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Spin-density-functional-based search for half-metallic antiferromagnets

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We present results based on local-spin-density calculations of a computational search for half-metallic (HM) antiferromagnetic (AFM) materials within the class of double-perovskite-structure oxides La$M'M''$O$_3$ that incorporate open-shell 3d (or 4d) transition-metal ions M',M''. The pairs $M'M''$=MnCo, CrFe, CrRu, CrNi, MnV, and VCu are studied. Three HM AFM results are found for the (fixed) cubic double perovskite structure. This work provides the first viable candidates for this unusual magnetic phase. La$_2$VMnO$_6$ is the most promising candidate, with the HM AFM phase more stable by 0.17 eV/cell than the ferromagnetic phase. La$_2$VCuO$_6$ is another promising possibility but, because V^{4+} and Cu^{2+} are spin-half ions, quantum fluctuations may play an important role in determining the ground state magnetic and electronic structure. This study indicates that HM AFM materials should not be prohibitively difficult to find. [S0163-1829(98)07517-1]

I. INTRODUCTION

A nonmagnetic metal whose electrical conduction is 100% spin polarized seems like an oxymoron. However, this is only one of the peculiar properties[1–3] of the unusual phase yclept half-metallic (HM) antiferromagnet (AFM) by van Leuken and de Groot.[2] A HM AFM is also a metal with zero spin susceptibility, a property normally associated with insulators, whereas conventional metals have $\chi \propto N(E_F)$, the Fermi level density of states. Due to mixing of atomic orbitals with neighboring nonmagnetic ions such as oxygen, magnetic ions commonly take on nonintegral values of the magnetic moment. Yet in a HM AFM distinct ions have antialigned moments that cancel exactly.[2] The prospect of getting a fully magnetized current from a metal that has no magnetic field provides not only fertile ground for research but conceivable new ''spin electronics'' devices that rely on the spin polarization of the carriers. Recently the likelihood of a novel form of superconductivity in HM AFM's has been proposed,[1] which further intensifies theoretical interest in these unique systems. To date, there is no confirmed example of a HM AFM. Is there a real likelihood of discovering, or even predicting, new HM AFM's, or are they destined to remain a theoretical curiosity?

Characterization of a material as ''half-metallic'' specifies that one spin channel is metallic while the other channel is insulating.[3] For a stoichiometric compound this results in a spin magnetization that is an integer number[1] $\mathcal{M}$ of Bohr magnetons (μ_B) per cell. The present objective is to predict compounds where $\mathcal{M}\equiv 0$, and therefore will have the special properties mentioned above. For an initial study one should consider only the simplest case of two magnetic ions whose spins (S) are antiparallel. In this case the moments will be distinct in shape and extent (different spin densities) but will cancel precisely in each cell due to the half-metallic nature of the system.

The only suggestion at present for a HM AFM material is the Heusler-like quintinary ordered alloy V$_7$MnFe$_8$Sb$_7$As.[2] Due to the complexity and intricacy of the unit cell, and to the intermetallic nature of the constituents, it is unlikely to be made in stoichiometric form. The perovskite crystal structure AMO$_3$, due to its simple crystal structure, potentially very large number of members, and strong coupling between magnetic ordering and electronic properties, appears to be an ideal system for a search for HM AFM members. We report here results of a computational search for candidate HM AFM's, based on a linearized augmented plane wave implementation of spin-density-functional theory,[4] in the double-perovskite crystal structure La$_2M'M''$O$_6$. More than 300 compounds in this structure, shown in Fig. 1, have been reported;[5] however, very few of those reported contain two magnetic ions. A=La was chosen for this study because of experience with this cation[4] and also due to the fact that LaMO$_3$ compounds in the perovskite structure are known to exist for all ions M in the 3d series.

