LATTICE EFFECTS IN PEROVSKITE AND PYROCHLORE CMR MATERIALS

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ABSTRACT
Colossal magnetoresistance (CMR) in doped lanthanum manganese thin films (La1-xMxMnO3, where M is a divalent ion) has been shown to result in a factor of 10^6 suppression of the resistance. The driving force for the CMR transition is thought to be the double-exchange (DE) interaction. Many studies of both the crystal structure and the local structure of the La1-xMxMnO3 (with M = Ca, Sr and Ba, as well as Pb) system have now been carried out. As expected, these systems all show a strong coupling of the lattice to the CMR transition. On the other hand, neutron diffraction data and x-ray absorption studies for the Tl2Mn2O7 pyrochlore, which also exhibits CMR, shows no deviations from ideal stoichiometry, mixed valency, or Jahn-Teller distortions of the MnO6 octahedron. We present results of crystallographic and local structural studies of these two important classes of CMR materials. compare the differences in structural response, and discuss the implications of these findings to our understanding of these materials.

INTRODUCTION
The existence of colossal magnetoresistance (CMR) in the doped lanthanum manganese oxides La1-xMxMnO3 (where M is a divalent ion) has been known for some time [1], but the recent intense interest follows the discovery of approximately a factor of 10^6 suppression of the resistance in thin films and their possible application in magnetic recording technology [2]. The driving force for the ferromagnetic (FM) transition, and the coincident metal-insulator (MI) transition, is thought to be the double-exchange (DE) interaction where the mobility of the conduction electrons between heterovalent Mn3+/Mn4+ pairs is greatly enhanced when the magnetic moments on adjacent Mn ions are aligned [3]. The mixed valency also leads to the formation of small polarons that leads to incoherent hopping and the large resistivity in the insulating phase [4]. These small polarons have their origin in breathing-mode instabilities arising from Mn3+/Mn4+ valence changes and Jahn-Teller (JT) distortions involving Mn3+

Neutron diffraction studies of the crystal and magnetic structures of the doped perovskite LaMnO3 system were first reported some time ago [5,6]. More recently, volume contraction at the MI transition has been reported in temperature dependent studies of La0.60Y0.07Ca0.33MnO3 [7] and La1.4Ca0.6MnO3 (x=0.25 and 0.5) [8], and Dai et al. [9] have published a study of La0.65Ca0.35MnO3 emphasizing the temperature dependence of the thermal (or displacement) parameters (also referred to as Debye-Waller factors). Structural and magnetic studies of insulating La0.87Sr0.13MnO3 have shown changes in both lattice parameters and Mn-O bond lengths near Tc, suggesting an increase of the JT distortion of the MnO6 octahedra, and found coexisting canted ferromagnetism and antiferromagnetism [10]. We have studied the detailed structural response for a large number of La1-xCaMnO3 samples with x ranging from 0 to 1, of which the work described here is just a small part [11]. Small lattice-polaron formation in La1-xCaMnO3 has been observed from pair-distribution function (PDF) studies of the local structure using the same neutron scattering data [12]. Changes in peak heights for Mn-O and O-O correlations in x=0.21 and 0.25 samples (which display CMR) near Tc were well modeled by a breathing-type collapse of the MnO6 octahedron in approximately one of the four Mn sites in each of the unit cells, corresponding to the Mn3+/Mn4+ mixed valence [12]. As would be expected, the PDF for the insulating x=0.12 sample did not show such a change of peak heights. Similar behavior has been observed in the x-ray absorption fine structure studies [13].
The lead substituted manganites have been less thoroughly studied, but are of interest because of their higher Curie temperature [14]. Our neutron diffraction studies of the crystal and magnetic structures of these compounds show that, except for a difference in Tc, they behave quite similarly, although a number of features, including the structure, are slightly different [15].

