The mixed manganite-cuprate \( \text{CaCu}_3\text{Mn}_4\text{O}_{12} \) is found, using density functional methods, to be a narrow gap (90 meV calculated) ferrimagnetic semiconductor. \( \text{Cu} \) (formally \( S = \frac{3}{2} \)) antialigns with \( \text{Mn} \) (formally \( S = \frac{3}{2} \)), and the net spin moment is \( 9 \mu_B \) consistent with the formal spins. Holes have \( \text{Cu} \) \( d_{xy} - \text{O} \) \( p_d \) (i.e. antibonding \( dp \)) character with spins aligned antiparallel to the net magnetization; electrons have the opposite spin and have mixed \( \text{Cu} \) \( d_{xy} - \text{Mn} \) \( e_g \) character. Thermally excited electrons and holes will each be fully spin polarized, but in opposite directions. The properties of this material are strongly tied to the distorted quadruple perovskite structure, which is closely related to the skutterudite structure. The observed resistivity, magnetoresistance, and magnetization are discussed in terms of our results.

I. INTRODUCTION

Reports in the past few years of very high values of magnetoresistance (MR) in manganite perovskites have stimulated a tremendous interest in those compounds \cite{1}, already well known from seminal works in the 1950s. These colossal magnetoresistance (CMR) materials are based on a closely related transition metal oxide perovskite structure. With the development of more and more complex materials by both conventional growth procedures, it was inevitable that the combination of \( \text{Cu} \) and \( \text{Mn} \) oxides would be explored.

From the basic point of view, attractiveness of these systems is due to the richness of their very complex phase diagrams, which in both cases may be viewed from the undoped antiferromagnetic (AFM) insulator (I) parent compound. In manganites, \textit{viz.} \( \text{La}_{1-x}\text{Ca}_x\text{MnO}_3 \), the phase diagram shows a strong relation between lattice, spin, charge and orbital degrees of freedom. From the \( \text{La} \)-rich end, the AFM-I phase gives way to a ferromagnetic (FM) metal, while from the Ca-rich side the system remains insulating down to \( x = 0.50 \) while displaying a variety of charge, spin, and orbitally ordered phases. In layered cuprates the AFM-I phase gives way to a metallic phase that becomes superconducting at remarkably high temperatures, over 100 K in several cases.

The high values of MR observed in the manganites may become important as components of magnetoelectronic devices. However, before widespread practical applications can be made some of their properties have to be improved. In particular, there are two limiting factors in their performance: one is that the highest values of MR can be reached only at relatively low temperatures and high magnetic fields (typically 250 K and several Tesla for \( \text{La}_{3/4}\text{Ca}_{1/4}\text{MnO}_3 \), the second is that the magnetoresistance is large only in a narrow interval around the Curie point.

Both from the point of view of the manganite-cuprate combination and for the possibility of improving device characteristics, the recent report by Zeng et al. \cite{2} constitutes an interesting new development. This group has shown that the hybrid cupromanganite \( \text{CaCu}_3\text{Mn}_4\text{O}_{12} \) (CCMO), which is an ordered perovskite with quadrupled primitive unit cell, presents a quite large MR in polycrystalline samples (up to several tens of percent) at low magnetic fields without the presence of either mixed valency or metal-insulator transition. Moreover, this colossal MR extends over a wide temperature range.

This compound contains two magnetic ions, formally given as \( \text{Mn}^{4+} (d^{5}, S = \frac{3}{2}) \) and \( \text{Cu}^{2+} (d^{9}, S = \frac{3}{2}) \), on two crystallographically distinct sites. Both its resistivity \( \rho(T) \) and magnetization \( M(T) \), measured on polycrystalline samples, show unconventional temperature dependencies. \( \rho(T) \) is semiconducting in behavior, but has no visible anomaly at the Curie temperature \( T_C = 355 \text{ K} \). \( M(T) \), on the other hand, shows a steep, nearly first-order-like jump at \( T_C \) to \( \sim 80\% \) of its saturation value. The temperature dependence of the activated resistivity (over a limited temperature range) suggests an energy gap of \( \sim 0.12 \text{ eV} \).

