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Electronic structure of the pyrochlore metals $Cd_2Os_2O_7$ and $Cd_2Re_2O_7$

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First-principles density-functional calculations within the local spin-density approximation and the generalized gradient approximation are reported for pyrochlore $Cd_2Os_2O_7$ and $Cd_2Re_2O_7$. The transition-metal t_{2g} manifolds are found to be well separated in energy from the O $2p$ bands and from the higher-lying e_g and Cd derived bands. The active electronic structure in the t_{2g} manifold near the Fermi energy E_F is found to be significantly modified by spin-orbit interactions, which we include. Both materials show semimetallic band structures, in which the E_F lies in an pseudogap. The band structure of $Cd_2Os_2O_7$ near E_F is dominated by very heavy-hole and electron bands, though at E_F the electron sections are lighter. $Cd_2Re_2O_7$ has heavy-hole bands but moderate mass electron states. The results are discussed in terms of measured transport and thermodynamic properties of these compounds as well as the very different ground states of these two materials.

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I. INTRODUCTION

Investigations of transition-metal oxides with metal-insulator transitions in their phase diagrams have revealed a remarkable range of interesting, complex, and often unanticipated phenomena, including high-temperature superconductivity, various charge, spin, and orbital ordered states, triplet superconductivity, giant magnetoelastic effects, and heavy Fermion behavior. A good example is provided by the perovskite manganites. Although known for several decades, these compounds were re-investigated in detail during the last few years because of interest in the colossal magnetoresistive effect, which is basically a metal-insulator transition occurring at or near the magnetic ordering temperature for some compositions. What has been revealed is a complex phase diagram including charge, spin, and orbital ordered phases resulting from an interplay of strong correlations, strong lattice coupling, and band-structure effects.

The pyrochlore oxide $Cd_2Os_2O_7$ is metallic at room temperature, but undergoes a metal-insulator transition at 226 K.[1,2] Upon cooling through the transition, the resistivity $\rho(T)$ crosses over from a metallic temperature dependence to an insulating (ρ strongly increasing as T is reduced) shape, though it does not fit a standard activated form. Instead, Sleight and co-workers[1] fit $\rho(T)$ to a form consistent with a second-order transition where the gap goes smoothly to zero at the critical temperature. Consistent with this, Mandrus and co-workers[2] report that the specific-heat anomaly resembles a mean-field transition and shows neither latent heat nor hysteresis. They also reported extensive crystallographic data, showing very little coupling of the transition to lattice degrees of freedom and confirming the purely electronic character of the transition. The specific heat shows a very small but possibly still finite Sommerfeld coefficient (note that the reported lattice part does not fit a simple Debye model complicating the analysis); $\gamma\sim 1$ mJ/mol K^2 in the range 2–4 K and the low T susceptibility is high for an ordered antiferromagnetic insulating phase. The thermopower above the transition is holelike and small. Just below the transition, the thermopower increases to $+40$ μV/K, but then decreases and crosses zero. A very large electron-like thermopower, up to $S=-300$ μV/K, is seen well below the transition.[1,2] This is not expected from the simplest picture of a fully gapped Fermi surface due to a spin-density wave. On the other hand, supposing that the metal-insulator transition is magnetic in character, the ground state could be very complicated especially in view of the strong geometric frustration of the pyrochlore lattice and the fact that the interactions are most likely antiferromagnetic. The related compound, $Cd_2Re_2O_7$, which differs from $Cd_2Os_2O_7$ by one electron per transition metal, was recently reported to be superconducting at ~ 1 K with a substantial diamagnetic signature.[3,4] It displays metallic properties up to 200 K where an apparently isostructural transition of unknown character occurs.[3,5–7] Like $Cd_2Os_2O_7$, this transition shows signatures in electrical transport and susceptibility, though the details differ. Very recently, it was reported[8] that there is a structural signature at this transition in $Cd_2Re_2O_7$. As mentioned, such a structural signature is not seen in $Cd_2Os_2O_7$. Interestingly, the low-temperature linear specific-heat coefficient for $Cd_2Re_2O_7$, $\gamma=30$ mJ/mol K^2 (Ref. 3) is similar to the value $\gamma\sim 20$ mJ/mol K^2 estimated for the high-temperature phase of $Cd_2Os_2O_7$ (Ref. 2) in spite of the difference in electron count and the very different low-temperature properties.

