Electronic structure and half-metallic transport in the La_{1-x}Ca_xMnO₃ system

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Possible origins of "colossal magnetoresistance" (CMR) behavior in the $La_{1-x}Ca_xMnO_3$ system are studied using the local spin-density method. These calculations allow the quantification of the effects of Mn d–O phybridization that have been largely neglected in previously published work. As regards the end-point compounds CaMnO₃ and LaMnO₃, the very different structural and magnetic symmetries of their ground states are predicted correctly. The distortion from the cubic perovskite structure of the LaMnO3 lattice is necessary to produce an antiferromagnetic insulating ground state. The distortion also strengthens the Mn magnetic moments. Application to ferromagnetic and constrained ferrimagnetic phases of $La_{1-x}Ca_xMnO_3$ in the CMR regime $x \approx \frac{1}{4} - \frac{1}{3}$ suggests, as observed, that magnetic coupling switches from antiferromagnetic to ferromagnetic. Hybridization between Mn d states and O p states is found to be strongly spin dependent, because the majority Mn d bands overlap the O p bands while the minority Mn d bands are separated by a gap from the O p bands. Both ferromagnetic and ferrimagnetic orderings are obtained and compared. We identify strong local environment effects arising from neighboring cation charge differences (La^{3+} or Ca^{2+}) that suggest localization of the low density of minority carriers, leading to effective half-metallic ferromagnetism in the CMR regime. This behavior supports in some respects the popular "double exchange" picture of Zener but indicates the Mn d-O p hybridization is much too strong to be considered perturbatively. Half-metallic character promotes the possibility of very large magnetoresistance, and may well be an essential ingredient in the CMR effect.

I. INTRODUCTION

Nearly a half century ago Jonker and van Santen^{1,2} (JvS) discovered a striking correlation between magnetic order and conductivity in the $\text{La}_{1-x}D_x\text{MnO}_3$ system (*D* being a divalent alkaline earth Ca, Sr, or Ba). These manganite alloys are insulating and antiferromagnetic (AFM) at the end points x=0 and x=1, but in the 0.2 < x < 0.5 region they are ferromagnetic (FM) and their conductivity at low temperature (*T*) is better described as metallic. The crystal structures are cubic perovskite (or close variants thereof; see Sec. II) so Mn ions are connected by oxygen ions, with negligible direct Mn-Mn hopping of carriers. JvS suggested that this was the first occurrence of a positive indirect exchange interaction in an oxide material.

Zener³ identified a double exchange process to explain this behavior. In Zener's picture, the oxygen ion is closed shell (O^{2-}) , but somehow hopping must occur via this ion. This can happen if an electron jumps onto a Mn ion (on its right, say) simultaneously with an electron hopping onto the oxygen ion from the Mn on the left. This double hopping event requires that both hopping electrons have the same spin, that of the active spin orbital on the oxygen ion. If in addition the Mn ions (which will be Mn^{3+} and Mn^{4+} for these systems) are presumed to be "Hund's rule" ions in which all electron spins are aligned, then the hopping event requires both Mn ions to have parallel moments. This mechanism necessarily connects the parallel alignment of Mn moments (ferromagnetism) with hopping of carriers (metallic conduction) and nicely accounts for the primary observations of JvS. The result is an effective positive exchange coupling induced by the carriers, and was named "double exchange" (DEX) to contrast it with direct exchange and superexchange.

This DEX mechanism was investigated more thoroughly by Anderson and Hasegawa⁴ and de Gennes,⁵ who found that carriers (nonintegral x) necessarily cause a distortion of the ordered spin arrangement and indeed lead to a FM phase at a critical concentration. de Gennes especially indicated the likelihood of canted spin arrangements in certain regions of the phase diagram. Anderson⁶ elaborated on the perturbative nature of this picture, and noted that the expansion is not likely to be rapidly convergent. The many-body treatment of DEX-like models was extended by Kasuya⁷ and Kubo and Ohata,⁸ and more recently by Furukawa,⁹ Inoue and Maekawa,¹⁰ and Millis, Littlewood, and Shraiman¹¹ who renewed investigations of noncollinear spin arrangements and spin-disorder scattering.

Early on, Goodenough¹² had begun to address this same exchange coupling problem with his discussion of Mn d–O p hybridization, leading to "semicovalent exchange." His theory led to generally successful interrelationships between the magnetic order, the crystallographic structure, the electrical conduction, and the Curie temperature (T_C) .^{12,13} There are other related questions: the observation of ferromagnetism in the system $(\text{La}_{1-x}^{3+}\text{Ba}_x^{2+})(\text{Mn}_{1-x}^{3+}\text{Ti}_x^{4+})\text{O}_3^{2-}$ (Ref. 14) where there are (formally) no Mn⁴⁺ ions present, rules out simple DEX as the sole cause of ferromagnetism in such systems.

The magnetic order in the D=Ca manganite system was elucidated in the pioneering studies of Wollan and Koehler,¹⁵ who used differences in neutron diffraction spectra above and below the Néel temperature (T_N) to infer the type of magnetic order and the magnitude of the magnetic moments. Their conclusions extended the findings of JvS that the mo-

ments on the Mn ions are near (but in some cases somewhat below) their Hund's rule values, and identified a variety of types of AFM order that occur in this system.

types of AFM order that occur in this system. The recent discovery $^{16-27}$ of a huge magnetic-fieldinduced reduction of resistivity $\rho(T,H)$ in La_{1-r}Ca_rMnO₃, now termed colossal magnetoresistance (CMR), was entirely unanticipated by the previous studies and introduces new problems in the description of this class of manganese oxides. CMR occurs in a region near $x = \frac{1}{3}$, where the materials are FM metals at low temperature. As the temperature T is lowered to a temperature T^* (the resistivity maximum) near the Curie temperature T_C (70–300 K depending on preparation conditions), the resistivity increases by 2-3 orders of magnitude and then drops again, within a few tens of kelvin. Near T^* , the application of magnetic fields can recover the low-resistance metallic state. An example is presented in Fig. 1, which gives experimental data of Liu et al.²⁷ These data are the first obtained on a single-crystal sample, and the magnetoresistance peak occurs at room temperature. In this sample, it is clear that the resistivity peak and the CMR peak coincide with the Curie temperature. The variations in transport behavior are reminiscent of the resistive anomalies in ferrites²⁸ near the magnetic ordering temperature, but in manganites the effect can be orders of magnitude larger. Evidently the transport properties are extremely sensitive to temperature (T) and to magnetic field (H) in the neighborhood of T^* , reflecting strong magnetoelectronic coupling. Magnetostructural coupling has been confirmed in La_{0.825}Sr_{0.175}MnO₃ (Refs. 26 and 29) where a magnetic field can switch the lattice between orthorhombic and rhombohedral phases near 220 K.

The quoted magnetoresistance ratio \mathfrak{R}_m defined by

$$\mathfrak{R}_m = [\rho(T,0) - \rho(T,H)] / \rho(T,H)$$
(1)

follows that used by Searle and Wang³⁰ in (La,Pb)MnO₃, who reported a value of 20% ($\Re_m = 0.2$). The values of magnetic field H are typically ~ 5 T, and such large fields are actually needed to reach low resistivity. The "sensitivity" $d \log \rho(T,H)/dH$ at low fields is the figure of merit in many applications, and typically the manganites have sensitivities that are no larger than the "giant magnetoresistance" layered magnetic structures. However, extremely large \Re_m ratios have been reported. Perhaps the first report of CMR in the manganite system was the value of $\Re_m \approx 100$ for $Nd_{0.5}Pb_{0.5}MnO_3$ at $H \approx 10$ T by Kusters *et al.*¹⁶ For laser ablated films of (La,Ca)MnO₃, McCormack et al.¹⁸ and Jin et al.¹⁹ reported $\Re_m = 1270$, and noted changes when La is partially substituted by Y.²⁰ Liu et al.²⁷ have reported the first single-crystal value, $\Re_m = 3$ for La_{0.65}(PbCa)_{0.35}MnO₃ (see Fig. 1). A value of $\mathfrak{R}_m \approx 10$ for pulsed laser deposited films of La_{0.7}Ca_{0.3}MnO₃ was reported by Lawler and Coey.²³ For the other divalent dopants, the effects are smaller but still "giant." von Helmolt *et al.*¹⁷ reported $\Re_m = 0.6$ (i.e., 60%) for La_{0.67}Ba_{0.33}MnO₃. Mahendiran *et al.*²¹ measured $\Re_m = 0.5$ for ceramic samples of $La_{1-x}Sr_xMnO_3$ for a range of x around 1/3, while the much larger $\Re_m = 10$ was reported by Tokura *et al.*²⁴ for single crystals of this material. Xiong et al.²² have recently reported $\Re_m = 10^4$ for the non-La material Nd_{0.7}Sr_{0.3}MnO₃ and a field of 8 T. It is evident that the