The pyrochlore $\text{Tl}_2\text{Mn}_2\text{O}_7$ was recently found to show very large magnetoresistance [16]. Although this behavior is similar to the perovskite manganites, the physics appears to be very different [17]. Our neutron diffraction data and x-ray absorption studies for the $\text{Tl}_2\text{Mn}_2\text{O}_7$ show no deviations from ideal stoichiometry, the existence of mixed valency, or Jahn-Teller distortions of the MnO$_6$ octahedron [17,18]. The pyrochlore structure is also different in that there are two intertwined structural sublattices: one consisting of corner-joined MnO$_6$ octahedra responsible for the magnetism and another consisting of Tl-O chains responsible for the conductivity. Thus the pyrochlores should provide an important new class of compounds where magnetism and electrical properties can be separately tuned.

In this article, we present crystallographic analysis of neutron scattering data that provides magnetic moment, lattice contraction and thermal parameters that clarify the behavior of the perovskites; we also present results of a PDF analysis of the same data to give local structural changes with the CMR transition and direct evidence for polaron formation. Neutron diffraction is also used to give the structure and stoichiometry of the pyrochlore system, x-ray absorption near-edge spectroscopy (XANES) is used to provide information about the Mn and Tl valence, and x-ray absorption fine structure (XAFS) is used to determine changes in thermal motion near Tc. These results provide a greater insight into the physical basis for CMR in these systems and the hope that this improved understanding may lead to the discovery of other classes of materials.

EXPERIMENT

Briefly, the perovskite samples were prepared using solid state chemical techniques and the pyrochlore samples were synthesized at high pressure and temperatures. All samples were characterized with susceptibility measurements using a SQUID magnetometer. More detailed information is available in the references. The structural studies were carried out using neutron powder diffraction, with the spallation sources at Los Alamos or at Argonne, with standard Rietveld crystallographic refinement or with PDF analysis. The x-ray absorption studies to determine valence (XANES) or local structure (XAFS) were carried out at the synchrotron source at Stanford.

Figure 1. Schematic view of the structure of $\text{La}_{0.7}\text{Pb}_{0.3}\text{MnO}_3$ emphasizing the structural arrangement of the MnO$_6$ octahedra. Corner-shared oxygens connect the octahedra, forming an Mn-O-Mn bond angle close to 180°.
RESULTS

1. Substituted Perovskites: Comparison of Ca and Pb substituted $La_{1-x}M_yMnO_3$ Systems

   The structures for both $La_{1-x}Ca_xMnO_3$ and $La_{1-x}Pb_xMnO_3$ are represented by slight distortions of the cubic perovskite structure (where Mn occupies the cell corners, La/Ca/Pb the center, and O the cell edges). The structure of $La_{1-x}Ca_xMnO_3$ has an orthorhombic distortion and is represented by the space group $Pbnm$ for all values of $x$; this is a $a\sqrt{2}xb\sqrt{2}xc$ supercell of the primitive perovskite lattice. The structure of $La_{1-x}Pb_xMnO_3$ has a rhombohedral distortion of the cubic cell and conforms to the space group $R\bar{3}c$ over the entire range ($x = 0.1-0.5$) we have studied. A schematic view of the structure of $La_{1-x}Pb_xMnO_3$ is shown in Figure 1; the structure for $La_{1-x}Ca_xMnO_3$ can be approximately represented by tilting the figure.

   Resistivity was measured using a standard four probe dc technique and magnetic susceptibility was measured with a commercial dc magnetometer at fields of 0.5-0.6 T. The results are shown in Figure 2. Arrott plots (i.e. $M^2$ vs $H/M$) give values of $T_c$ of $164\pm4$ and $186\pm4$ for the $x = 0.12$ and $0.21$ samples, respectively. Resistivity plots show peaks that coincide

   ![Figure 2](image)

   Figure 2. The dependence of resistivity and magnetization on temperature for $La_{1-x}Ca_xMnO_3$ with $x = 0.12$ and 0.21.

   ![Figure 3](image)

   Figure 3. Magnetic moment for $La_{1-x}Ca_xMnO_3$ with $x = 0.12$ and 0.21 obtained from neutron diffraction data.