II. BASIC CONSIDERATIONS OF THE SEARCH

Magnetic 3d ions are characterized by a nominal d^n configuration where $1 \leqslant n \leqslant 9$. Since each such configuration can

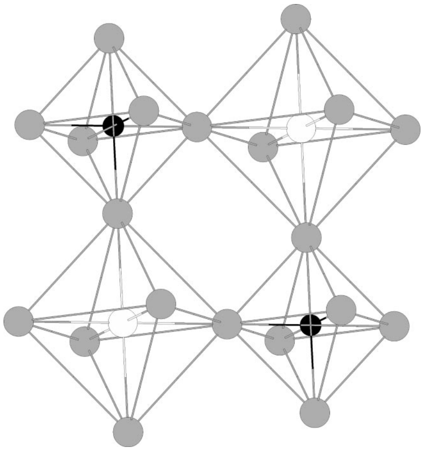

FIG. 1. The double-perovskite crystal structure. The black and white spheres are transition metal (M', M'') ions, the gray oxygen ions form an octahedron around each metal ion, and the cation (viz., La, but not shown) lies between eight MO$_6$ octahedra. The figure illustrates that the octahedra around different M ions are allowed by symmetry to be different sizes.

be realized by more than one ion (in different charge states), and there are several uni-, di-, and trivalent cations A to choose from, there are thousands of magnetic double-perovskite compounds that might be considered. Although attributes of a material that make it a better candidate comprise a substantial list,[1] there is one overriding requirement: the moments must be *equal* in magnitude so that they may cancel to give $\mathcal{M}=0$. This requirement of equal spins narrows the number of choices considerably.

A. Combinatorics of $A'A''M'M''O_6$

To illustrate the combinatorics in the class of compounds $A_2M'M''O_6$, we consider the number of double-perovskite-structure compounds that might be relevant for our search. There are nine possible open d^n configurations, giving $(9\times8)/2$ distinct pairs of $3d$ ions. However, $4d$ ions are also likely to be magnetic in these compounds, and including them the number of possibilities becomes $(18\times17)/2$ pairs. Since an ion can be in a few different charge states, each $3d^n$ or $4d^n$ configuration can be attained by more than one ion; we take as an average two charge states per ion, giving another factor of 2^2. The cation A can be chosen from di- and tripositive cations (including the rare earths) and even some univalent ions, amounting to some 25 ions. The number of compounds then is of the order of

$$25\times2^2\times\frac{18\times17}{2}\approx15\,000. \tag{1}$$

Considering also the possibility of splitting the cations $A\rightarrow A'A''$ leads to an addition factor of $\frac{24}{2}$ or a total of the order of 2×10^5 possibilities.

This vast number reduces drastically if one considers the requirements imposed by the HM AFM state. Most crucially, the magnetic moments of the ions must be equal in magnitude; so they have the possibility of canceling. To do this, one separates the ions into the five classes $S=\frac{1}{2},1,\frac{3}{2},2,\frac{5}{2}$, and only pairs with equal spins need be considered. Supposing the ions separate evenly into these classes (not really the case) with about four per class, the factor $(18\times17)/2$ in Eq. (1) drops to $5\times(4\times2/3)$. The cation charge further restricts the pairs of ions. Let us consider only the case $A=\mathrm{La}^{3+}$, which is all we consider in this paper anyway [removing the factor of 25 in Eq. (1)]. Specification of this trivalent cation implies that the charge states of the two d cations must sum to 6, effectively limiting the choice to (3+,3+) or (2+,4+) pairs [(1+,5+) is much more rare]. Due to complexities in trying to predict the spins of each ion (which may be environment dependent; see below), we will not attempt to enumerate the possibilities, but the number of possible La-based double perovskites is perhaps no more than 25.

B. Estimation of stable moments

To use the constraint of equal moments it is necessary to be able to make a realistic prediction of the spin moment of a given ion in the crystal. For a magnetic ion with an open $3d$ shell, the moment m (in μ_B) is

$$m=\sum_{\alpha,s} s n_{\alpha,s}=n_+-n_-, \tag{2}$$

where $s=\pm1$ denotes the spin direction, $n_{\alpha,s}$ is the occupation number of the $3d$ crystal field level $\alpha=e_g$ or t_{2g}, with spin s, and n_s is the total s occupation. The energy of an ion in the perovskite octahedral field is