FIG. 1. Example of experimental data on a CMR material, taken from Liu *et al.* (Ref. 27) for a single crystal of La_{0.65}(CaPb)_{0.35}MnO₃. The panels show (top) the magnetization M(T) in a magnetic field of 1 T, (middle) the resistivity in zero field and in a 5.5-T field, and (bottom) the normalized magnetoresistance. The magnetoresistance ratio as defined in the text approaches 3 for this sample.

magnetic and transport properties depend, sometimes very strongly, on the method of preparation, as well as on the cations involved.

The general phenomenology of the lanthanum manganite system is as follows. The end points of the $La_{1-x}Ca_xMnO_3$ system consist formally of Mn^{3+} (d^4) ions (x=0) and Mn^{4+} (d^3) (x=1), and both are antiferromagnetic insulators but with different crystal structures and magnetic symmetries. Based on fitting of neutron diffraction data,¹⁵ these end points form the high spin configurations, reduced somewhat

from the Hund's rule values by hybridization. Since in the octahedral crystal field experienced by the Mn ion in the perovskite structure, the t_{2g} orbitals lie lower than the e_g orbitals, the majority t_{2g} orbitals are fully occupied for x=1, all minority orbitals are unoccupied, and the cubic structure is stable. The magnetism in CaMnO₃ is *G* type,¹⁵ i.e., a rock-salt arrangement of moments, with $T_N \approx 120$ K.

For LaMnO₃ there is one additional electron to populate the two majority e_g orbitals, leading to a Jahn-Teller (JT) instability,^{12,13} and indeed LaMnO₃ is found to be in a strongly distorted orthorhombic form of the perovskite structure (Sec. II). The magnetic order below T_N =141 K, termed A type,¹⁵ is spin aligned in layers and alternating from layer to layer.^{14,15,31,32} A JT instability has been the most common explanation for the distortion in the literature. There may be other driving forces, for example, the same structure is assumed by CaTiO₃, which has a nominally empty Ti *d* shell and therefore is subject to no JT instability. CaTiO₃'s distortion is understood in terms of a mismatch in atomic sizes, which is also present in LaMnO₃ as discussed in Sec. II.

The La_{1-x}Ca_xMnO₃ system becomes FM for concentrations 0.2 < x < 0.5, and it has metallic *T* dependence of conductivity near $x \approx \frac{1}{3}$ below the resistivity peak (designated by *T**). Approaching *T** from above, the resistivity increases strongly, then at $T^* \approx T_C$ it drops rapidly, and the saturation magnetization indicates the onset of FM ordering. It is in the region of *T** that application of a strong magnetic field results in a drop in the resistance by up to three orders of magnitude in La_{2/3}Ca_{1/3}MnO₃. Related behavior occurs in the Sr- and Ba-substituted materials, but specific differences are seen and "colossal" effects have been seen only in La_{1-x}Ca_xMnO₃ with $x \approx \frac{1}{3}$. One can categorize the scientific problem as a series of questions.

(a) How does the resistivity achieve such a low value $(\sim 100 \ \mu\Omega \text{ cm}$ in single-crystal films,^{33,34} with $d\rho/dT$ strongly positive) at low temperature, when there is extensive charge disorder (La³⁺,Ca²⁺) to cause scattering, and conduction must proceed through a nominally closed shell O^{2^-} ion? A perturbative picture in terms of highly correlated hopping processes (Zener's DEX picture) is unlikely to be sufficient to explain the transport quantitatively.

(b) Does the resistivity at high temperature $T \ge T_C$ follow a universal form? Some workers report an activated form, with activation energy $E_a \approx 50-120$ meV, while others claim that a variable-range hopping form $T^{-\nu}$, $\nu = \frac{1}{4} - \frac{1}{3}$, is a better fit. And why is the resistivity derivative negative at all in this regime, in the midst of what would appear to be increasingly strong spin scattering from the disordered moments?

(c) What determines the temperature T^* where the resistivity drops? It seems that $T^*(H=0) \approx T_C$, i.e., the resistivity drop coincides with FM ordering. Oxygen treatment can change T^* from 70 to 300 K; how should such a variable exchange interaction be described?

(d) How does the application of fields of a few Tesla reduce the resistivity by three orders of magnitude or more, especially considering that μH is much less than kT_C and other energy scales such as the exchange constant J? Once the difficult questions (a)–(c) are answered, the CMR question (d) may not be such a conundrum. In fact, it has already been noted that the decrease in ρ often seems to be

related directly to the magnetization M ($\delta \rho \propto -M^2$), whether it is achieved by lowering the temperature (below T_C) or by applying a magnetic field.

One rather benign factor that contributes to obtaining large CMR values $\mathfrak{R}_m(T^*)$ is the upward shift of $T^*(H)$ with field, since the field enhances the FM order and thus reduces spin scattering. Typical shifts of the peak position are $dT^*/dH \approx 10 \ K/T$. This shift alone will lead to large negative magnetoresistance at $T^*(H=0)$, in exactly the same way one obtains large positive magnetoresistances at a superconducting transition T_s as T_s shifts with field. However, in CMR materials the magnetoresistance is usually negative everywhere, which would not be the case if the $\rho(T)$ curve were simply shifted upward in temperature by the field. In a related vein, a magnetic-field-induced structural phase transition has been observed by Asamitsu et al.²⁹ in La_{0.83}Sr_{0.17}MnO₃, where the rhombohedral-orthorhombic structural transition versus concentration and temperature occurs at the Curie temperature.

In this paper we lay the groundwork for answering these questions from a first-principles point of view. We explicitly address the question of covalence, by calculating the magnitude and learning the implications of Mn d–O p hybridization in these manganites. We find an interplay between magnetic ordering, electronic structure, and crystalline distortions in La_{1-x}Ca_xMnO₃ that reveals the importance of covalency. We confine ourselves to the determination of the electronic and magnetic structure in (meta)stable states within the local spin density approximation (LSDA).

We will show that the LSDA description is quite realistic. The structures and methods are discussed in Secs. II and III, respectively. In Sec. IV, we discuss the end points x=1 and x=0, where we find that LSDA provides a very good overall description of these compounds, including predicting the correct ground-state crystal structures and magnetic symmetries. In Sec. V, we address the CMR region $x = \frac{1}{4} - \frac{1}{3}$. A crucial feature that arises is the half-metallic $(\frac{1}{2}M)$ character of FM CaMnO₃ and the effective $\frac{1}{2}M$ character in the $x = \frac{1}{3}$ region. The application of fixed spin moment calculations allows us to evaluate the robustness of the magnetic solutions that we obtain. Spectral data and some previous calculational results are discussed in Sec. VI. In Sec. VII we discuss possible connections of the strong magnetoelectronic and magnetostructural coupling to the resistivity data on CMR materials. Mn-O covalency and the half-metallic character of the electronic system play a central role in our considerations.

Hamada, Sawada, and Terakura³⁵ have presented related work, including studies of trends in the electronic structures of several perovskite transition metal oxides. Satpathy, Popović, and Vukajlovic³⁶ have addressed the applicability of beyond-LSDA functionals to these compounds. Butler, Zhang, and MacLaren³⁷ have used coherent potential approximation calculations to study alloy disorder effects and estimate the resistivity arising from A site cation disorder. We return to these calculations in Sec. VI.