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well with $T_c$ for $x = 0.21$. The strong interdependence of $\rho$ and $M$ results from the DE interaction where the mobility of the conduction electrons is greatly enhanced with FM ordering. The CMR results from the field-dependence of $T_c$, $dT_c/dH > 0$. The $x = 0.12$ sample does not exhibit CMR; instead, it remains insulating at all temperatures, with a low-temperature resistivity 6 orders of magnitude greater than the $x = 0.21$ sample.

The temperature dependence of the magnetic moment obtained from Rietveld structure refinement using the neutron diffraction data for $x = 0.12$ and 0.21 is shown in Figure 3. The saturation moment for both samples is about $3.1\mu_B$, a little smaller than the $3.9-3.8\mu_B$ expected.

The dependence of the cell volumes for $La_{1-x}Ca_xMnO_3$ on temperature show a lattice contraction near the resistive and magnetic transitions for $x = 0.21$ (Figure 4), as would be expected with the increased strength of metallic bonding. In contrast, the sample with $x = 0.12$, which remains insulating, the cell volume varies smoothly with temperature, even through the FM transition. Similar volume contraction at the MI transition has been previously observed for $La_{0.6}Y_{0.07}Ca_{0.33}MnO_3$ [6], $La_{0.75}Ca_{0.25}MnO_3$ [7], and $La_{0.65}Ca_{0.35}MnO_3$ [9].

![Figure 4. Dependence of cell volume on temperature for $La_{1-x}Ca_xMnO_3$ with $x = 0.12$ and 0.21.](image)

Since $Mn^{3+}$ is a Jahn-Teller ion, the MnO$_6$ octahedra in LaMnO$_3$ are distorted so that the axial bonds are elongated compared with the planar bonds [19]. When $Ca^{2+}$ is substituted for $La^{3+}$, the Mn$^{4+}$ ions formed by this doping are not JT active and have considerably smaller ionic radii than Mn$^{3+}$, the Mn$^{4+}$O$_6$ octahedra no longer undergo the JT distortions and they contract in size. Thus Mn$^{3+}$/Mn$^{4+}$ mixed valence results in both breathing-mode and dynamic JT distortions, and bond frustration, that should manifest itself in increased structural disorder [4]. Local distortions that are not long-range ordered will not be visible in measured average bond lengths, but will be evident in the form of enlarged thermal parameters (or mean-square displacement parameters). The thermal parameters for the oxygens and the cations in $La_{1-x}Ca_xMnO_3$ are shown in Figs. 5 and 6, respectively. Figure 5 shows that the oxygen thermal parameters in the insulating phase have large values at low temperatures that reflect mostly static distortions and account for roughly half of the atomic displacements at room temperature; this suggests that the structure must be substantially disordered, even at low temperatures. In well-ordered materials, such as metallic thorium, the value of the low-temperature thermal parameter is close to zero. For this sample, the temperature dependence of the thermal parameters for both the planar oxygens (shown in the left-hand panel) and the axial oxygens (right-hand panel), show the expected Debye-Waller (DW) behavior (i.e. curved at low temperatures, then becoming nearly linear at higher temperatures), with comparable DW temperatures of 597 and 684K, respectively. These values are comparable to those found for insulating $La_2CuO_4$ with atomic DW temperatures of 511 and 661K for the planar and axial oxygens, respectively [20]. For the $x = 0.21$ sample, which has an MI transition near 186K, there is a break in the temperature dependence followed by a substantial decrease in the thermal parameters below this transition.

Although the $x = 0.12$ sample is disordered as a result of the mixed Mn valence, these distortions remain the same at the different temperatures and are only evident in the large value of the low temperature thermal parameters. The substantial decrease at low
temperatures for the \( x = 0.21 \) sample is more intriguing: as suggested in the PDF analysis described later [12], this corresponds to an ordering of the structure as the sample becomes metallic and the holes now hop freely among Mn ions. At low temperatures, the difference in the oxygen thermal parameters for \( x = 0.12 \) and 0.21 is approximately 0.0020\( \text{Å}^2 \) corresponding to an rms displacement of 0.045\( \text{Å} \) for the axial oxygens, and approximately 0.0013\( \text{Å}^2 \) corresponding to an rms displacement of 0.036\( \text{Å} \) for the planar oxygens. These values represent averages over all Mn sites. If we assume that only sites containing a hole (Mn\(^{4+} \) sites) are contributing to this excess rms displacement, these values should really be multiplied by \( \approx 4.8 \). This would then give oxygen displacements of 0.20 and 0.17\( \text{Å} \) for the axial and planar oxygens, respectively, in MnO\(_6\), in agreement with the PDF results [12].