The basic electronic, and even magnetic, structures of this compound are not known. In this work we present the electronic features of this material, relating them to its transport and magnetic properties. In Sec. II we describe the distorted quadruple perovskite structure and outline our method of calculation. The results for the band structure, density of states, and magnetism are given in Sec. III. In Sec. IV we discuss the avenues for magnetic coupling in CCMO, and magnetotransport is discussed briefly in Sec. V. Our results are summarized in Sec. VI.
II. CRYSTAL STRUCTURE AND METHOD OF CALCULATION

A. Structure

The crystal structure, shown in Fig. 1 and discussed in detail by Chenavas et al. 25 years ago [3], is a strongly distorted ordered version of a perovskite with formula Ca$_{1/4}$Cu$_{3/4}$MnO$_3$. Formal valence ideas suggest a Cu$^{2+}$ ion, so the system is isovalent with CaMnO$_3$ and hence expected to be insulating, as observed. Here the Cu$^{2+}$, but not the Mn$^{4+}$, ion is expected to be a Jahn-Teller ion, leading to an oxygen sublattice that corresponds to a tilted three-dimensional network of MnO$_6$ octahedra. The Mn-O-Mn angle becomes $\approx 142^\circ$, instead of 180$^\circ$ as in the ideal perovskite structure. Two types of polyhedra are present at the A position: a slightly distorted Oicosahedron around the Ca site and a roughly square planar O-coordinated Cu site with a Cu-O distance of 1.94 Å. The quadrupled perovskite cell has space group Im$ar{3}$ (≡ I2/m3, No. 204 in the International Tables).

The quadrupling and distortion of the perovskite structure leads to low site symmetries. The cations nevertheless all sit on the usual ideal positions of the cubic perovskite lattice. The symmetry lowering arises, first, from the replacement of 75% of the Ca (in CaMnO$_3$) by Cu and second, by the rotation of the O octahedra which leaves O sites of the form (0, y, z) (y = 0.3033, z = 0.1822) and mirror site symmetry only. The Mn site at (1/4, 3/4, $\frac{1}{2}$)a has 3 symmetry, because each MnO$_6$ octahedron rotates to orient a triangular face perpendicular to a $<111>$ direction. The Cu site retains mmm symmetry, while the Ca site is in a m3 position. The lattice constant $a$ is approximately twice the related simple perovskite cell, and the Bravais lattice is bcc.

This structure is closed related to that of skutterudite CoSb$_3$ [4]. Both are members of a class that can be generally denoted as $\Lambda'$A$''_3$T$_4$D$_{12}$, where $\Lambda'$, A$''$ are cations, T is a metal (usually transition metal) ion, D is an anion, and the underlying structure is perovskite. The relation of CoSb$_3$ to the CaCu$_3$Mn$_4$O$_{12}$ structure is: Co→Mn; Sb→O; the Sb$_4$ square becomes the CuO$_4$ square; the Ca ion fills the La site in filled skutterudites (like LaCo$_4$Sb$_{12}$). The Cu site is not filled in the skutterudites.

It must be noted for the analysis that follows, that the CuO$_4$ “square” is in fact not actually a square although all Cu-O bondlengths are equal and all O sites are equivalent. Rather it is a rectangle whose O-Cu-O angles are 85.6$^\circ$ and 94.4$^\circ$. As a result the Cu d$_{xy}$, d$_{xz}$, and d$_{yz}$ orbitals are not related by symmetry. Nevertheless, we will use the term “CuO$_4$ square” and when we discuss it, we will have in mind a local coordinate system in which it lies in the $x-y$ plane.

FIG. 1. The crystal structure of the quadruple perovskite compound CaCu$_3$Mn$_4$O$_{12}$. Two primitive cells of the bcc structure are shown. Oxygen atoms lie at the vertices of the MnO$_6$ octahedra. Small black spheres denote Cu atoms, large gray spheres are Ca atoms.

Due to the low site symmetry arising from the distortion, the Mn d-orbitals cannot be exactly associated with the standard $t_{2g}$/e$_g$ symmetries. Instead, the 3 symmetry of Mn dictates that, in the local coordinate system where the threefold axis is the $z'$ axis, the irreducible representations of the five 3d states are $z'^2$, $\{x'y', y'z',\}$, and $\{x'y', x'^2 - y'^2\}$. We will call in this work the standard decomposition as “local frame” and the last, symmetry-determined, one the “symmetry adapted frame”.