II. CRYSTAL STRUCTURE

CaMnO₃ forms in the cubic perovskite ABX_3 structure, with a lattice constant of 3.73 Å. Mn ions are sixfold coordinated with oxygen ions along the Cartesian axes, while Ca





FIG. 2. The distorted Pnma crystal structure of LaMnO₃, giving an impression of the substantial distortion from the cubic perovskite structure. Small black spheres are Mn, gray spheres are La, white spheres are O. The region shown comprises the volume of four perovskite primitive cells. The bounding box corresponds closely but not exactly to the cell boundary.

ions are twelvefold coordinated with oxygens lying along its $\langle 110 \rangle$ directions. Six oxygen ions form an octahedral cage for the Mn ions, and cages are linked by oxygen ions.

LaMnO₃ was found by Elemans *et al.*¹⁴ in a strongly distorted orthorhombic *Pnma* structure (D_{2h}^{16}) the gadolinium orthoferrite (GdFeO₃) structure type,³⁸ space group No. 62 in the International Tables) below $T_s \approx 875$ K with (at low temperature) $a = \sqrt{2} \times 4.060$ Å, $b = 2 \times 3.834$ Å, $c = \sqrt{2} \times 3.912$ Å. We use this structure, whose volume is that of a cube with edge 3.934 Å, for our calculations of distorted LaMnO₃. This *Pnma* structure is shown in Fig. 2, where it is contrasted with the ideal perovskite structure. There have been reports of other cell symmetries, for example, Wollan and Koehler¹⁵ reported a monoclinic structure. However, these are all closely related structures, and it is clear that both oxygen and cation stoichiometry affects the crystal structure and symmetry.

The *Pnma* lattice structure can be derived from the perovskite structure by the following.

(i) First rotating an oxygen octahedron around the z axis. Since the octahedrons remain connected, the attached octahedrons in the x-y plane rotate oppositely, resulting in a $\sqrt{2} \times \sqrt{2}$ doubling of the cell (conventionally taken as the *a*-*c* plane) and a reduction to tetragonal symmetry with $b \neq a = c$.

(ii) Tilting an octahedron along the Mn-O-Mn direction in the a-c plane, leading to opposite tilting of the neighboring layers and thereby resulting in a further doubling of the primitive cell along the b axis. This leads to orthorhombic symmetry and shortens the lattice along the b axis and one in-plane lattice constant (taken along the c axis). Since volume tends to be conserved, the a axis increases.

The result is a total of seven internal structural parameters: two each for the La ions and the O_I ions, which lie on the Wyckoff 4*c* sites with mirror symmetry, none for the Mn ions, which lie on the 4*a* sites with inversion symmetry, and three for the O_{II} ions that lie on the general 8*d* sites. The structural parameters are given in Table I. In this structure

TABLE I. Structural parameters of the *Pnma* (D_{2h}^{16}) , No. 62 in the International Tables) structure of LaMnO₃ as reported by Elemans *et al.* (Ref. 14), *a*=5.742 Å, *b*=7.668 Å, *c*=5.532 Å at 4.2 K.

	x/a	v/b	z/c
 Lo	0.549	1/4	0.010
Mn	1/2	0	0.010
O _I	-0.014	1/4	-0.070
O _{II}	0.309	0.039	0.224

the O octahedron rotates and distorts strongly: the Mn-O bond lengths, which are 1.97 Å in the isovolume cubic perovskite structure, become 1.91, 1.96, and 2.18 Å.

The distortion from cubic has been ascribed to two causes. An obvious one is the Jahn-Teller instability of the d^4 ion in the ionic picture: three electrons fill the t_{q} orbitals that lie low in energy, and the fourth electron goes into the doubly degenerate e_g orbital, leading to an instability. This JT instability would favor a local tetragonal distortion of the MnO_6 octahedron, which could be repeated periodically in various ways but would not in itself lead to the low Pnma symmetry. It has also been noted, simply on the basis of packing of spheres,³⁸ that this compound should be noncubic: the sum of Mn-O layer ionic radii $R_{Mn}+R_O$ do not match the related quantity for the La-O layer $(R_{La}+R_O)/\sqrt{2}$, closely enough to make the cubic structure stable.^{1,2,39} Such size misfits make instabilities against rotations of oxygen octahedra common in perovskites. Since the mineral perovskite itself (CaTiO₃) assumes the same space group symmetry^{39,40} but has a nominal Ti⁴⁺ (d^0) configuration with spherical symmetry, the distortion of LaMnO3 need not necessarily be driven by the JT instability.

LaMnO₃ has a combination of atomic size mismatch and electronic instability that leads to the low-symmetry structure, and the dominant driving force is not evident *a priori*.⁴¹ A difference with CaTiO₃ is that in that crystal the distortion is nearly a pure rotation of TiO₆ octahedra that preserves the Ti-O bond lengths, while in LaMnO₃ these bond lengths change to give the MnO₆ octahedron an aspect ratio of 1.12 (~1.004 for CaTiO₃). Hence the JT distortion is strong, whether or not it should be considered the driving force.

We note some structural complications that should be mentioned, since they may be related to the CMR phenomenon in some way. Structural variations with preparation conditions have been discussed by Yakel,42 with nonstoichiometry being a common occurrence. Tofield and Scott⁴³ used powder neutron diffraction to study a series of samples, and concluded that cation vacancies commonly occurred on both the A and B sites. Cerva⁴⁴ used transmission electron microscopy to image defects in La_{0.8}Sr_{0.2}MnO₃, concluding that there were extended missing layers of La/Sr cations on the scale 25 nm. In the same system Andersen et al.45 also concluded there were La/Sr vacancies on the basis of wet chemimethods. van Roosmalen et al.⁴⁶ studied the cal La₂O₃-Mn₂O₃ phase diagram and concluded that LaMnO₃ is the only compound containing both La and Mn, but that it is not a line compound; i.e., nonstoichiometry occurs. These studies all indicate that the common designation $(La,D)MnO_{3+\delta}$ can be misleading: cation vacancies may be more common than excess (interstitial) oxygen.

III. COMPUTATIONAL METHODS

The electronic structures, charge and spin densities, and total energies were calculated with the general potential linearized augmented plane-wave (LAPW) method.^{47–49} This method makes no shape approximations to the density or potential and retains high variational freedom in all regions, so it is well suited to open crystal structures with low site symmetries such as those considered here. The set of basis functions was supplemented with local orbitals for additional flexibility in representing the Mn 3*d* states, La 4*f* states, and semicore states (Ca 3*s*,3*p*; La 5*s*,5*p*; O 2*s*), and for relaxing linearization errors generally. The La 4*f* states were treated fully self-consistently with the band states, and were found to lie 2–3 eV above the Fermi level E_F , having no evident effect on the results.

The LAPW sphere radii were taken to be 2.0 a.u. for Mn, Ca, and La, and 1.55 a.u. for O. Self-consistency was carried out on special *k*-point meshes; for LaMnO₃, for example, we used 84 points in the irreducible Brillouin zone for the FM case (single formula unit per cell, 20 and 28 points, respectively, for the A-type and G-type AFM cells that require two formula units, and 8 points for the *Pnma* structure with four formula units. The basis set cutoffs were of the order of K_{max} =4.5 a.u. (energy of 20 Ry), and considering also the local orbital extensions the computations are extremely well converged in the basis set expansion.

It is not uncommon to find that LSDA does not provide a correct description of transition metal oxides (TMO's). However, these manganites have not yet been tested, and they lie on the left-hand side of the 3d series where LSDA is less problematic. One of the purposes of this study was to assess the realism of the LSDA description of this system. Most calculations have been carried out with the von Barth– Hedin-Lundqvist form⁵⁰ of exchange-correlation potential; certain calculations repeated with the Vosko-Wilk-Nusair⁵¹ form led to no appreciable difference.

Unless stated otherwise, the calculations assume a volume/formula unit corresponding to the cubic perovskite lattice constant at $x = \frac{1}{3}$ (3.890 Å). Because of the large spin moments that arise, the variation of the results with volume should be continuous and uninteresting for the properties we discuss here.