The response of the cation sublattices is less pronounced. Fig. 6 shows thermal parameters for the La/Ca ions: where for the \( x = 0.21 \) sample the behavior again shows evidence of ordering below the MI transition. Fig. 6 also shows data for the Mn ions where the thermal parameters for both samples show the normal Debye temperature dependence, but a shift relative to each other. It is not surprising that Mn ion displacements do not change at the MI transition for \( x = 0.21 \). The breathing mode distortions do not involve the central Mn ions, and the JT distortions are anticorrelated from site to site, thus the main changes are in the Mn-O distances but not in the Mn positions. The La/Ca thermal parameters do show a change and this

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**Figure 5.** Temperature dependence of the oxygen thermal parameters for La\(_{1-x}\)Ca\(_x\)MnO\(_3\) for \( x = 0.12 \) and \( x = 0.21 \). The left-hand panel shows data for the planar oxygens, while the right-hand panel shows data for the axial oxygens.

**Figure 6.** Temperature dependence of the cation thermal parameters for La\(_{1-x}\)Ca\(_x\)MnO\(_3\) for \( x = 0.12 \) and 0.21. The left-hand panel shows data for La/Ca, while the right-hand panel shows data for Mn.
suggests that buckling modes of the Mn-O-Mn bonds are also important because simple JT distortions do not couple to the La/Ca distortions to leading order, but the buckling modes do. This is to be expected since buckling distortions in the octahedral network relieve bond mismatches in perovskites and will undoubtedly respond to changes in the Mn-O bond-length distribution.

Dai et al. [9] obtain a qualitatively different thermal parameter dependence for the constituents of $La_{0.67}Ca_{0.33}MnO_3$, obtained from Rietveld refinement with reactor source powder neutron diffraction data. In particular, they observe breaks in the Mn data but not in the La/Ca data, while we observe the opposite for $x=0.21$ and $0.25$. This raises the interesting possibility that these differences may actually arise from differences in the band filling factor.

The first evidence for a change in the local structure at the MI transition came from atomic pair-distribution-function (PDF) analysis of our neutron diffraction data [12]. In these studies, an increase in the heights (or a narrowing of the widths) of the O-O correlation peaks at 2.75Å (corresponding to the distance between nearest neighbor oxygens in MnO$_6$) can be correlated with an increasingly ordered structure below the MI transition in the $x=0.21$ sample.

This can be seen in Figure 7 which shows the temperature dependence of the 2.75Å peak height; this shows a break for $x=0.21$, but not for $x=0.12$ (which follows the normal Debye-like evolution of peak heights with temperature). The structural change for the $x=0.21$ sample can be modeled as an isotropic collapse of oxygen towards Mn of magnitude $\delta = 0.12\AA$ occurring in about one quarter of the Mn sites. This provided the first direct evidence for the formation of small lattice polarons in the insulating phase, and is consistent with the transport measurements which are well explained by a small polaron hopping mechanism in that phase.

Temperature dependence of the Debye-Waller parameters for near-neighbor interactions can also be obtained from XAFS. In this case, the measured quantity differs from the previous measurements because the XAFS measurement includes a term from correlated motion and because corrections have to be made for multiple scattering paths. Mn-O Debye-Waller parameters $\sigma^2$ have been reported for $La_{1-x}Ca_xMnO_3$ and $La_{1-x}Pb_xMnO_3$ by Booth et al. [13] and are shown in Figure 8. The results resemble the PDF results in that there is a narrowing in the peak widths (or increase in the peak heights) around the MI transitions for the compounds $La_{1-x}Ca_xMnO_3$ ($x=0.25$ and $0.33$) and $La_{0.67}Pb_{0.33}MnO_3$, but not for $La_{0.5}Ca_{0.5}MnO_3$ which remains an AF insulator and has no CMR transition.