Here we report the electronic structures of these two compounds as calculated within the local density approximation (LDA) and the generalized gradient approximation (GGA), using the general potential linearized augmented plane-wave

(LAPW) method including spin orbit, which we find important.[9–13] The calculations were done with well converged zone samplings and basis sets (including local orbitals to relax linearization errors and treat semicore states). The experimental crystal structure at 180 K of Mandrus and co-workers, [i.e., $a=10.1598$ Å and $x(\mathrm{O}1)=0.319$] was used throughout for $Cd_2Os_2O_7$.[2] The calculated Hellman-Feynman force on the symmetry unconstrained structural parameter was found to be small with this choice supporting the experimental crystallography. Total-energy minimization, within the LDA, yields a value $x(\mathrm{O}1)=0.3198$. Donohue and co-workers[5] refined the crystal structure of $Cd_2Re_2O_7$ obtaining $a=10.219$ Å and $x(\mathrm{O}1)=0.309$. However, this yields rather short Re-O bond lengths, and we note that the refinement is difficult because the compound contains heavy elements and the presence of Cd mandated the use of x rays rather than neutrons. We performed a relaxation of the internal coordinate within the LDA keeping the lattice parameter fixed at its no doubt reliable experimental value. We obtained $x(\mathrm{O}1)=0.316$ in this way. The energy of this relaxed structure was 0.35 eV/cell (four Re atoms) lower in energy than with the reported value of $x(\mathrm{O}1)=0.309$, which is well outside the normal LDA errors. The Raman-active a_{1g} phonon frequency corresponding to this coordinate is calculated as 463 cm^{-1}. The corresponding frequency for $Cd_2Os_2O_7$, also calculated in the LDA, is almost the same, $\omega=459\ \mathrm{cm}^{-1}$, indicating that the Re compound is not softer than the Os regardless of the unusual Re valence, at least as measured by this particular phonon mode.

In many aspects, the calculations we present are like those presented by Mandrus and co-workers for $Cd_2Os_2O_7$. However, there is one important difference. We find that spin-orbit interactions are significant because of the presence of heavy elements in the structure, and so include them by the usual second variational approach. The inclusion of spin orbit substantially changes the electronic structure near the Fermi energy. In addition, we allow for magnetism in $Cd_2Os_2O_7$, which we investigated using self-consistent unconstrained and fixed spin moment calculations. These were done by the method described in Ref. 14. Not surprisingly, our calculated non-spin-polarized band structure for $Cd_2Os_2O_7$ *without including spin orbit* is practically identical to that given by Mandrus and co-workers and so is not displayed here. Significantly, it is very metallic and has four Os d derived bands crossing the Fermi energy E_F and other bands. It is difficult to envisage what kind of instability might make it insulating. In the remainder of this report we discuss the band structure *including spin orbit*, which while similar in many basic aspects differs significantly near E_F.

II. BAND STRUCTURE

The crystal structure of $Cd_2Os_2O_7$ features Os ions (nominally Os^{+5}, $5d^3$) at the center of O octahedra. $Cd_2Re_2O_7$ is similar but with one less $5d$ electron per transition-metal atom. Within an ionic model, assuming nominal charges, one expects a manifold of occupied O $2p$ bands, followed by a partially filled transition-metal t_{2g} manifold and a higher-lying unoccupied set of e_g bands. Furthermore, since the actual transition metal site symmetry is weakly rhombohedral (due to the second neighbor coordination), a further crystal-field splitting of the t_{2g} manifold is possible.

The calculated LDA band structure of $Cd_2Os_2O_7$ is shown in Fig. 1, while that of $Cd_2Re_2O_7$ is in Fig. 2. The corresponding non-spin-polarized densities of states (DOS) near E_F are shown in Figs. 3 and 4. The GGA band structures (not shown) are very similar. As shown by the band structure the t_{2g} and e_g manifolds are cleanly separated from each other, and from the O $2p$ bands by clean gaps, as in the ionic model. However, despite this there is quite strong hybridization between Os d and O p states, reflecting the covalent tendency of $5d$ transition metals relative to $3d$ oxides. Although the actual Os site symmetry is rhombohedral, this part of the crystal field is weak and the band structure shows no apparent further splitting of the t_{2g} derived manifold. It is exactly half filled and contains 12 bands (note that there are four Os ions per unit cell). The t_{2g} bandwidth is 2.85 eV. Considering that the effective Hubbard U is likely 2 eV or less, based on the trends for transition-metal oxides, and noting the multichannel character of the t_{2g} manifold, $Cd_2Os_2O_7$ should not be classified as a strongly correlated material in the sense of having on-site Coulomb correlations play a dominant role in the formation of the electronic structure. This is consistent with the observation of a high-temperature metallic phase.[15]