IV. END-POINT STOICHIOMETRIC COMPOUNDS

The first step in our study is to apply LSDA methods to $CaMnO_3$ and $LaMnO_3$ where the experimental facts are relatively unambiguous, to establish whether LSDA provides a realistic description. Generally LSDA does quite well in transition-metal-based compounds, but in the classes called Mott insulators its performance may be unacceptable. These problem cases generally occur toward the right end of the 3*d* series, however, and since Mn occurs in the middle of the transition series one may not expect serious problems. In comparing with experiment, it must be kept in mind that we assume precise stoichiometry, whereas the absolute oxygen content, and defect types and concentrations, are always po-



FIG. 3. Total and atomic density of states (majority and minority) of CaMnO₃ with the observed *G*-type AFM ordering. By symmetry, only the Mn ion has a net polarization, and the essentially complete polarization of the Mn *d* (t_{2g}) complex is evident. Ca *s* and O *s* character is minuscule, and Ca *d* character is very minor. Some curves are plotted as dashed lines simply for clarity.

tential complications in these compounds.

CaMnO₃, with its JT stable d^3 ion, is the simplest member of this system both electronically and structurally. FM spin polarization leads to a 0.86 eV/Mn energy gain relative to the nonmagnetic case (energies will be quoted per formula unit, or equivalently, per Mn). The A-type AFM state is 57 meV lower than the FM state, and has a metallic band structure. The observed G-type magnetic structure is 116 meV below the FM case, and it is insulating with a 0.42-eV calculated gap. Thus LSDA predicts the correct ground state. The Mn *d*-band exchange splitting is $\Delta_{ex} \sim 3$ eV, and the Mn 3s and 3p core states, which can easily be observed spectroscopically, are similarly exchange split. The Mn t_{2g} manifold is essentially completely polarized (Fig. 3), in accord with Hund's rule. In the region of interest, Ca 3s and 3d character and O 2s character are negligible. Comparison of the density of states (DOS) with the band structure presented in Fig. 4 illustrates the features more completely: oxygen p spectral density extends throughout a 7-eV region to the bottom of the gap, and also appears through hybridization in the conduction bands (Fig. 3) although it is absent at the conductionband edge. The band gap is direct at the X point, but corresponds to a gap between occupied majority and unoccupied minority Mn t_{2g} states accessible only by spin-flip transitions. The measured optical gap (spin-conserving transitions) will be larger than the absolute gap of 0.42 eV.

In Fig. 5, we illustrate the magnetic behavior by plotting contours in the x-y plane of spin-up valence electron density (the up and down densities are related by a $\langle 100 \rangle a/2$ translation) and the net spin (magnetization) density m(r) (spin up minus spin down). The spin-up density is large on one Mn ion and dominated by the occupied t_{2g} orbitals (e.g., d_{xy}), while on the neighboring Mn ions the spin-up density is



FIG. 4. Insulating band structure of the observed G-type AFM state of CaMnO₃, corresponding to the densities of states shown in Fig. 3. The gap is direct at the X point. The designation "110" indicates another X point lying outside the first Brillouin zone. Note that the AFM order introduces a second gap 2.5 eV above the fundamental gap.

small and slightly e_g -like. An asymmetry in the oxygen density is visible. The spin-density plot shows very clearly its t_{2g} character, and shows also the small but nonvanishing polarization on the oxygen ion. The spin density on each side of the O ion is opposite to that of the nearest Mn ion, giving rise to a node in m(r) between the Mn and O ions as well as the node through the O nucleus as dictated by symmetry. This contribution to m(r) will affect the "experimental" moment arising from a fit to polarized neutron scattering data that assumes only a Mn moment.

An essential role of band-structure calculations is to obtain the degree of hybridization. One measure is to contrast the value of the magnetic moment with that of the free ion, i.e., the Hund's rule value. We quote the moment μ^{sph} within the Mn sphere of 2.0 a.u. and the oxygen sphere of 1.55 a.u. used in our calculations. Mn moments are reflected realistically in μ^{sph} , but due to ~5% of the Mn d orbital extending out of the sphere, these values are not a precise prediction of the total Mn moment. Without hybridization the Mn moment will be integral (we neglect orbital contributions), and the oxygen moment will vanish. Hybridization, which occurs most strongly in the majority states because the exchange splitting of ~ 3 eV results in overlapping Mn d and O p majority states, results in a decrease from integral values of the moment. We report in Table II the moments μ^{sph} for the magnetically ordered states we have studied. In FM cases, in which the total moment is defined precisely in terms of a difference between majority and minority charges in the unit cell, up to $0.5\mu_B$ of the moment lies outside this Mn sphere. However, the interstitial contribution to the moment is smaller for AFM states because they have nodes in the spin density between the atoms. In the FM, A-type AFM, and G-type AFM states the values are $\mu_{Mn}^{sph}=2.64\mu_B$, $2.56\mu_B$, and 2.48 μ_B , respectively; in this case the differences arising from differences in hybridization are rather small, indicating a strong atomiclike moment. The calculated G-type groundstate moment of 2.48 μ_B is in very reasonable agreement with $\mu_{expt}=2.65\mu_B$,¹⁵ especially considering that this sphere value is an underestimate of the total moment.

For contrast, we show in Fig. 6 the band structure for



FIG. 5. The (001) plane of CaMnO₃ containing Mn and O ions. Upper panel: single spin density in its observed *G*-type AFM state, with contour from 0.5 to 0.5 a.u.⁻³, in steps of 0.05 a.u.⁻³ (solid) and from 0.0 to 0.045 a.u.⁻³ in steps of 0.005 a.u.⁻³ (dashed). Lower panel: the net spin density, with contour coding identical for both signs. Long dashes denote the zero contour. Solid contours run up to 0.045 a.u.⁻³ in steps of 0.005 a.u.⁻³, and dashed contours run to 0.3 a.u.⁻³ in steps of 0.05 a.u.⁻³. The long dashed lines indicate nodes in the spin density, and relative signs of the spin density in different regions are indicated.

A-type ordering of spins with tetragonal crystal symmetry. Note that there appears to be no possibility of opening a gap at the Fermi level with a moderate change in the electronic structure (such as a different approach to the exchangecorrelation potential, e.g., including gradient corrections). Notably, there is a Mn *d*-band crossing E_F from 1 eV below at *M* to 4 eV above at Γ , although *d*-band dispersions are less than this value (5 eV) elsewhere. An interesting point is that with this spin arrangement the bands at the $Z=(0,0,\pi/2a)$ point are pure spin states. (For *G*-type ordering, that is, a rocksalt arrangement of Mn moments, states are the *L* point are pure spin states.) The band structure for this A-type spin alignment becomes important when we discuss LaMnO₃ below.

We note now the outcome for (experimentally inaccessible) FM CaMnO₃ because already it is indicative of the provocative behavior that may be expected of the FM phases. The calculated moment is precisely $3\mu_B/Mn$, as the formal valence would predict, in spite of considerable d-p hybridization. This integral value occurs because FM CaMnO₃ is "half-metallic" $(\frac{1}{2}M)$, with metallic majority bands but insulating minority bands.⁵² $\frac{1}{2}M$ FM is in fact a rather rare occurrence⁵² and we argue below that its connection to the also rare CMR effect is not accidental. The band structure is presented in Fig. 7, where it can be seen that the

TABLE II. Values of the magnetic moment (in μ_B) inside all inequivalent Mn and O inscribed spheres for the various magnetically ordered states discussed in the text. Values of 0.0 indicate moments that vanish by symmetry. Values of the moment inside Ca and La spheres (not listed) are not larger than $0.02\mu_B$ and arise only from tails of neighboring atoms. The lattice constants used are those for CaMnO₃ (7.0558 a.u.), the $x = \frac{1}{3}$ alloy (7.3535 a.u.), and the cube will the same cell volume as observed for LaMnO₃ (7.4370). FiM' denotes the ferrimagnetic solution for which one Mn moment is essentially zero.