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The thermal parameters obtained from crystallographic analysis show that the onset of structural ordering is sharp and coincides with the MI transition in the $x = 0.21$ sample. On the other hand, local structural determinations of the displacement parameters, both from our PDF work for $x = 0.21$ and 0.25 [12] and from EXAFS studies for $x = 0.25$ and 0.33 [13], show a more gradual change occurring over 60-80K and centered on the MI transition. Similarly, Figure 2 shows that the development of the magnetic moment also begins well above the MI transition and continues past the transition. Thus, the length scales for magnetic and local structural ordering are similar, as would be expected. When the length scales for this ordering becomes comparable to the crystallographic length scale (several hundred angstroms), the system goes through a sharp MI transition and the long-range crystallographic parameters, such as cell volume and thermal parameters, reflect this sharp transition.

These experiments have shown that the measured structural response of $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ through the coincident FM and MI transition is well understood in terms of the theoretical descriptions of DE [3] and JT-assisted small polaron formation [4].

The lead-substituted lanthanum manganites form an interesting class of compounds because Pb doping, like Sr doping, leads to $T_c$'s above room temperature, which might make them more useful in device applications. As shown in Figure 1, the rhombohedral distortions from the primitive perovskite structure are slightly different from the orthorhombic distortions in $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ and result from the larger ionic radius of Pb$^{2+}$. Figure 9 shows the dependence of $T_c$ on Pb dopant level.

Figure 9. $T_c$ as a function of dopant composition for $\text{La}_{1-x}\text{Pb}_x\text{MnO}_3$ showing the large increase in $T_c$ with increased Pb doping.
Neutron scattering data for this system were collected in separate experiments on two
different diffractometers for high- (furnace) and low- (closed cycle He refrigerator) sample
temperatures, with a region of overlap between 300 and 345K. Structural refinement with these
data were carried out to obtain the temperature dependence of the magnetic moment, cell
volume and thermal parameters. The magnetic moment data are displayed in Figure 10. As can
be seen, the magnetic moment begins to increase below 400K (consistent with a T_c of ~328K)
with a saturation moment of about $3.8\mu_B$, which is close to the expected value of $3.7\mu_B$.

![Figure 10. Temperature dependence of the magnetic moment refined from neutron
diffraction data (right-hand panel).](image)

As in the $x = 0.21 \text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ sample, the cell volume (shown in Figure 11) shows a
break at $T_c$.

![Figure 11. Temperature dependence of cell volume for $\text{La}_{0.7}\text{Pb}_{0.3}\text{MnO}_3$.](image)

The thermal parameters obtained from structural refinement are shown in Figure 12. As
with the CMR $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ system, the thermal parameters for O show evidence of ordering
of the MnO$_6$ octahedra below the MI transition while those for La/Pb may also show a small
break. However, in contrast to $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$, the thermal parameters for Mn show an unusual
increase in the region approximately 100 deg above the MI transition that may be real;
unfortunately, there is some uncertainty in the data where high and low temperature data overlap.

II. Pyrochlores: The $\text{Tl}_2\text{Mn}_2\text{O}_7$ System

Although heterovalency and possibly Jahn-Teller (JT) effects are necessary to produce
CMR in the $\text{La}_{1-x}\text{A}_x\text{MnO}_3$ compounds, only slightly weaker magnetoresistance has been found
for $\text{Tl}_2\text{Mn}_2\text{O}_7$ [16,17], which has the pyrochlore structure. Because $\text{Tl}_2\text{Mn}_2\text{O}_7$ also contains Mn
as the magnetic constituent, it was first thought that this compound would also contain
significant amounts of the JT-split cation Mn$^{3+}$ and that it was again Mn$^{3+}$/Mn$^{4+}$ DE that gave
rise to ferromagnetism. Mixed-valence could result from oxygen deficiency, as was suggested by Shimakawa et al. [16]. However, our structural analysis on Tl$_2$Mn$_2$O$_7$ showed that if this were the case, oxygen deficiency would have to be below the 3.5% level, consistent with Shimakawa et al.'s Hall-derived carrier density, <0.5% assuming two electrons per defect.