$$E_{\mathrm{ion}}=\sum_s\left[n_{e_g,s}\left(\frac{3}{5}\Delta_{\mathrm{CF}}-\frac{s}{2}I_{\mathrm{St}}m\right)\right. \tag{3}$$

$$\left.+n_{t_{2g},s}\left(-\frac{2}{5}\Delta_{\mathrm{CF}}-\frac{s}{2}I_{\mathrm{St}}m\right)\right], \tag{4}$$

where Δ_{CF} is the crystal field splitting between the e_g and t_{2g} levels, I_{St} is a Stoner-like parameter giving the exchange (magnetic) energy $\pm\frac{1}{2}\Delta_{\mathrm{ex}}$,

$$\Delta_{\mathrm{ex}}=I_{\mathrm{St}}m, \tag{5}$$

proportional to the moment m on the ion, and $n=n_++n_-$. This energy can be expressed as

$$E_{\mathrm{ion}}=\Delta_{\mathrm{CF}}\sum_s n_s\overline{\nu_s}-\frac{1}{2}I_{\mathrm{St}}m^2, \tag{6}$$

$$\overline{\nu_s}\equiv\sum_\alpha n_{\alpha,s}\nu_\alpha\Bigg/\sum_\alpha n_{\alpha,s}. \tag{7}$$

Here ν is $\frac{3}{5},-\frac{2}{5}$ for e_g,t_{2g}, respectively, and this formula for the energy illustrates the balance between the crystal field energy and magnetic energy that must be minimized to obtain the stable configuration of the ion.

The ratio $\gamma=I_{\mathrm{St}}/\Delta_{\mathrm{CF}}$ determines whether the ion takes on a high-spin or low-spin configuration. $S=\frac{5}{2}$ is attained only by a d^5 ion (viz., Mn^{2+}, Fe^{3+}, or Co^{4+}). $S=2$ occurs only for d^4 and d^6 ions, and $S=\frac{3}{2}$ only for d^3 and d^7 ions. $S=1$ is attained not only by d^2 and d^8 high-spin ions, but also by the low-spin d^4 ion $(t_{2g,+}^3t_{2g,-}^1)$ if γ is small. $S=\frac{1}{2}$ occurs for low-spin d^5 and d^7 ions as well as for the single-electron d^1 and single-hole d^9 ions.

These guidelines hold in the strong crystal field limit. Within a crystal there are additional effects. The kinetic energy, which results from electron hopping from ion to ion (via the intervening oxygen ion in the perovskite structure), drives the moment away from integer values and has very substantial effects in perovskite materials. One may also have to consider structural distortions that lower symmetry and alter hopping amplitudes. There is in addition the possibility of ions changing their charge state (determined by differences in site energies and by intra-atomic repulsion). However, these single-ion energies, with I_{St} and Δ_{CF} given from density-functional calculations or from experiment, have been used to guide our initial choice of ion pairs that we have examined more closely using self-consistent calculations.

Figure 2 indicates the behavior of the ion energy in the strong crystal field limit for two values of γ, for each integer occupation n as the moment m varies over allowed values ($m\leqslant n$ for $n\leqslant5$, $m\leqslant10-n$ for $5\leqslant n\leqslant10$). All occupations $n_{\alpha,s}$ were varied within the limits of their constraints until the energy was minimized for fixed n and m (for the isolated ion, and neglecting spin-orbit coupling, $m=2S$). The energy reflects the downward parabolic energy gain from polarization, together with a linear increase in energy when one crys-