	<i>a</i> (a.u.)	Mn	0	
CaMnO ₃				
FM	7.3535	2.64	0.057	
AFM A type	7.3535	2.56	0.056, 0.0	
AFM G type	7.3535	2.48	0.0	
AFM G type	7.0558	2.34	0.0	
LaMnO ₃ : cubic				
FM	7.3535	2.99	0.05	
AFM A type	7.3535	2.99	0.052	
AFM A type	7.4370	3.18	0.054	
AFM G type	7.3535	2.89	0.0	
LaMnO ₃ :Pnma				
FM	(7.4370)	3.37	0.067, 0.079	
AFM A type	(7.4370)	3.37	0.067, 0.079	
$x = \frac{1}{4}$				
FM	7.3535	3.07	0.062	
$x = \frac{1}{3}$				
FiM	7.3535	2.93,3.04	0.078, -0.001, 0.058, -0.050	
FiM'	7.3535	3.00,0.02	0.075, 0.034, 0.010, -0.004	
FM	7.3535	3.05,3.09	0.089,0.053,0.062,0.058	

Fermi energy E_F falls very near the middle of a 1.2-eV gap in the minority channel between O p bands and Mn d bands. The minority bands also are instructive because the valence bands, which are nominally O p, do not overlap the nominally Mn d (t_{2g}) bands. The O p bands are nearly 6 eV wide, with the dispersion arising from a combination of nearestneighbor O p-O p hopping and O p-Mn d hopping. The Mn d bands are 4.5 eV wide, and this dispersion must result from O p-Mn d hopping because direct Mn d-Mn d hop-



FIG. 6. Metallic band structure of the (metastable) A-type AFM state of CaMnO₃, which should be contrasted with the band structure for the observed ordering shown in Fig. 4. Note the broad bands (\sim 4 eV wide) crossing the Fermi level (shown as the dashed line), and the absence of any hint of an energy gap.

ping is negligibly small. This fact indicates that there is important O p character in the conduction bands, as is seen in the local DOS. In the minority channel the lower part of the Mn d bands overlaps with the O p bands (whose position is spin independent) and band edges are harder to identify.

As a result of the Mn t_{2g} exchange splitting (~3 eV), the Mn d-O p hybridization is strongly spin dependent. Since the majority d bands overlap with the O p bands and hybridize strongly, they form a highly conducting majority spin network. The minority d bands, which lie 3 eV higher in energy, hybridize more weakly across the aforementioned minority spin gap. The majority-minority spin distinction could not be greater than it is in this $\frac{1}{2}M$ situation, and the differences are intimately tied to the spin-dependent hybridization.

Increased band filling accounts for most of the differences between LaMnO₃ and CaMnO₃, and for this reason $\frac{1}{2}M$ character does not persist in FM cubic LaMnO₃ in spite of the similarity to the CaMnO3 band structure. Hybridization is evident in the computed FM moment of $3.38\mu_B/Mn$, a 15% decrease from the Hund's rule value of $4\mu_B$. For both of the AFM orderings the Mn d exchange splitting is \sim 3.5 eV but does not lead to full polarization, so the local moments are well below their Hund's rule value $(\mu_{Mn}^{sph}=2.89\mu_B)$ in both cases). For this (idealized) cubic structure, the AFM solutions are 110 meV (A type) and 365 meV (G type) higher in energy than the FM state, and all solutions for the cubic perovskite structure are metallic. These energy differences are collected in Table III with those of CaMnO₃. As in CaMnO₃ discussed above, the (observed) layered A-type AFM alignment displays one d band (among others spanning



FIG. 7. Minority (upper) and majority (lower) band structures of half-metallic FM CaMnO₃. Note the overlap of O p bands and Mn d bands for the majority states, while for the minority states they are separated by a gap and hybridize much more weakly. The bottom of the oxygen bands lies at the same energy for both spins.

 E_F) that is nearly 5 eV wide, which at first sight appears to preclude the possibility of obtaining an insulating A-type AFM solution as observed.

The actual structure of LaMnO₃ is, however, the strongly distorted *Pnma* structure shown in Fig. 2, rather than the cubic structure. We have carried out calculations including the observed large structural distortion¹⁴ involving a $\sqrt{2} \times 2 \times \sqrt{2}$ quadrupling of the unit cell, internal atomic displacements, and considerable strain (Sec. II and Table I). We find that the *Pnma* distortion gives an energy gain of 0.23 eV per formula unit at constant (experimental) volume.

Based on the picture of a Jahn-Teller instability of the d^4 Mn ion in LaMnO₃, a substantial energy gain by the distortion is expected. The unanticipated result is that this distortion leads to two other crucial changes: (1) it lowers the energy of the A-type AFM state below that of the cubic FM state (by 156 meV), thus making it the lowest-energy solution, and (2) it induces new band splittings and large band shifts that result in an insulating band structure with a 0.12-eV indirect gap. A reported thermal gap is 0.24 eV.²¹ Arima, Tokura, and Torrance⁵³ noted the weak oscillator strength in their optical conductivity data for LaMnO₃, and suggested an optical gap of ~1 eV. In La_{1-x}Sr_xMnO_{3+ δ} with $x \approx 0.1$ and $\delta > 0$, a gap of ~0.2 eV was reported by Chainani, Mathew, and Sarma.⁵⁴

TABLE III. Calculated relative energies (in meV per primitive perovskite cell) of various phases of the manganites. In each case the energies are referenced to the ferromagnetic phase.

CaMnO ₂		
5	Paramagnetic	+860
	Ferromagnetic	0
	A-type AFM	-57
	G-type AFM	-116
LaMnO ₃		
	G-type AFM	+365
	A-type AFM (cubic)	+110
	Ferromagnetic (cubic)	0
La _{2/3} Ca _{1/3} MnO ₃		
	Ferrimagnetic	+70
	Ferromagnetic	0

The mechanism of the gap opening due to the distortion is addressed by plotting the bands for a structure in which the internal atomic displacements from high-symmetry sites are only 25% of the experimental values. The gap could arise simply because the lowered symmetry introduces new gaps near E_F , or it could arise from the shifting of bands across E_F without additional band splitting. As shown in Fig. 8, it is actually a combination of these two factors: two bands are hybridized and split at E_F by the symmetry lowering, while a third is simply shifted above E_F by the potential shifts arising from the distortion (the first band below E_F at Γ). From these band figures it appears that more than half of the observed amplitude of the *Pnma* distortion is required to open the gap.

The DOS of the *Pnma* structure is shown in Fig. 9 compared with the metallic spectrum of the cubic structure (both with A-type AFM). The distortion from cubic to *Pnma* results in (i) two chemically distinct O sites whose 1s core levels are split by 0.2 eV, and (ii) removal of minority carriers, giving a considerably higher local moment of $\mu_{Mn}^{sph}=3.31\mu_B$ as well as a moment of $\mu_o^{sph}=0.07\mu_B$ within the sphere of the O ion that is allowed by symmetry to polarize. Wollan and Koehler¹⁵ report $\mu_{Mn}=3.89\mu_B$ from their fit to diffraction data. Recalling that there is also spin density outside the spheres, and that Wollan and Koehler assumed a moment only on the Mn ion, it is difficult to say just how much real discrepancy there is between the LSDA description and observation. Direct comparison of calculated and measured spin densities could clarify this point.

The indirect gap in *Pnma* LaMnO₃ [Fig. 8(c)] involves a conduction-band minimum at Γ and valence-band maximum near $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ in reciprocal lattice vector units, with another valence band at $(0, \frac{1}{2}, 0)$ nearly equal to the valence-band maximum. This indirect gap would be measurable in transport studies of clean (i.e., stoichiometric and therefore undoped) samples unless the thermally excited carriers form small (localized) polarons. From our band structure of Fig. 8, it appears that the optical gap will be $\gtrsim 0.7$ eV. However, due to the AFM order and the fact that optical transitions are spin conserving, the direct gap may be difficult to assign.

In all three respects—energy, spectrum, and magnetism the distortion is necessary, and sufficient, to give a good



FIG. 8. Band structure near the Fermi level (energy gap) for LaMnO₃ with the observed A-type AFM order, for (a) no internal distortion, (b) 25% amplitude of distortion, and (c) fully distorted experimental structure. The gap arises from a combination of band splitting due to additional hybridization and to displacements of band edges across the Fermi level (dashed line).

account of the experimental data. The large changes in energy and the development of an energy gap resulting from the distortion reflect strong magnetostructural coupling. This coupling suggests that the enhancement of CMR and shift of T^* by ~10% substitution of La by Y, attributed by Jin *et al.*²⁰ to the 0.2% decrease in lattice constant, may be more readily explained in terms of strong magnetostructural coupling to local strains that are altered by the incorporation of the smaller Y ion.