B. Calculations

We have applied the linearized augmented plane wave method [5] (LAPW) that utilizes a fully general shape for density and potential. The WIEN97 code [6] has been used in the calculations. The experimental lattice constant of 7.241 Å = 2 × 3.62 Å was used. LAPW sphere radii (R) of 1.90 a.u. were chosen for the Cu and Mn atoms, 2.00 a.u. for Ca and 1.60 a.u. for O, with cutoffs of RK$_{\text{max}}$ up to 7.0, providing basis sets with more than 1800 functions per primitive cell. Self-consistency was carried out on k-points meshes of up to 60 points in the irreducible Brillouin zone (1000 points in the complete BZ). The generalized gradient approximation (GGA) exchange-correlation functional of Perdew et al. [7] was used in the present work, except where noted.

A previous study of the electronic structure of CCMO has been reported by Wu, Zheng, and Gong [8] using both LDA and the LDA+U (corrections due to strong on-site
repulsion) within a local combination of atomic orbitals scheme. They concluded that LDA gives a metallic behavior, in disagreement with the experimental situation, and that it was necessary to apply the LDA+U method to open a band gap. We will show here that the semiconducting behavior is well reproduced just considering GGA within density functional theory. Discrepancies between our results and those of Wu et al. are due to approximations made in their methods, and possibly to their choice of basis set (see [9]).

III. COMPUTATIONAL RESULTS

A. Band Structure

The important valence-conduction band region contains over 60 bands, hence the full band structure will not be presented. The majority and minority band structures bounding the gap are shown in Fig. 2, and the densities of states (DOS) in Fig. 3. The calculated gaps are 0.50 eV for spin up (majority) and of 0.18 eV for spin down (minority), and each is direct. For the minority carriers the gap occurs at H between pure Cu $d_{xy}$ states below the gap to pure Mn $t_{2g}$ character above. The thermal gap is quite small, 0.09 eV, and is both indirect and spin-asymmetric (i.e. bounded by the spin down valence band maximum at H and the spin up conduction band minimum at $\Gamma$). It is common for the band gap in density functional calculations to be smaller than the true gap, but the band character and shape on either side of the gap are nonetheless given reasonably. In this case the calculated gap is quite similar to the experimental estimate.

The bands at the valence band maximum (spin down) have a strong Cu $d$ character. They arise from the $dp\sigma$ antibonding interaction of the $d_{xy}$ (see below) with O $p\sigma$ orbitals in the CuO$_4$ square, and are the analog of the $d_{z^2}$ states in the layered cuprates. This bonding makes a band with a dispersion of almost 1.5 eV. The other Cu $d$ orbitals are concentrated in a small region between 1 and 2.5 eV below the gap. As expected for the Mn$^{3+}$ ($d^3$) ion the corresponding $t_{2g}$ and $e_g$ orbitals (in the local octahedron-adapted coordinates) are well separated, with the $t_{2g}$ majority orbitals filled.

The dispersion of the bands bounding the gap influences transport coefficients. As discussed above, the valence bands are derived primarily from a $dp\sigma$ antibonding combination of the Cu $d_{xy}$ and the four neighboring O $p\sigma$ orbitals, which we will denote $D_{xy}$. If the CuO$_4$ unit were actually a square, $D_{xy}$ would not couple with other Cu $d$ – O $p$ combinations. Since the unit is not exactly a square, the Cu $d_{xy}$ orbital will also mix with inplane O $p\pi$ orbitals via $dp\pi$ coupling, which may not be negligible.

From the depiction of the CuO$_4$ squares in Fig. 4, it can be seen that the $D_{xy}$ functions on neighboring squares are orthogonal by symmetry. As a result, the dispersion, which is 1.2 eV along H-$\Gamma$, cannot develop from direct $D_{xy}$ – $D_{xy}$ hopping.
FIG. 3. Bottom: Partial density of states (DOS) for the Mn atom, decomposed according to the symmetry adapted frame, which in the text is denoted with primes ($x'y'$, etc.). Top: A detail of the partial density of states around the gap, with Cu as solid line and Mn as dashed line. The majority DOS is plotted upward, the minority is plotted downward. The zero of energy lies within the gap.