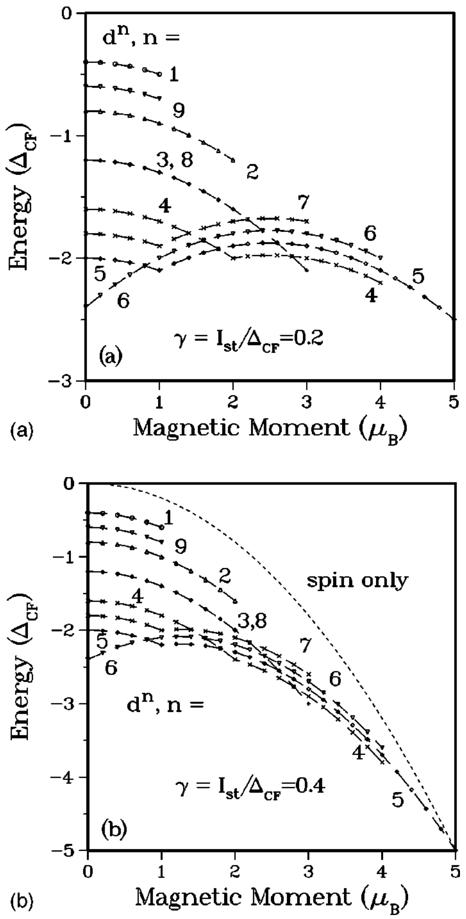

FIG. 2. Energy of a magnetic ion in a crystal field Δ_{CF}, vs magnetic moment, for various ionic configurations d^n. (a) γ=0.1 and (b) γ=0.2. The ''spin-only'' dotted curve indicates the asymptote as the crystal field term vanishes. Each curve is the sum of a piecewise linear increasing crystal field term and a negative quadratic magnetic term.

tal field level is filled and a higher one begins to become occupied. There is a strong tendency toward the ''high-spin'' (largest possible m, Hund's rule) configuration; however, for large Δ_{CF} relative to I_{St} a low-spin configuration can become stabilized: note the $n=6$ curves in both plots, where a nonmagnetic $m=0$ result is stable or metastable. Low-spin configurations may also occur for $n=4$, 5, or 7, as noted above. The curves of Fig. 2 are only guidelines; fully self-consistent local-spin-density calculations reported below vary both n and m for a given spin alignment until the energy is minimized. For the perovskite structure, values of Δ_{CF} are 2–3 eV.

III. METHOD OF CALCULATION

The present calculations were performed using the general potential linearized augmented plane wave (LAPW) method[6–8] as applied in several previous studies of LaMO$_3$ perovskites.[9,10] Calculations were performed for the ten-atom double-perovskite unit cell using a good convergence criteria (below). Our LAPW method uses no shape approximation for the charge density or the potential, and retains high variational freedom in all regions of the cell. The set of normal LAPW basis functions is supplemented with local orbitals for additional flexibility[7] in treating the Mn d states, the La f states (unoccupied), and the semicore orbitals (O 2s, La 5s and 5p, and 2p states of some of the lighter 3d transition-metal ions). The LAPW sphere radii were taken to be 2.0 a.u. for La, 1.90 a.u. for the transition-metal ions, and 1.55 a.u. for O. Self-consistency was carried out on evenly spaced meshes of 60 k points in the irreducible Brillouin zone for the ferromagnetic state done with the basic perovskite structure. Larger meshes used in selected cases verified that the energy was not changed appreciably. Equivalent samplings were used for the antiferromagnetic state calculations, which were done using a rocksalt ordering of transition-metal ions (hence an fcc Bravais lattice). An LAPW cutoff K_{max} corresponding to $R_O K_{max}=6.8$ was used (R_O is the oxygen sphere radius) corresponding to 575 basis functions for the five-atom cell.

The von Barth–Hedin exchange-correlation[11] functional was used. Energies might be improved somewhat by using the generalized gradient corrections perfected by Perdew and coworkers,[12] as was the case for iron.[13,14] However, nearly all of the energy differences reported in Sec. IV are larger than expected changes due to gradient corrections.

Except for one selected test (a Jahn-Teller type of distortion involving movement of O ions along the crystal axes; see Sec. V), we have performed calculations only in the ideal cubic-perovskite structure with a lattice constant of 3.89 Å. Structural distortions of both the rotational type common in ferroelectrics and of the Jahn-Teller type centered on nonsymmetric magnetic ions may become important for some of the compounds studied here. We have not included complex distortions in this initial study, for three reasons. First, this set of calculations was done with the objective of learning whether any (at least metastable) HM AFM states can be found. Structural distortions may change things, but they may just as well change a ''near miss'' into a HM AFM as they are to change a HM AFM into a ''near miss.'' Second, a really thorough investigation of relaxation should include at least the structure of LaMnO$_3$, an orthorhombic $Pnma$ structure with six variable internal coordinates and the three lattice constants, as well as a quadrupled cell. This is a task that probably will never be done directly, but can (with substantial computational work) be done with the approach of Rabe and co-workers.[15,16] Finally, for the (half-)metallic phases being pursued here, distortions are likely to be less drastic than if the systems were simply magnetic insulators.