V. INTERMEDIATE CONCENTRATIONS $x = \frac{1}{4}$ AND $x = \frac{1}{3}$

To begin to address the question of CMR, we must treat mixed La-Ca manganates. This system has the cubic perovskite crystal structure in the CMR regime $x \approx \frac{1}{3}$. We have treated two cases, which are particular ordered realizations of the $x=\frac{1}{3}$ and $x=\frac{1}{4}$ systems. As was the case for the end-point compounds discussed above, we find negligible Ca or La character in the states near or below E_F , so they merely



FIG. 9. Density of states for cubic (dashed) and energetically favored orthorhombic Pnma (solid) LaMnO₃ with the observed A-type AFM ordering. Note the opening of the gap at the Fermi level (vertical dashed line) in the total DOS, and the vanishing of minority occupation in the distorted Pnma structure. The Mn d exchange splitting of 3 eV is evident.

contribute their valence electrons to the Mn-O system and become electronically inactive spectator ions of differing size and charge.

 $x=\frac{1}{3}$: For a tetragonal three formula unit La₂CaMn₃O₉ supercell with repeating (-La-Ca-La-) layers, the FM moment of $3.51\mu_B/Mn$ is near the reported value¹⁵ of $3.4\mu_B/Mn$. Two distinct Mn sites occur in this supercell: Mn_{La-La} site sandwiched between La³⁺ and La³⁺ layers, and a Mn_{La-Ca} site lying between La³⁺ and Ca²⁺ layers. The charge is 0.05e larger than on Mn_{La-Ca}; since this difference resides in majority charge the moment is correspondingly larger on Mn_{La-La} ($\mu^{sph}=3.08\mu_B$). These differences between the ions are much smaller than what arises in the ionic picture of only d^3 and d^4 configurations. This description thus leads not to a strong mixed-valent model, but rather to a picture of strongly polarized, nearly half-metallic, Mn *d* bands as suggested very early on by Searle and Wang.³⁰

Fermi surface averages are important for beginning to interpret transport data, so we have calculated the densities of states $N(E_F)$ and Fermi velocities v_F . Due to the artificial tetragonal symmetry of our supercell (compared to the disordered, but cubic on average, $x = \frac{1}{3}$ material), in-plane and perpendicular velocities differ somewhat, but the directionally averaged values are $v_{F,\uparrow}=7.4$, $v_{F,\downarrow}=2.2$, in 10^7 cm/s. The densities of states are $N_{\uparrow}(E_F)=0.58$ states/eV Mn ion, with 23% and 21% within the Mn_{La-Ca} and Mn_{La-La} spheres, respectively; $N_{\downarrow}(E_F)=0.27$ states/eV Mn ion, with 15% and 44% within the Mn_{La-Ca} and Mn_{La-La} spheres. Thus the minority DOS is not only smaller but is distributed very unevenly between the two Mn sites.

It is possible to obtain self-consistent solutions with other magnetic configurations in this $x = \frac{1}{3}$ supercell. A ferrimagnetic (FiM) solution in which the Mn_{La-La} moment of 2.98 μ_B is antiparallel to the majority Mn_{La-Ca} moments (3.04 μ_B) has an energy that is 70 meV higher. If interpreted simply in terms of nearest-neighbor Heisenberg-like local moment coupling, the interatomic exchange coupling is J=35 meV and favors ferromagnetism.

We have another "FiM" solution to the LSDA equations, corresponding to a Mn_{La-La} ion that is paramagnetic; as a result the energy is greater than the FM state by roughly the exchange energy of a single Mn ion (~1 eV) in the LSDA. The fact that this state is metastable, rather than completely unstable against moment formation, is evidence of the com-



FIG. 10. The total DOS and local DOS on each inequivalent Mn ion for the $x=\frac{1}{3}$ supercell for the FM ordering and for the FiM ordering. The subscripts denote the types of cation planes sandwiching that layer of Mn ions.

petition between the drive to form an atomiclike moment (the exchange energy) and the tendency toward covalency (band energy, which is given up as a moment forms). Physically, low-energy variations of the magnetic system are expected to involve noncollinear spin canting rather than changes in the magnitude of the moment. This fact is reflected in the very high energy of our latter FiM solution. We return to these questions when we discuss the fixed moment calculations below.

The differentiation of the $\mathrm{Mn}_{\mathrm{La-La}}$ and $\mathrm{Mn}_{\mathrm{La-Ca}}$ ions is a local environment effect that is important to understand, since it will have its counterpart in the disordered solid. In Fig. 10 we show the Mn d DOS for each ion for both the FM and FiM orderings. There are three items to note, which reveal an unusual constancy of behavior in the region near E_F . First, the local densities of states (LDOS) are strongly spin differentiated in the range -2 eV to 0 (relative to E_F), and the moment flip results simply in a flip in the LDOS of the affected atom in this region, while leaving its shape and the LDOS of the neighboring Mn atoms practically unchanged. Hence the difference is a local environment effect, without substantial band-structure contribution in this energy range. Second, the small fraction of minority carriers is associated entirely with the Mn_{La-La} ion, which is the one surrounded entirely by trivalent cations and therefore is a more attractive site for electrons. The concentration of minority carriers on the Mn_{La-La} ion is roughly twice as large for the FiM ordering, suggesting that FM ordering minimizes the minority carrier concentration at this concentration. Third, the Mn_{La-Ca} ion remains $\frac{1}{2}M$ as in the FM CaMnO₃ case discussed above, hence it will provide no minority conduction. We return to these considerations in Sec. VII.

This supercell with inequivalent Mn ions allows the study of the stiffness against fluctuations in the magnitude of the moment, for different relative (but collinear) spin orientations (FM and FiM). For this study we use constrained moment calculations, in which the total moment in the cell is fixed. The results for the value of μ^{sph} for each of the inequivalent Mn ions, and the total energy, are presented in Fig. 11. The two states discussed above are evident as minima: FM at $M = 10.6\mu_B$ and FiM at $M = 2.7\mu_B$, with the FM state more stable by 70 meV. For the FM orderings, the approach to self-consistency became difficult in the $M = (6.5-7)\mu_B$ region (hence the breaks in the curves in Fig. 11), arising from fluctuations of the spin between the two inequivalent Mn ions. The Mn_{La-La} ion that carried the higher moment above this range switched to having the lower moment below. Since these calculations are for FM alignment, the main distinction between the two Mn sites is the number of neighboring divalent and trivalent metal ions.

This region of spin instability is also the same region in which the Mn_{La-La} ion's moment vanished for the FiM ordering (see Fig. 11). This behavior indicates some interesting behavior of the LDSA equations, but the relatively high energies in this range seem to exclude any physical significance so we have not pursued the behavior any further. The FiM ordering was only followed in the $2.3\mu_B \leq M \leq 6.9\mu_B$ range. It is interesting that the larger moment (in magnitude) switches over between the two Mn ions near, but not at, the minimum of energy for the FiM ordering. The FiM deep (relative) minimum might lead one to conclude that the FiM state achieves its relatively low energy due to all Mn ions becoming fully polarized. However, there must be strong competing effects from covalency, because at the energy crossover ($M \approx 4.5 - 5.0$) the FiM state has much higher atomic moments than the FM state (and yet equal energy).

The change in slope of the energy and of the Mn moments at $M = 11 \mu_B$ is related to the $\frac{1}{2}M$ character discussed above. Below this point the magnetization arises predominantly from Mn moments. However, above this range all of the valence electrons consistent with retaining (nominally) O^{2^-} ions have been polarized. When larger *M* is forced, as is done in the fixed moment calculations, the additional magnetization must come primarily from the O ions, and we find that the moments on the O sites are increased substantially at $M = 12\mu_B$ over their values for smaller *M*. As is evident in



FIG. 11. Plot of the Mn moments (lower panel) and the total energy of the system (upper panel) versus the imposed fixed total moment *M* of the supercell. Both ferromagnetic and ferrimagnetic orderings are shown; recall that the moments are oppositely directed in the ferrimagnetic case. Solid (dashed) lines in the lower panel represent the Mn_{La-La} (Mn_{La-Ca}) ion moment. The discontinuity at a moment of $11\mu_B$ in the ferromagnetic case results from the forced polarization of O ions that begins at this point.