The symmetry character of the Mn $d$ shell is important to identify, since it affects magnetic coupling. The natural presumption is that, since the MnO$_6$ octahedron is not strongly distorted, then with respect to the local coordinate frame in which the axes extend from Mn through the neighboring O ions (or nearly so), the configuration can be described as $t^3_{2g}$, the fully polarized $d^5$ configuration. While this picture is certainly roughly true, there is a related and precise aspect to the exact site symmetry of Mn. The Mn $d$ DOS, decomposed into the symmetry adapted frame (Sec. II.A) indicates that it is the $z^2$ state alone that is completely occupied in the majority bands, and very nearly completely unoccupied in the minority bands. The other two twofold irreducible representations are strongly mixed in both the majority occupied and unoccupied states. This full polarization of the $z^2$ orbital reflects the fact that it is directed along a $<111>$ axis and therefore is an equal combination of (only) the $t_{2g}$ orbitals in the local frame: $z^2 = (xy + yz + zx)/\sqrt{3}$. Thus the $t_{2g}$ orbitals are fully occupied as expected.

B. Magnetic Structure

The calculations were initiated with magnetic Cu and Mn ions, aligned in ferromagnetic fashion. Both Mn and Cu ions remain magnetic, but the Cu moments strongly favor being antiparallel to the Mn moments, resulting in a ferrimagnetic spin ordering. Both the Mn moments ($S = 3/2$, ideally 3 $\mu_B$) and the Cu moment ($S = 1/2$, ideally 1 $\mu_B$) are reduced by hybridization with the O $2p$ states, with the Mn moments being near 2.42 $\mu_B$ and -0.45 $\mu_B$, respectively. The net moment is 9 $\mu_B$ per formula unit, which is what would be obtained from the formal moments aligned ferromagnetically (4 Mn $\times$ 3$\mu_B$ - 3 Cu $\times$ 1$\mu_B$). The magnetic moment on the Cu ion is a result of the exchange splitting on the $D_{xy}$ orbital, which in this coordinate system is the orbital with lobes pointing to the nearest neighbor oxygens. The almost electronically isolated CuO square favors this configuration as was shown previously in other zero or one dimensional copper oxides [11-13]. Magnetism in the Mn ion comes as expected from the splitting of the $t_{2g}$ orbitals and filling only of the spin up states.

Experimental study of the magnetic arrangement in CaCu$_3$Mn$_2$O$_{12}$ has been reported. Neutron scattering has established that some samples are nonstoichiometric, with the (also Jahn-Teller active) Mn$^{4+}$ ion substituting partially on the Cu site. [12] It was suggested that in these samples the order may be ferromagnetic or canted. In a nearly stoichiometric sample, the total magnetization decreased and ferrimagnetic ordering was inferred.

To investigate how strong this ferrimagnetic configuration is, we have done fixed spin moment calculations that impose ferromagnetic alignment of the spins. Due to the Mn$^{4+}$ assignment the magnetic moment of the idealized Mn ion in this compound is 3 $\mu_B$, so we fixed the total moment to 15 $\mu_B$ to include aligned moments of the three Cu ions. Our results show that this state is almost 1 eV higher in energy that the ground state, with little change of the individual magnetic moments. Supposing a near neighbor spin Hamiltonian with a Cu-Mn coupling of the form

$$H^{Cu-Mn} = \sum_{<ij>} J^{Cu-Mn}_{ij} \mathbf{S}^{Cu}_i \cdot \mathbf{S}^{Mn}_j,$$

with the sum being over pairs, the three Cu ions per cell and eight Mn neighbors per Cu would lead to an AFM exchange coupling of $J^{Cu-Mn} = 20$ meV.

FIG. 4. A skeleton drawing of the CaCu$_3$Mn$_2$O$_{12}$ structure, emphasizing the CuO$_4$ squares. [11] Small light grey dots represent the Mn ions, while the squares represent the CuO$_4$ units with black O ion. The Cu ion lies at the center of the square and is not shown. The large light gray sphere denotes Ca. This figure is displaced by $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ from the regions shown in Fig. 1.