IV. RESULTS FOR THE CHOSEN COMPOUNDS

The double-perovskite compounds that have been studied are listed in Table I. We discuss them in turn. Note that, while we denote global spin directions by up (+) and down (−), the terms ''majority'' and ''minority'' refer to each specific ion (more occupied or less occupied) and do not specify a direction of the spin. Also, due to strong hybridization with the oxygen 2p states, it is not possible even to define an ionic moment precisely. Values given in Table I and below provide the nominal charge and an estimate of the effective ionic moment, which often is not very near any integral value.

TABLE I. Local-spin-density-functional results for magnetic double perovskites $La_2M'M''O_6$. Approximate calculated d occupations n are given as d^n. Approximate spin-only moments $m(M')$, $m(M'')$ (in μ_B) are not always near an integer value, due to strong hybridization with oxygen. Half-metallic character is denoted by an integer value of $\mathcal{M}_{\text{tot}}$, and HM AFM's are denoted by AFM†. Relative energies are per transition-metal ion, with the first quoted magnetic alignment taken as the reference. FiM ≡ ferrimagnetic.

M'	M''	Order	$m(M')$	$m(M'')$	$\mathcal{M}_{\text{tot}}$	E_{rel} (eV/M ion)
$Mn^{3+}d^4$	$Co^{3+}d^6$	AFM†	2.8	−2.8	0	0.00
		FM	3.3	1.3	4.60	−0.46
$Cr^{3+}d^3$	$Fe^{3+}d^5$	FiM1	2.6	−0.6	2	0.00
		FiM2	2.0	−4.0	−2	−0.12
		FM	3.0	4.0	7.15	−0.03
$Cr^{3+}d^3$	$Ru^{3+}d^5$	FiM	2.5	−0.5	2	0.00
		PM	0	0	0	+0.67
$Cr^{3+}d^3$	$Ni^{3+}d^8$	FiM	2.0	−1.4	0.60	0.00
		FM	2.4	1.6	4	−0.15
$Mn^{3+}d^4$	$V^{3+}d^2$	AFM†	1.6	−1.6	0	0.0
		FM	1.9	1.1	3.00	+0.17
$V^{4+}d^1$	$Cu^{2+}d^9$	AFM†	0.7	−0.7	0	0.00(!)
		FM	0.7	0.7	1.38	0.00(!)
		PM	0	0	0	+0.06

A. Mn^{3+},Co^{3+}: d^4,d^6

These ions were chosen as a likely $S=2$ pair. In the ionic picture, the Mn^{3+} ion is expected to be high spin ($4\mu_B$), while Co^{3+} may be high spin ($4\mu_B$) or nonmagnetic; see Fig. 2. In fact, nominally trivalent Co ions are known sometimes to occur in a low- but nonzero-spin [$(1\text{–}2)\mu_B$] state as well. When the Mn and Co moments are antialigned, indeed a HM AFM state is obtained, although the moments are only $\approx 2.8\mu_B$. The densities of states (DOS), shown in Fig. 3(a), indicate that the ionic picture is followed closely ($\Delta_{\text{CF}}=1.5\text{–}2$ eV, $\Delta_{\text{ex}}\approx 2$ eV). The conducting channel has 75% Co d, 25% Mn d character at the Fermi level. When the spins are aligned, a high-spin Fe and low-spin Co result was obtained, reflecting the strong difference in hybridization that arises due to the type of magnetic alignment. The spin-aligned phase is 0.46 eV per M ion lower in energy than the HM AFM phase, and so the sought-after HM AFM phase is at best metastable.