As mentioned, the t_{2g} manifold, which consists of 12 bands, is exactly half filled. Unlike the scalar relativisitic band structure, the band structure including spin orbit shows a semi metallic structure in the sense that there is a gap between the sixth and seventh bands throughout the Brillouin zone, but because of the dispersions it is not an insulating gap. Instead, there are two electronlike Fermi surfaces. One, from the lowest conduction band, is a shell around the Γ point, while the other consists of ellipsoids along the Γ-X lines. Corresponding to these electron surfaces there are hole surfaces at the zone boundary around the W points. This band structure can, at least conceptually, be made insulating in two ways: (i) by increasing the gap between the sixth and seventh bands, or (ii) by depressing the sixth band at the zone boundary and or raising the, degenerate at Γ, seventh and eighth bands near the zone center. The heavy masses of these narrow bands is consistent with high thermopowers if a gap is opened. From the band structure, it may be seen that the electron sheets of Fermi surface are lighter (higher velocity) than the hole sections. For the paramagnetic metallic state, the calculated average Fermi velocity is low, reflecting these heavy bands, $\langle v_x^2\rangle^{1/2}=\langle v_y^2\rangle^{1/2}=\langle v_z^2\rangle^{1/2}=5.9\times10^6$ cm/s.

The calculated electronic DOS, $N(E)$ for $Cd_2Os_2O_7$, has a large peak just above E_F with $N(E_F)=9.24\ \mathrm{eV}^{-1}$ on a per formula unit (2 Os atom) basis. The GGA yields a somewhat higher value $N(E_F)=11.4\ \mathrm{eV}^{-1}$. However, while these numbers are smaller than the scalar relativistic value of $12.7\ \mathrm{eV}^{-1}$ reported by Mandrus and co-workers,[2] our LDA specific-heat coefficient $\gamma=22\ \mathrm{mJ/mol\,K}^2$ is still consistent within the range of electronic specific heats above the transition as estimated from experiment.[2] This leaves little room