Fig. 11, the energy cost of polarizing O atoms is distinctly different from that of polarizing Mn ions. Note also that the energy curve E(M) is rather flat in the $10\mu_B < M < 11\mu_B$ region, indicating the magnitude of the moments can fluctuate somewhat without much cost in the high-spin FM region. The curvature $d^2E/dM^2=17$ mRy/ $\mu_B^2=1/\chi$ leads to a susceptibility in the FM state of $\chi=0.22\times10^{-6}$ emu/g. Interestingly, this value is roughly equal (within ~20%) to the Pauli susceptibility of a paramagnetic system with the same total $N(E_F)$. The energy cost of spin fluctuations, both in direction and in magnitude, needs further study.

 $x = \frac{1}{4}$: A bcc supercell of the type La₃CaMn₄O₁₂ presents one example of an ordered $x = \frac{1}{4}$ phase. Each Mn ion has two Ca and six La neighbors, and each Mn ion is equivalent. An average FM moment of $3.53\mu_B/\text{Mn}$ ($\mu^{\text{sph}}=3.06\mu_B$) results, very similar to the FM $x = \frac{1}{3}$ case above and to the experimental value. The DOS, shown in Fig. 12, reveals the intraatomic Mn *d* exchange splitting of ~3.5 eV. There is a 2-eV gap in the minority states just below E_F , with the result that minority *d* states are again only slightly occupied ($E_{F\downarrow}\approx0.2$ eV). The hybridization with O *p* states in the majority bands near E_F is clearly evident: both Mn and O contribute to the



FIG. 12. The density of states for the ferromagnetic $x = \frac{1}{4}$ supercell. Solid and dashed lines denote majority and minority states, respectively. The minority Fermi level is ~0.15 eV. The Mn *d* spin splitting of ~3.5 eV is evident. The peak in the total DOS at 2.5 eV is due to the La 4*f* bands, which were always included in the calculations.

DOS at E_F . We have not attempted to generate AFM or FiM ordered solutions for the $x = \frac{1}{4}$ concentration. The directionally averaged Fermi velocities are $v_{F,\uparrow} = 7.2$, $v_{F,\downarrow} = 2.8$, in 10^7 cm/s, similar to those obtained above for the $x = \frac{1}{3}$ supercell. The densities of states are $N_{\uparrow}(E_F) = 0.45$, $N_{\downarrow}(E_F) = 0.54$, in states/eV primitive cell. The differences between these values and those given above for the $x = \frac{1}{3}$ supercell indicate that the minority DOS near E_F is particularly sensitive to atomic ordering.

VI. RELATION TO OTHER WORK AND SPECTROSCOPY DATA

A. Other theoretical work

Hamada, Sawada, and Terakura³⁵ have reported LAPW studies of LaMnO₃, and on La_{0.5}Ba_{0.5}MnO₃ using the virtual crystal approximation. They observe the same type of strong Mn d-O p hybridization as we have emphasized, and also conclude that there is half-metallic (or very near) character in the FM phase. They also concur that the distortion is instrumental in obtaining an insulating gap in LaMnO₃. One difference remains to be resolved. For undistorted LaMnO₃ they report the A-type AFM ordering to be only 1 meV above the FM ordering, whereas we have found a 110-meV difference. Possibly the difference is partly in the structures assumed in the calculations (not reported in detail in their short paper). They find for their $x = \frac{1}{2}$ virtual crystal alloy that the FM state is stabilized in the cubic phase over the A-type AFM state, which is still the lower-energy phase for $x = \frac{1}{2}$. This result is consistent with the observation of the cubic structure in the FM CMR region.

Using the linearized muffin-tin orbital method in the atomic-sphere approximation, Satpathy, Popović, and Vukajlović³⁶ focused on the application of the LDA+U method⁵⁵ of treating a strong on-site Coulomb interaction U ("Hubbard U") in a mean-field manner. The exchange pa-

rameter J was included as well. They calculated U=10 eV, J=0.9 eV, and reported the changes in the electronic spectrum compared to the LSDA. Specifically, in agreement with our results and those of Hamada, Sawada, and Terakura, they find that LSDA is sufficient to account for the antiferromagnetic insulating state, once the crystal distortion is taken into account. The LDA+U method produces spectral changes and increases in magnetic moments that must be compared with experiment before conclusions are drawn. The reported LDA+U moment of $3.3\mu_B$ in CaMnO₃, which is well above the Hund's rule value, clearly seems to be too large.

Butler, Zhang, and MacLaren³⁷ applied the layer Korringa-Kohn-Rostoker method with spherical potentials inside space-filling spheres. They reported the DOS for nonmagnetic, cubic LaMnO₃, which may be useful in constructing tight-binding Hamiltonians for manganites. They find the occupied O p bands to be separated from the partially occupied Mn d bands by ~ 2 eV, but that hybridization results in substantial O p character in the conduction bands. A large peak in N(E) falls precisely at E_F , suggesting a Stoner instability of the nonmagnetic state. They confirm the $\frac{1}{2}M$ character in the FM state. Calculations of the resistivity of La_{0.67}Ba_{0.33}MnO₃ arising from substitutional (cation) disorder gave 6 $\mu\Omega$ cm for majority spin conduction and essentially infinite (insulating behavior) for minority spins. They report Ca character at the Fermi level, whereas for the cases we have studied the Ca (and La) character is negligible.

Well before the CMR behavior was discovered, Mazzaferro, Balseiro, and Alascio⁵⁶ suggested a Hamiltonian to model the behavior of (La,Sr)MnO₃. The Hamiltonian included the usual on-site and hopping contributions with both Mn and O ions treated explicitly. They treated the Mn⁴⁺ ion as a spin- $\frac{1}{2}$ ion with an exchange coupling (J) to favor parallel alignment of an added electron, and a large Hubbard repulsion U to rule out the occurrence of Mn^{2+} ions. Additionally, they included a term that the present calculations suggest is important: a Mn site energy shift depending on the environment (number of neighboring divalent versus trivalent cations). Their model is a very complicated one, which they treated in the Bethe lattice approximation for nonmagnetic and ferromagnetic phases. Their main conclusions for this model were (1) the FM phase is stable for any concentration x; (2) the conductivity may be either metallic or semiconducting at intermediate x depending on the parameters (giving single-band or split-band behaviors, respectively); (3) the FM phase will be the most conducting; (4) in the FM phase the model predicts $\frac{1}{2}M$ behavior, but Mn site disorder is the cause of this result. The (admittedly preliminary) results they obtained for this model are promising enough that more detailed study seems warranted.

B. Spectroscopy data

The only photoemission spectroscopy (PES) data on the $La_{1-x}Ca_xMnO_3$ that we are aware of are that of McIlroy and collaborators.^{57,58} For a film of the x=0.35 material, spectral shifts were observed across the nonmetal-metal transition that were interpreted in terms of changes in the Mn d–O p hybridization and the charge distribution, roughly consistent with the predictions of band calculations. They also identified a relative value of " $N(E_F)$ " (averaged over their reso-

lution) that varied roughly as the magnetization, clearly associating conducting states with magnetic order.

Studies of the $La_{1-x}Sr_xMnO_3$ system have been reported by Chainani, Mathew, and Sarma⁵⁴ and by Saitoh *et al.*⁵⁹ The ceramic samples of Chainani, Mathew, and Sarma were highly resistive and did not show a clear nonmetal transition across the critical region, but changes in spectra versus *x* were observed. Their data were interpreted in terms of strong Mn *d*-O *p* hybridization, a charge transfer energy Δ =5 eV, and a Mn *d* repulsion energy of *U*=4 eV. This value of *U* is much smaller than that calculated by Satpathy, Popović, and Vukajlović³⁶ (see above).

