *A* atoms) in these compounds are located in the corners of tetrahedral units which share corners to form infinite, intersecting chains. Such an arrangement leads to a very high degree of magnetic frustration if the nearest-neighbor interactions are antiferromagnetic.

All the A₂Mn₂O₇ phases show a sharp increase in magnetic susceptibility at low temperatures with positive Curie–Weiss constants, suggesting long-range ferromagnetic interactions. However, electrical, field-cooled and zero-field-cooled ac susceptibility, specific heat, and small angle neutron diffraction studies indicate that the A₂Mn₂O₇ phases with *A* = rare earth, Y, Sc (not Tl) are electrical

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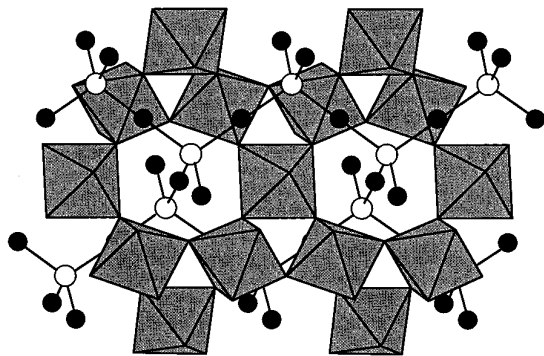


FIG. 1. Schematic view of the structure of $\text{Tl}_2\text{Mn}_2\text{O}_7$ showing the interpenetrating arrangement of MnO_6 and $\text{Tl}_2\text{O}'$ networks. Corner-shared oxygens connect the octahedra, forming Mn–O–Mn bond angles close to 134° . Small filled circles represent Tl ions, while the large open circles represent the O' oxygens.

insulators and do not display long-range magnetic order (7–10). They all seem to show complex magnetic properties in common with spin glass materials. This is in contrast to the $\text{Tl}_2\text{Mn}_2\text{O}_7$ phase, which is not only a good electrical conductor (with a room temperature resistivity in the range 0.1 to 0.01 Ω cm) but also shows long-range ferromagnetic ordering ($T_c \sim 120$ K) (11, 13). The resistivity as a function of temperature of this phase shows a very sharp drop in resistivity at the magnetic ordering temperature, and is very similar to electrical properties observed for CMR perovskites. Interestingly, the CMR effect (comparable to perovskite manganites) also has been observed for $\text{Tl}_2\text{Mn}_2\text{O}_7$ (14). This is very intriguing due to the fact that, unlike perovskite manganites, this phase requires no aliovalent or external doping for the observation of ferromagnetism and of the CMR effect. Our recent crystal structure determination (single-crystal X-ray and powder neutron diffraction) of $\text{Tl}_2\text{Mn}_2\text{O}_7$ exhibiting the CMR effect showed that the compound is very close to being ideal or stoichiometric, with no appreciable vacancies at the Tl and O sites (15). In addition, the observed Mn–O distance is ~ 1.90 Å, which is much shorter than the Mn–O distances observed in CMR perovskite and suggests that the average manganese valence in $\text{Tl}_2\text{Mn}_2\text{O}_7$ should be very close to $4+$ (15). This indicates that the double-exchange mechanism, which requires large proportions of mixed valency at the Mn sites (Mn^{3+} and Mn^{4+}) and is operative in perovskite manganites, may not be responsible for the observed ferromagnetism and the CMR effect in $\text{Tl}_2\text{Mn}_2\text{O}_7$.

To further substantiate the above, we have performed X-ray absorption near edge spectroscopy (XANES) using the Mn K edge for $\text{Tl}_2\text{Mn}_2\text{O}_7$ at bremsline X23B, National Synchrotron Light Source (NSLS), Brookhaven National Laboratory (BNL). The details of the sample preparation and characterization are described elsewhere (6, 15). In addition, the absorption spectra for MnO_2 ($\sim 0\%$ Mn^{3+}),

Mn_2O_3 ($\sim 98\%$ Mn^{3+}), $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ ($\sim 70\%$ Mn^{3+}), and $\text{Er}_2\text{Mn}_2\text{O}_7$ ($\sim 100\%$ Mn^{4+}) are also recorded for comparison.