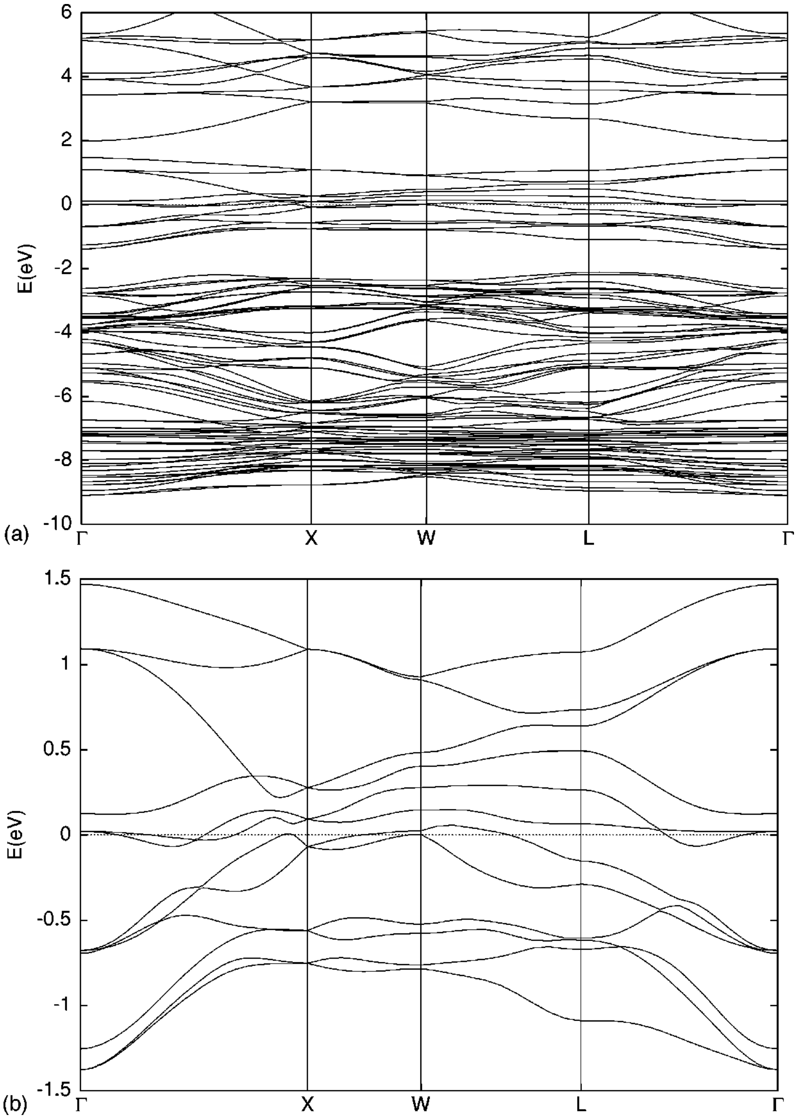

FIG. 1. LDA paramagnetic band structure of $Cd_2Os_2O_7$. Spin-orbit interactions were included via a second variational step. The horizontal reference denotes E_F. The bottom panel is a blowup around E_F showing the Os t_{2g} manifold.

for enhancement by electron phonon interactions or beyond density-functional many-body correlations.

The band structure and corresponding DOS for $Cd_2Re_2O_7$ are shown in Figs. 2 and 4, respectively. As may be seen from the upper panel of Fig. 2, the large energy scale electronic structure is like that of $Cd_2Os_2O_7$, and in particular the nominal ionic model is valid, with E_F falling in an isolated manifold of transition-metal t_{2g} states. However, a closer examination (lower panel of Fig. 2) shows that the differences from the Os compound are not at all well described by a rigid-band model. The band structure, like that of the Os compound, is semimetallic. In particular, there is a clean pseudogap between the fourth and fifth bands, and since there are eight d electrons per cell the nominal Fermi energy lies between them. The Fermi surfaces consist of nearly spherical, moderate mass Γ centered electron pockets from the fifth and sixth bands in the t_{2g} manifold ($m^* \sim 1.2$), and very heavy-hole sections from near the zone boundary. These enclose a total of 0.15 e/cell and an equal number of holes. As may be seen, this is less symmetric than the situation in $Cd_2Os_2O_7$. However, because of the semi-metallic character, which places E_F near the band edges, the velocity is still rather low, $\langle v_x^2 \rangle^{1/2} = 7.5 \times 10^6$ cm/s. Jin and co-workers[4] report that the Hall number is quite T dependent, but is electron-like at low temperatures. This is consistent with our band structure, which has both electron and hole sheets, but with much lighter electron sheets, which will dominate the conductivity due to their higher velocities.

The calculated $N(E_F)$ for $Cd_2Re_2O_7$ is 5.3 eV^{-1} per formula unit, and is derived mainly from the heavy-hole bands. This corresponds to a bare band specific heat $\gamma = 12.4$ mJ/mol K^2. Comparing with the measured value of 29.6 mJ/mol K^2 (Ref. 4) one obtains an enhancement $(1+\lambda_{total}) = 2.4$ or $\lambda_{total} = 1.4$, a reasonable value for a known superconductor.

The plasma frequency for $Cd_2Re_2O_7$ from the calculated $N(E_F)$ and $\langle v_x^2 \rangle$ is $\hbar\omega_p = 1.3$ eV. Within Boltzmann tranport theory for conventional metals, the slope of the intrinsic resistivity, in the moderate temperature linear regime, is given by $\partial\rho/\partial T = (8\pi^2 \hbar k_B \lambda_{tr})/(\hbar\omega_p)^2$, where λ_{tr} is the transport electron phonon coupling, often a reasonable approximation to the superconducting coupling λ. Jin and