Saitoh *et al.*⁵⁹ also reported strong covalency and suggested the gap of LaMnO₃ should be considered to be of the charge-transfer type. Band shifts observed upon replacing La with Sr are not rigid band, and the doped hole states were interpreted as having strong O p character. Intensity at the Fermi level remained low at all concentrations studied, with the onset occurring closer to E_F in the middle of the range.

In all of the PES studies mentioned above, the main valence spectra have a strong increase around 1.5-2-eV binding energy, remaining large in the region 2-6 eV, and falling off in the range 6-8 eV. In our calculations, we find a strong increase at 1–1.5 eV below E_F (see the FM phase DOS curves in Figs. 10 and 12), O p states occupying the range down to a lower peak around 6 eV below E_F , and then a falloff to zero near 8 eV. While this may be roughly in accord with the data, two differences should be noted. First, the observed intensity at the Fermi level is not nearly as strong as our DOS curves would suggest. Matrix element effects have not been calculated, but we do not expect them to give such a strong reduction in intensity. The second noticeable difference between our DOS and the data is the strong Md dpeak around 2 eV below E_F . Experimental resolution is unlikely to account for this difference. In the case of the hightemperature superconducting cuprates, such as YBa₂Cu₃O₇, it took nearly three years to master the techniques of surface preparation that revealed the existence of states at the Fermi level. Surface problems could be just as serious in these manganites.

VII. RELATION OF THE LSDA RESULTS TO CMR PHENOMENA

We now turn to the question of CMR, which occurs in the FM phase. For FM alignments, majority spin bands are strongly covalent combinations of Mn d and O p that span the Fermi level. The more interesting minority band structures for FM $x=0, \frac{1}{4}, \frac{1}{3}$, and 1 along the common Γ -X direction are shown in Fig. 13. As noted above, FM CaMnO₃ is half metallic (i.e., E_F falls within a minority spin band gap), while LaMnO₃ has a small minority carrier density. The x = $\frac{1}{4}$ and $x = \frac{1}{3}$ cases are intermediate; i.e., they have even lower minority carrier density. For the $x = \frac{1}{3}$ supercell, Mn_{La-La} character dominates the lowest above-gap band, while the Mn_{La-Ca} -derived bands are the pair above E_F . The intermediate pair, just below E_F , derives from both Mn ions. These differences are due to shifts in potentials due to the nearby cation charges (La³⁺ neighbors create a more favorable environment for an electron), a local environment effect that has not been emphasized heretofore.



FIG. 13. The minority band structure along Γ -*X* for the series of FM phases La_{1-x}Ca_xMnO₃, $x=0, \frac{1}{4}, \frac{1}{3}$, 1. For the five bands near E_F for $x=\frac{1}{3}$, the lower band is purely Mn_{La-La} character, the upper pair is purely Mn_{La-Ca}, and the middle pair involve all Mn ions. There is a strong decrease in minority gap with increasing Ca content *x* that arises from the raising of the O *p* bands as the average neighboring cation charge decreases. Note that for CaMnO₃ (*x*=1) the actual Fermi level (determined by the majority bands) lies near midgap. The majority band structures (not shown) are strongly metallic in this region.

The nature of the Ca/La disorder and local strains and relaxations, which we have not considered, will affect the precise electronic structure of the minority carriers. Tofield and Scott⁴³ have made the interesting observation that the reduction in ionic radius from Mn^{3+} to Mn^{4+} (0.65 Å to 0.54 Å) is much larger than for other transition-metal ions, and this enhances local distortions. Several features we have found should be robust, however.

(1) The electronic structure is very nearly half metallic. This implies the lack of a Stoner continuum (low-energy continuum of spin-one electron-hole excitations) that distinguishes the $\frac{1}{2}M$ FM from conventional metallic FM's. There is, however, a possibility of new low-energy excitations involving a hole in the majority spin band and an electron in a localized minority spin state, or vice versa.

(2) Hybridization is very spin dependent: for the minority channel the O p bands and Mn d bands are nonoverlapping and hybridize much more weakly than is the case for the majority O p and Mn d bands that do overlap and mix very strongly at E_F .

(3) The Ca/La local environment disorder leads to variations in the Mn *d* site energy that creates a tendency towards incoherence (i.e., localization) in the minority states near E_F . These effects for the relatively broad majority bands should be minor. The likely result is that E_F lies below a mobility edge giving nonconducting minority states.

(4) The half metallicity is a local effect that persists near flipped Mn spins (e.g., abrupt "domain walls"). The lack of a Stoner continuum and the possibility of minority spin polarons in a $\frac{1}{2}M$ FM provide possibilities for transport anomalies and for a large negative magnetoresistance (MR).

In addition, compositional variations or tendency toward local ordering of cations with La:Ca ratio differing from the sample average will lead to inhomogeneities, and their occurrence may be sensitive to the method of preparation. Such inhomogeneities can account for broadening of transitions and complex critical behavior as local regions become ferromagnetic at different temperatures.

Within this framework, Ca doping induces local FM (and potentially metallic) regions, consistent with the "ferromagnetic molecule" picture that Matsumoto³¹ suggested to account for the behavior in the small-*x* region. The real interest is in the FM phase $0.2 \le x \le 0.5$. At low temperature $T \le T_C$ and strong fields the magnetization is saturated and a low metallic resistivity is observed (no more than 100 $\mu\Omega$ cm in the better samples³³). The residual resistivity is presumably due to disordered La³⁺ and Ca²⁺ ions and the accompanying local lattice distortions in a background of parallel spins. As T_C is approached from below the resistivity rises dramatically. At the same time, the magnetic behavior is unusual in the sense that high fields are necessary for saturation.

The essentially $\frac{1}{2}M$ FM character provides a way to account for high resistivity in zero field. Due to conduction only in the majority spin channel, hopping of carriers between FM regions with opposite magnetization directions will be suppressed. The effect is related to that discussed for heterogeneous giant MR (GMR) materials such as Co-Cu (Refs. 60 and 61) where maximum suppression occurs for antialigned domains because the spin states at the Fermi level are maximally mismatched. However, the impeding effect is not like a scattering event that randomizes the direction of propagation, but rather a barrier (wave-function mismatch) that leads to reflection (no forward scattering). Unlike for heterogeneous GMR systems, however, where there is both majority and minority conduction but of differing magnitudes, the half-metallic nature of $La_{1-x}Ca_xMnO_3$ results in a more strongly insulating electronic system, and hence larger values of the MR $[\rho(H) - \rho(0)]/\rho(H)$.

In one dimension disordered, antialigned domains of $\frac{1}{2}M$ character would readily halt conduction. In three dimensions it is less easy, although perfectly cubic, antialigned domains would provide strict localization, as long as tunneling through the domains (which provide barriers) is vanishingly small, and conduction through the cube (domain) edges is negligible. Some disorder in such a system would not leave any percolation path for conduction, but simply act to increase size of some domains. A strongly antialigned configuration of $\frac{1}{2}M$ domains is realizable and should lead to a high resistivity. Well below T_C , magnetic coupling between the microdomains will grow as the magnetization grows, which will favor larger aligned regions and higher conductivity. The proximity to a FM-AFM transition, the expectation of local disorder in the cation environment, the sensitivity to processing, and the high saturation fields suggest very small domain sizes and thin domain walls. In this scenario there is a clear relation between the zero-field resistivity and the number of domain walls that must be traversed, i.e., inversely with the mean linear domain size. Applying a field lowers the resistivity by aligning the domains.

VIII. SUMMARY

We have presented a variety of results based on the *ab initio* local spin-density approach that is broadly in agree-

ment with ground-state properties, and provides several clues to the underlying processes involved in the colossal magnetoresistance phenomena. While this picture does not yet provide a theory of transport, it does provide a theoretical approach to the CMR problem that accounts for hybridization and is consistent with the electronic structures, the magnetic properties, and qualitative aspects of the behavior of $\rho(T,H)$. The near- $\frac{1}{2}M$ nature of the Mn ion provides some microscopic justification of the Hund's-rule-ion picture that has been presumed to hold in previous work. However, the strongly metallic majority spin bands in the FM materials, arising from the large hybridization, provide the needed explanation of the low resistivity at low temperature that has

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been missing. Further accounting of hybridization and of magnetostructural coupling is likely to be essential to extend our understanding of the CMR phenomenon.

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