The magnetism of CaCu$_3$Mn$_2$O$_{12}$ presents several interesting questions. First of all, the exchange splitting of the Cu $d_{xy}$ state is $\Delta_{ex}^{Cu} \sim 1.2$ eV from the Cu $d_{xy}$ DOS (not shown). Given its moment of $m_{Cu}=0.45$ $\mu_B$, this gives a ratio $\Delta_{ex}^{Cu}/m_{Cu} = 2.7$ eV/$\mu_B$, a very large value considering this ratio (roughly the Stoner $I^{Cu}_{ex}$) is
usually less than unity in transition metal magnets. The exchange splitting of the other Cu d orbitals is smaller, of the order of 0.4 eV. This difference reflects a strongly anisotropic exchange potential on the Cu ion.

The exchange splitting on the Mn ion is harder to estimate, due to the strong dissimilarity of the majority and minority d DOS (Fig. 3a). This is a rather common occurrence in ferrimagnets, where the spin up bands cannot be regarded as an exchange shifted version of the spin down bands, even to zeroth order.

IV. MAGNETIC COUPLING

The magnetic coupling in CaCu$_3$Mn$_4$O$_{12}$ is potentially quite complex to unravel due to the two types of magnetic ions and the large cell with low symmetry sites. The bond angles involved in the various exchange processes in CaCu$_3$Mn$_4$O$_{12}$ are: O-Cu-O, 85.6° and 94.4°; O-Mn-O, 90.0°; Mn-O-Mn, 142°; Cu-O-Mn, 108.7°. Nearest neighbor bond distances are $d$(Mn-O) = 1.915 Å, $d$(Cu-O) = 1.942 Å, $d$(Cu-O) = 2.56 Å. Note that in the undistorted structure with twofold coordinated Cu, $d$(Cu-O) would be $\sqrt{2}a/4 = 2.56$ Å; i.e. the rotation of the MnO$_6$ octahedra decreases the Cu-O distance by 0.62 Å.

Lacroix [14] has discussed the couplings in the isostructural compound CaCu$_3$Ti$_4$O$_{12}$, where Ti is $\delta^0$ and there are only Cu-Cu interactions to consider. The observed magnetic order is antiferromagnetic, [14] but with a three sublattice, non-collinear structure in which three Cu spins in a (111) plane have projections on that plane that lie at 120° angles to each other. The three Cu spins in the next (111) layer are antiparallel to the first three. Lacroix argues that, because the exchange coupling path is through the TiO$_6$ octahedron, first, second, and third neighbor Cu-Cu coupling $J^C$ may be comparable in magnitude. This should be true if direct O-O hopping within a MnO$_6$ octahedron or within a CuO$_4$ square is neglected. Non-collinearity of the spins was attributed to spin-orbit coupling. In CaCu$_3$Mn$_4$O$_{12}$ the Cu-Cu geometry is the same, so all three couplings should again be considered. However, the MnO$_6$ octahedron will provide different coupling than would the TiO$_6$ tetrahedron.

In addition, Mn-Mn coupling is essential as well as the Mn-Cu coupling discussed in the previous section. Since Mn spins lie on a simple cubic lattice connected by a single O$^2-$ ion, the Goodenough-Kanamori-Anderson (GKA) rules can be applied to understand $J^{Mn-Mn}$. Further Mn-Mn couplings should be small and not affect qualitative behavior. Whereas 180° Mn$^{4+}$-O-Mn$^{4+}$ coupling is antiferromagnetic (viz. CaMnO$_3$), when this angle is reduced to 142° a ferromagnetic sign is expected. Parallel alignment of the Mn spins is observed, and is the only situation we have considered in our calculations.

Finally, there is the question of Mn-Cu coupling. In this structure all oxygen ions are equivalent and are coordinated with two Mn ions and one Cu ion. We assume that only a single Mn-Cu coupling is important; this interaction connects a Cu spin to eight Mn neighbors and each Mn spin to six neighboring Cu spins. The ferromagnetic/ferrimagnetic difference in energy in the last section identified $J^{Mn-Cu} = 20$ meV (antiferromagnetic).

V. DISCUSSION

The picture we obtain leads to a ferrimagnetic semiconductor with a calculated indirect gap of 90 meV. Electron carriers and hole carriers will have oppositely directed spins (up and down, respectively, with respect to the net macroscopic magnetization $\vec{M}$). Here we consider the experimental data of Zeng et al. in the light of our predicted electronic and magnetic structure.