B. Cr^{3+},Fe^{3+}: d^3,d^5

This pair was chosen in the anticipation that differing charge states [Cr^{2+},Fe^{4+}:d^4,d^4] might result, leading to either an $S=2$ pair or an $S=1$ pair. However, charge differentiation did not occur. Two distinct solutions for antialigned moments have been obtained; one has high-spin Fe ($4\mu_B$) parallel to the net moment, and the other has low-spin Fe (‘‘$1\mu_B$’’) antialigned with the net moment. Both are HM; however, they are ferrimagnetic (FiM) rather than AFM. A FM, high-spin solution also was found. Of these three spin configurations, the high-Fe-spin FiM state is lowest in energy. All three states can be characterized as Cr^{3+},Fe^{3+} (d^3,d^5) whose moments will not cancel. Thus current evidence is that this system is not a prospect for HM AFM. However, a HM FiM state is likely, and is itself worthy of study.

C. Cr^{3+},Ru^{3+}: d^3,d^5

The $4d$ Ru ion is isoelectronic with Fe, and so this pair provides another possibility for a $S=2$ or $S=1$ pair with unequal charges (Cr^{2+},Ru^{4+}). The unexpected behavior in Ru-based perovskite compounds [ferromagnetism (FM) in $SrRuO_3$ (Refs. 17 and 18), superconductivity at 1 K in Sr_2RuO_4 (Ref. 19)] also prompted us to check the pair Cr-Ru. However, like Cr-Fe, the Cr-Ru pair are predicted to be isovalent, and Ru is found to be magnetic with a low spin. With antialigned moments, the compound is a HM FiM with a net moment of $2\mu_B$. Using fixed spin moment methods it is possible to force the net moment to vanish slowly during continued self-consistency. Sometimes this results in the discovery of another phase, usually one that is metastable. In this case, however, forcing the net moment to vanish resulted in the destruction of the moment on both ions, at the energy cost of 0.67 eV/ion, rather than resulting in a (possibly HM) AFM state. As in all of these compounds, this pair may have magnetic states that we have not located in these calculations.

D. Cr^{3+},Ni^{3+}: d^3,d^7

This pair was chosen as a likely $S=\frac{3}{2}$ case. For a small crystal field, the d^7 ion may be high spin ($3\mu_B$), thereby balancing the d^3 moment. For these pairs the antialigned configuration resulted in a FiM net moment of $0.60\mu_B$, near but not at the HM AFM result. The FM alignment is lower in energy by 0.15 eV per ion. This is a case where relaxation of the structure (volume and/or distortion) might result in a HM AFM phase.

E. Mn^{3+},V^{3+}: d^4,d^2

This choice, if Mn^{3+} assumes low spin, is a possibility for an $S=1$ pair. A low spin indeed resulted, for both antialigned and aligned moments. The DOS are shown in Fig.

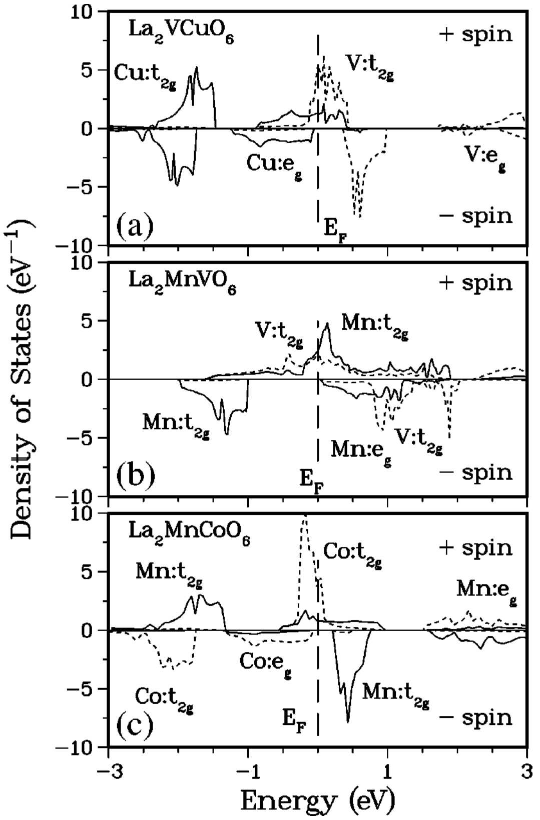

FIG. 3. Atom-projected densities of states for the three HM AFM states found in the double perovskites: (a) Mn-Co, (b) Mn-V, and (c) V-Cu. Note that in (a) and (c) the t_{2g} and e_g states are distinguishable for each ion and each spin, whereas this is not the case for the strongly mixed metallic channel in (b).