The structure of Tl$_2$Mn$_2$O$_7$ is shown in Figure 13. This structure can be thought of as being made up of two intertwined sublattices consisting of MnO$_6$ octahedra, connected at the corners, and TlO chains. Unlike the perovskites, where the Mn-O-Mn bond angle is close to 180°, the octahedra are connected in such a way as to give Mn-O-Mn bond angles close to 130°.

Figure 12. Temperature dependence of the isotropic thermal parameters $U_{iso}$ for La/Pb. Mn and O in La$_{0.7}$Pb$_{0.3}$MnO$_3$.

Figure 13. Schematic view of the structure of Tl$_2$Mn$_2$O$_7$ emphasizing the structural arrangement of the MnO$_6$ octahedra. Corner-shared oxygens connect the octahedra, forming an Mn-O-Mn bond angle of about 134°. Small circles represent Tl ions, while the large circles represent oxygens.

The resistivity as a function of temperature, $\rho(T)$, for the Tl$_2$Mn$_2$O$_7$ samples used in our studies [Figure 14, upper panel] are comparable to those reported by Shimakawa et al. [16]. A sharp decrease in $\rho(T)$ occurs at the FM transition $T_c(H=0) = 142$K, and a maximum
magnetoresistance between H = 0 and 8 T of 60% is comparable to values obtained in the bulk perovskite samples. At 142K we see a rise in dc magnetization, M(T), and a saturation moment at 10 K and 4 T of 2.74μB [Figure 14, lower panel], slightly less than expected for Mn^{4+} (3μB) and consistent with Shimakawa et al. [16]. This correspondence between a sharp resistance drop and a FM moment is also seen in the perovskites and is the hallmark of CMR compounds.

Structural analysis with powder neutron and single-crystal x-ray diffraction data shows no deviations from ideal stoichiometry. This analysis gives an Mn–O distance of 1.90 Å, which is significantly shorter than the Mn–O distances (1.94 to 2.00 Å) observed in phases based on LaMnO₃ perovskites which show CMR. Both the stoichiometry and the shorter Mn–O distance in Ti₂Mn₂O₇ indicate oxidation states very close to Ti²⁺Mn⁴⁺O₇. Thus, Ti₂Mn₂O₇ has neither mixed valency for a double-exchange magnetic interaction nor a Jahn-Teller cation such as Mn³⁺, which were both thought to play an essential role in CMR materials. For example, unlike the CMR pyrochlores, XAFS studies of the Debye-Waller broadening parameters for the Mn–O and Ti–O bonds show no anomalies near Tc (Figure 15), instead they are similar to those for the normal Er₂Mn₂O₇ pyrochlore [18].

Although the FM pyrochlore compound Ti₂Mn₂O₇ bears a similarity to the CMR manganese oxide perovskite compounds (i.e. both compounds are oxides, both have strong local moment magnetism arising from octahedrally coordinated Mn, and both exhibit dramatic decreases in the resistivity associated with the transition from high-temperature paramagnetic to low-temperature FM state that is associated with CMR), there are significant differences between the two compound families: on a microscopic level, we see no evidence for significant doping in the pyrochlore Mn–O sublattice. Such doping is necessary to produce the mixed valency responsible for DE in the perovskites - CMR occurs over the range 20 to 45% of hole concentrations (with respect to Mn), obtained by doping with an alkaline earth on the rare-earth site [21]. Second, there is no evidence for Jahn-Teller distortions among the Mn–O octahedra, consistent with the stoichiometry of the compound and the approximately homovalent Mn⁴⁺ population thus implied. Third, the above mentioned tendency for Ti to form 6s conduction bands is unlike the perovskite case where the rare-earth levels are inactive electronically.