Resistivity and MR. Zeng et al. interpreted their data in the neighborhood of $T_C$ in terms of a gap of around 120 meV. However, one should note that their measured resistivity does not behave in activated fashion over any extended temperature range; rather, in the range 25 – 300 K the resistivity of their sample can be described by the form

$$\rho(T) = \rho_0 e^{-T/T_0}; \quad \rho_0 = 10^5 \Omega cm, \quad T_0 = 180K. \quad (2)$$

Below 25 K $\rho$ deviates only slightly (upward) from this form. Since this data is from polycrystalline samples, $\rho(T)$ may be affected strongly by extrinsic factors, and the data would give only an upper bound on the intrinsic resistivity. Moreover, the variation of M(T) implies variation in carrier density with temperature due to the dependence of the gap on the ordered moment, complicating the interpretation of $\rho(T)$.

In a stoichiometric single magnetic domain sample of CaCu$_3$Mn$_4$O$_{12}$ in zero field, the equal number of thermally excited electron and hole carriers fixes the position of the chemical potential within the gap. In this compound, each type of carrier is fully polarized (electrons, up; holes, down) and there will be no spin scattering due to the absence of available spin-flipped states for each type of carrier. An applied field produces a relative shift of the up and down bands by $g\mu_B B$, where $g$ is the average of the electron and hole $g$ factors. If $\vec{B}$ is applied parallel to $\vec{M}$, the gap is narrowed; however, due to the requirement of equal number of electrons and holes there will be no induced magnetization (and therefore no spin susceptibility as long as $k_B T$ is much smaller than the gap). The field-induced change in the carrier density $n$ follows the form

$$n(B, T) = n(B = 0, T) e^{\frac{g\mu_B B}{k_BT}}. \quad (3)$$

Even if the measured $\rho(T)$ is not intrinsic, as long as it is proportional to the number of excited carriers, at low $T$
part the field-induced change in carrier density will contribute to the negative MR. If $g \sim 2$, the enhancement in the carrier density for $B = 6$ T (the highest field measured) is 35% for $T = 25$ K and 2.6% for $T = 300$ K. The (negative) MR at 5 T was reported to be 35% and 6-7% respectively. Since at $B = 5$ T the magnetization will surely be aligned with the field, the predicted decrease in gap and increase in carrier density with field can account for much of the observed MR. The temperature dependence of $\rho$ remains to be understood.

$M(T)$. Zeng et al. reported a normal hysteresis loop characteristic of a soft magnet, but the magnetization $M(T)$ shows an almost first-order-like jump to $\sim 75\%$ of the saturation magnetization just below $T_C$, and no observable structure in $\rho(T)$ at $T_C$. This behavior of $M(T)$ and $\rho(T)$ is likely to be strongly affected by the granularity of the sample.

VI. SUMMARY

Accurate band structure calculations predict that CaCu$_3$Mn$_4$O$_{12}$ is a very small indirect gap ferrimagnet, with Cu spins antialigned with the Mn spins and a net moment of $9 \mu_B$ per formula unit. The gap lies between majority spin conduction states and minority spin valence bands. As a result, application of a magnetic field parallel to the magnetization decreases the gap, and this effect will contribute to the low temperature magnetoresistance. This unusual spin arrangement around the gap makes it attractive for possible applications in spin electronics devices.

The basic electronic structure conforms to expectations based on the formal valence: the Cu$^{2+}$ ion is polarized due the $dp\sigma$ antibonding interaction with the surrounding four oxygen ions, and the Mn$^{4+}$ ion has fully occupied and fully polarized $t_{2g}$ orbitals, and no Jahn-Teller instability. The fourfold coordinated Cu ion distorts the perovskite structure, but in a way that constrains the normal floppy nature of the perovskite crystal structure.

An antiferromagnetic coupling $J^{Cu-Mn} \approx 20$ meV between the Cu and Mn spins is obtained from a fixed-spin-moment calculation. The ferromagnetic coupling between neighboring Mn ions can be rationalized by the strong departure of the Mn-O-Mn angle from $180^\circ$ (it is $142^\circ$) but a quantitative understanding of the magnetic coupling is still lacking.

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