3(b); we discuss the unusual structure of the metallic channel below. The antialigned ordering results in a HM AFM state; moreover, this state is 0.17 eV/ion lower in energy than the FM alignment. Thus this pair provides a strong candidate for the HM AFM that this search hoped to locate. This compound is discussed further in the next section.

F. V^{4+},Cu^{2+}: d^2,d^8

This was the choice for an $S=\frac{1}{2}$ pair. This pair is unique in our studies to date, in that differing charge states actually are obtained. The differing ionic radii as well as the differing charge states of this pair of ions should give a strong preference for well-ordered structures. Both aligned and antialigned moment solutions were obtained, with *identical* energies. Moreover, the antialigned phase is a HM AFM, whose DOS is compared in Fig. 3(c) with the other HM AFM states. Due to the identical energies of the different alignments and their small spins, this system appears to be a strong candidate for a three-dimensional quantum magnetic system as $T \rightarrow 0$ (viz., quantum spin liquids, heavy fermion metals, Kondo insulators), rather than a simple HM AFM or an exotic superconductor.

G. Synopsis

Of these six pairs of transition-metal ions giving the double-perovskite structure, three have led to at least an electronically metastable HM AFM phase (lattice stability is a further, complex problem). This amount of success is remarkable considering there was previously no viable candidate. One of these is clearly only metastable (the Mn-Co pair) while Mn-V and V-Cu in the La$M'M''$O$_3$ compound are not unstable towards ferromagnetic alignment of the moments.

The calculated DOS of these three HM AFM states, shown in Fig. 3, reveal that qualitatively different type of gaps can occur in the insulating channel. Correlated insulating oxide compounds are identified as Mott insulators, if the gap lies between d states on the metal ion or as charge-transfer insulators if the gap lies between occupied O p states and metal ion d states.[20] Without experimental input we cannot judge the strength of correlation effects in these compounds. However, adapting this terminology to the present materials, the Mn-V compound [Fig. 3(b)], with a gap between Mn t_{2g} and e_g states, is the analog of a Mott insulator. The Mn-Co and V-Cu compounds, on the other hand, are inter-transition-metal charge-transfer insulators, with the gap lying between occupied d states on one metal ion and unoccupied d states on the other metal ion.

V. DISCUSSION

Although the local-spin-density-functional calculations used here generally give good charge densities and in a majority of systems (including many perovskites[4]) predict magnetic properties as well, several questions remain. Whether the proposed compounds can be made can be answered only by experiment (competing phases are too numerous to calculate). Magnetic moments, type of spin ordering, and ionic charges can be sensitive to volume and calculations reported here were carried out only at the representative cubic-perovskite lattice constant of 3.89 Å. However, variations of the volume for the Mn-V and V-Cu compounds confirmed that this volume is realistic (near the minimum of energy) and that the HM AFM phases persisted at nearby volumes. Relaxation of the positions of the O ions as allowed by symmetry (see Fig. 1) was carried out for the Mn-V compound. The oxygen octahedron relaxed inward around the smaller Mn ion[21] by only 0.02 Å, and the frequency of O vibration about this minimum (an observable Raman-active A_g eigenmode) is calculated to be 465 cm^{-1}. This relaxation actually stabilizes the HM AFM state; conversely, displacing the oxygen octahedron toward the V ion (by 0.08 Å) drives the compound from the HM AFM phase to a FiM phase.