The origin of CMR in Ti₂Mn₂O₇ is fundamentally different from that of the perovskites. Instead of a single mechanism, DE, driving both the conduction and magnetic ordering processes

Figure 14. Temperature dependence of the resistivity (upper panel) and the magnetization (lower panel) for Ti₂Mn₂O₇ (from reference 17). The resistivity data are for 0 (top), 0.1, 1, 2, 4, 6 and 8T (bottom). The magnetization data are for 0.001 (bottom), 0.1, 1 and 4T (top).
as in the perovskites, in the pyrochlore compound, there are two processes. The magnetic ordering seems driven by superexchange, as in other FM pyrochlore insulators. The conduction band, however, most likely involves a large admixture of TI-based valence states. The interdependence of $\rho$ and $M$ results from unusually large incoherent scattering from spin fluctuations accompanying FM ordering. Then CMR again results from the field-dependence of $T_C$, $dT_C/dH > 0$, as in the perovskite compounds.

CONCLUSIONS

At present, we have two families of manganite compounds displaying colossal magnetoresistance (CMR): the substituted rare-earth manganite perovskites and the thallium manganite pyrochlores. Various studies have shown that the substituted mixed-valent perovskites undergo a simultaneous transformation from a paramagnetic insulator to a ferromagnetic metal at the CMR transition. Neutron diffraction studies have clearly shown a volume contraction accompanying the M-I transition and the development of a magnetic moment at $T_C$. Studies of the temperature dependence of the thermal parameters [from crystallographic or pair-distribution functions (PDF) analysis of neutron diffraction data, or x-ray absorption fine structure (XAFS)] show the existence of polaron formation over a broad range of experimental length scales. The theoretical understanding is reasonably complete: the dominant mechanism is double-exchange (DE), where alignment of the Mn spins lowers the energy for electron conduction, and small polaron formation in the insulating phase (helped by the Jahn-Teller distortions of the MnO$_6$ octahedra) that leads to hopping conductivity.

Neutron diffraction and x-ray near edge studies of the thallium manganite pyrochlore system shows that there is no mixed-valence, and XAFS studies show no anomalies in the thermal parameters involving the Mn-O bonds near $T_C$. The structure is different from the perovskites in that it can be thought of as consisting of two intertwined sublattices, one consisting of MnO$_6$ octahedra joined at the corners responsible for the magnetism and another consisting of TI-O chains responsible for the conductivity. The mechanism for CMR is also quite different. Instead of a single mechanism, DE, driving both the conduction and magnetic ordering processes, there are two processes: the magnetic ordering is driven by superexchange, as in other FM pyrochlore insulators, and conduction most likely involves a large admixture of TI-based valence states in the conduction band. The interdependence of $\rho$ and $M$ results from unusually large incoherent scattering from spin fluctuations accompanying FM ordering, and CMR results from the field-dependence of $T_C$, as in the perovskite compounds. The existence of two structural sublattices implies that the electrical and magnetic properties can be tuned separately to give greater

Figure 15. Temperature dependence of the nearest-neighbor peak heights for the Mn-O bonds in Tl$_2$Mn$_2$O$_7$ (■) and Er$_2$Mn$_2$O$_7$ (▲) and the Tl-O (●) bonds in Tl$_2$Mn$_2$O$_7$. The smooth Debye-like temperature dependence through the FM transition at 142K (vertical dotted line) differs markedly from the temperature dependence of the peak-height for La$_{0.75}$Ca$_{0.25}$MnO$_3$ (x) (from reference 18).
flexibility in optimize performance, as has been done by Ramirez and Subramanian [22] by partial substitution Sc into the Ti-O chains, where a 60-fold increase in CMR has been found. Other substitutions into either of the sublattices can be used to give other changes in properties. Eventually, we hope that other classes of compounds will be found that can provide an even broader range and flexibility in desired magnetoresistant properties.

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