Although the XANES spectra differ considerably above the edge, it is evident that the Mn K edge positions of Mn^{4+}O_2 and $\text{Tl}_2\text{Mn}_2\text{O}_7$ coincide and are shifted approximately 4 eV above the position of the edge observed in Mn^{3+}O_3 (Fig. 2). The above observation points to the fact that the Mn valence in $\text{Tl}_2\text{Mn}_2\text{O}_7$ should be very close to $4+$. Since the Mn K edge XANES is strongly influenced by Mn coordination (16) it is helpful to compare the $\text{Tl}_2\text{Mn}_2\text{O}_7$ spectrum with those of materials of known Mn valence and similar Mn coordination. That the average Mn valence state in $\text{Tl}_2\text{Mn}_2\text{O}_7$ is close to $4+$ is further substantiated by comparing its XANES spectra with those of the CMR perovskite $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ and pyrochlore $\text{Er}_2\text{Mn}_2\text{O}_7$ (Fig. 3). Again the Mn K edge in $\text{Tl}_2\text{Mn}_2\text{O}_7$ is coincident with that of $\text{Er}_2\text{Mn}_2\text{O}_7$, a compound known to contain only Mn^{4+} (6), and is several electron volts higher in energy than that of the CMR perovskite $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$, with an average manganese valence of $3.3+$. However, it is reasonable to argue that the structural, chemical, and spectroscopic investigations cannot completely rule out the possibility for the presence of a negligibly small degree of mixed valency ($\text{Mn}^{3+}/\text{Mn}^{4+}$ or $\text{Mn}^{4+}/\text{Mn}^{5+}$) in $\text{Tl}_2\text{Mn}_2\text{O}_7$ which may be responsible for ferromagnetism and for CMR. This is unlikely, due to the fact that the density of such pairs, if they exist, should be well below the percolation limit for nearest-neighbor hopping in the pyrochlore lattice. Based on our earlier structural study (15) and the present spectroscopic study, it is clear that this material has features which show only a superficial similarity to CMR perovskites. As mentioned earlier (15), instead of double exchange driving both the conduction and magnetic ordering processes as in

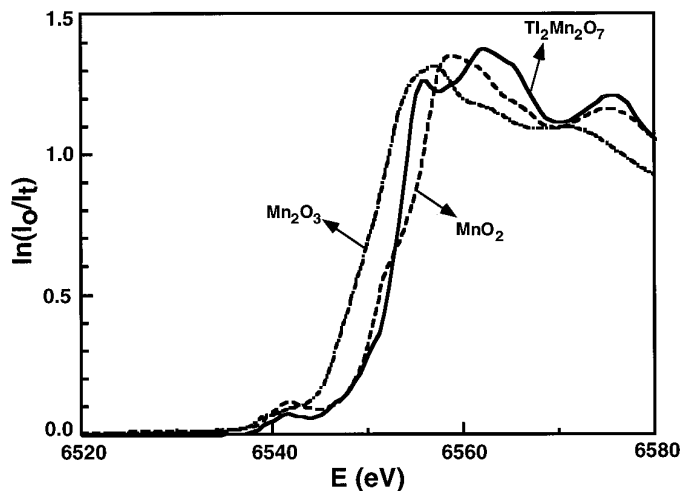


FIG. 2. Mn K edge XANES region of spectra for $\text{Tl}_2\text{Mn}_2\text{O}_7$, Mn_2O_3 , and MnO_2 .

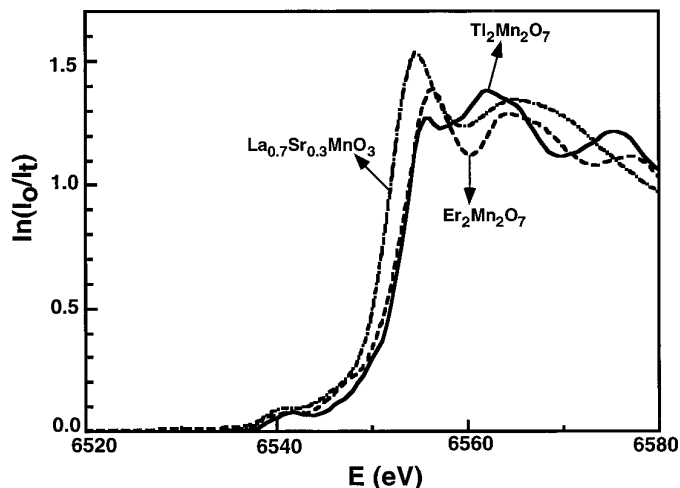


FIG. 3. Mn *K* edge XANES region of spectra for $\text{Tl}_2\text{Mn}_2\text{O}_7$, $\text{Er}_2\text{Mn}_2\text{O}_7$, and $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$.

the perovskites, the magnetic ordering in $\text{Tl}_2\text{Mn}_2\text{O}_7$ seems driven by superexchange; the conduction band, however, most likely involves a large admixture of Tl-based valence states.

It is evident that the observation of the CMR effect in nearly stoichiometric $\text{Tl}_2\text{Mn}_2\text{O}_7$ broadens the search for potential CMR candidate materials which fall “outside” the boundaries established by perovskite manganites.

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