Possible correlation effects deserve more comment. A limitation of local-spin-density-functional calculations used here is the inability to predict whether transition-metal compounds such as these are correlated electron systems. In the La$_2$VCuO$_6$ compound, for example, the bandwidth of the conduction band of the HM AFM state is only 1 eV wide, and strong on-site repulsion (‘‘Hubbard U’’) of electrons will tend to drive the metallic channel insulating. If this occurs, it may provide an example of yet another new phenomenon in these systems: a case in which one spin channel is a Mott insulator while the other is better described as a band insulator or possibly a generalized charge-transfer insulator. An extension of the local-spin-density approximation (LSDA), referred to as the LSDA+ U method,[22] often provides an improved mean-field description of correlated insulators. However, at present it is inapplicable to metals, and so its use is restricted to materials that are known to be insulators.

In La_2MnVO_6, on the other hand, the bandwidth of the metallic channel is more than 3 eV wide, and correlation effects should be much less important. The distinctions in Fig. 3(b) are easy to understand. The Mn majority t_{2g} states lie lower than any V states, and also hybridize less weakly with O $2p$ states than do e_g states. Hopping within this band therefore must go Mn-O-O-Mn; hence the band is quite narrow (1 eV). The minority Mn t_{2g} states lie in the same range as the majority V t_{2g} states; however, since the ionic moments are antiparallel, these states have the same spin direction [$+$ in Fig. 3(b)] and can form a mutual, relatively broad, band based on Mn-O-V-O-Mn-... hopping. Occupation of this comparitively broad band results in cancellation of part of the Mn moment, which by Eq. (3) results (self-consistently) in reduced exchange splitting and leads to the low-spin Mn ion. Hence it is reasonable to expect the conducting character of this band to survive correlation corrections.

An example of a spin density for a HM AFM phase is shown in Fig. 4 for the V-Cu compound. The spin-density isosurfaces illustrate very graphically the difference between the up- and down-spin densities. In fact, unlike conventional perovskite antiferromagnets where the oxygen is polarized only in a dipole form with no net moment, here the O ion has a net moment that lies in the same direction as the Cu spin. This unusual form of spin density for an AFM should be more readily apparent in the magnetic form factor measured in polarized neutron scattering experiments than in the typical case in which there is no net moment on the O ion. The O moment in this case is only of the order of $0.01\mu_B$, however.

This computational search indicates that the double-perovskite class of compounds provides a fertile environment for half-metallic antiferromagnets, a new type of magnetic material for which there were previously no viable possibilities. Although this search was confined to the La cation (which may be considered representative of trivalent cations), mixed-cation compounds such as $A^{2+}B^{3+}M'M''O_6$ show strong tendencies to form ordered structures[5] and may also provide good candidates. This work should not be interpreted as suggesting that perovskites provide the most likely possibility; certainly other crystal structures deserve strong consideration. The point here is that it should not be a formidable problem to fabricate HM AFM compounds, and so the study of their myriad unusual properties may commence.

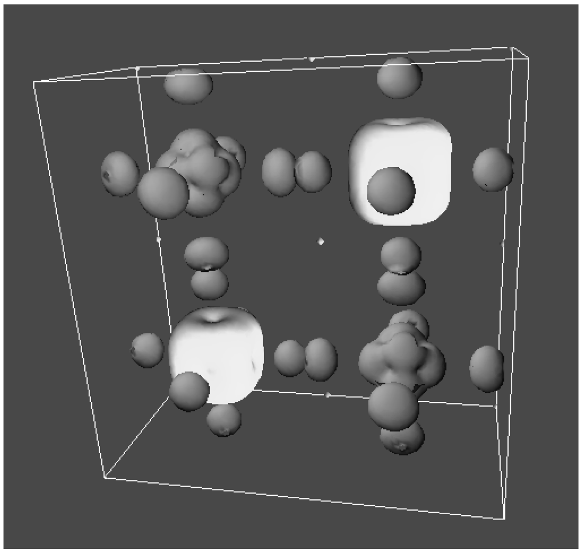

FIG. 4. Isosurfaces (at ±0.003 a.u.) of the spin density in the HM AFM state of La_2VCuO_6, illustrating the very different spin densities on the two magnetic ions. Two double-perovskite cells are shown; the complete structure is cubic. Upper: the largest (light shaded) surface surrounds the V ion. The O ions, which appear as dumbbells (truncated by the cell edges in some cases), are polarized in the same direction as the smaller (dark) Cu ion.

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