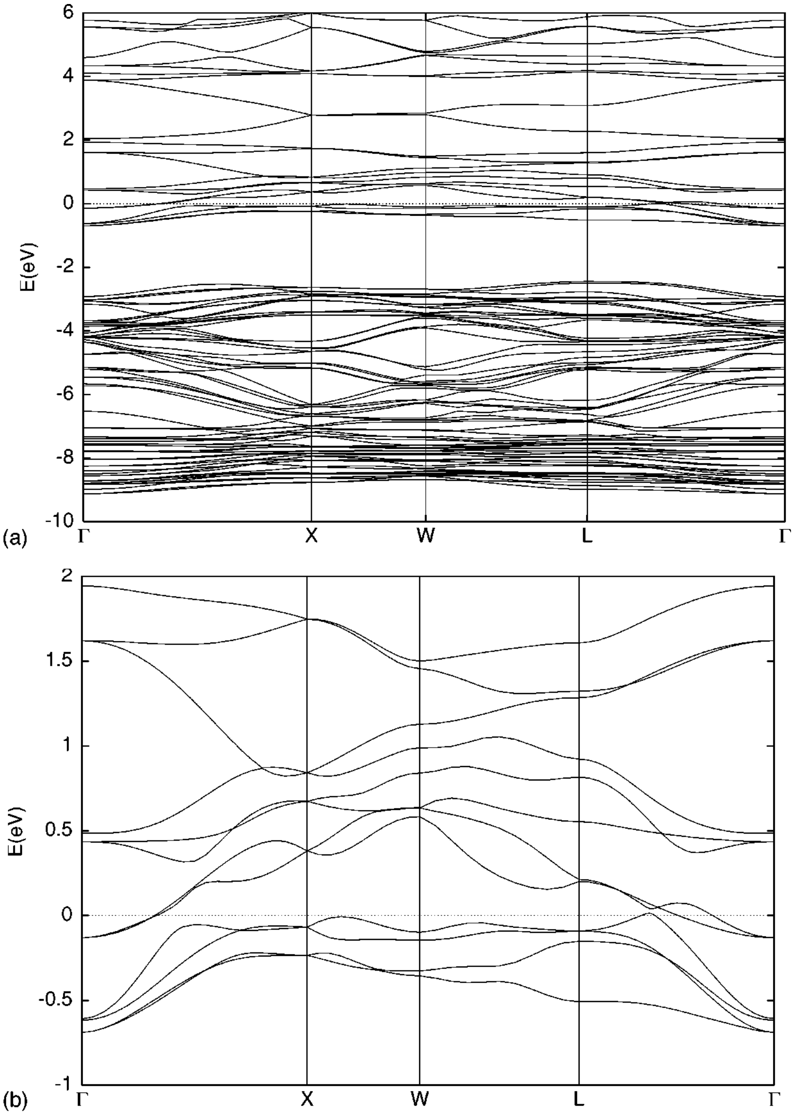

FIG. 2. LDA paramagnetic band structure of $Cd_2Re_2O_7$. Spin-orbit interactions were included via a second variational step. The horizontal reference denotes E_F. The bottom panel is a blowup around E_F showing the Re t_{2g} manifold. The heavy bands cross E_F yielding hole sections of Fermi surface, but these are not along the symmetry lines shown. Note the nonrigid band behavior relative to Fig. 1.

co-workers[4] report approximately linear ρ vs T from approximately 50–200 K. However, the two reported samples differ by a factor of more than 3 in $\partial\rho/\partial T$, providing a broad range of λ_{tr} from 0.75 to 2.5. This is problematic, as according to the experimental data $\partial\rho/\partial T$ displays unusual though fine structure in this temperature range, and then changes discontinuously to a value near zero at the transition. It is extremely hard to imagine such a drastic change in λ_{tr} originating from the conventional mechanism, as it would suggest a high-temperature phase with almost no electron phonon scattering, which crosses over into a moderate to strong coupled low-temperature phase.

The bare susceptibility from the value $N(E_F)$ is $\chi_B = 1.69\times 10^{-4}$ emu/mol. The experimental data show a large spread. Jin and co-workers[4] estimate the spin susceptibility $\chi(0) = 5.4\times 10^{-4}$ emu/mol, while Hanawa and co-workers[3] obtain 3.0×10^{-4} emu/mol for the total susceptibility at low temperature,[16] rising to $\approx 5\times 10^{-4}$ emu/mol above the 200-K phase transition. This corresponds to Wilson ratios R_W from 0.74 to 1.3, which are low for a transition-metal oxide, but would indicate weak electron correlations in the presence of a moderate electron-phonon coupling.

III. MAGNETISM IN $Cd_2Os_2O_7$

It should be noted that the high value of (N_F) obtained in $Cd_2Os_2O_7$ would lead to a strong magnetic instability in a $3d$ based material, but is marginal here. This can be understood in terms of the expected lower Stoner parameter I in a $5d$ compound. The peak near E_F derives from the flat practically dispersionless band that lies just above E_F over most of the zone. The relatively high $N(E_F)$ suggests the possibility of a Stoner instability against ferromagnetism. We checked for this both within the local spin-density approximation (LSDA) and GGA using fixed spin moment calculations, but found that $Cd_2Os_2O_7$ is predicted to be stable against ferromagnetism, so there is not such an instability. The calculated susceptibility is $\chi = 9.0\times 10^{-7}$ emu/g in the LSDA. This was determined from a fourth-order fit of the energy vs moment for the small moment part of Fig. 5. The bare Pauli susceptibility from $N(E_F)$ is $\chi_B = 4.2$

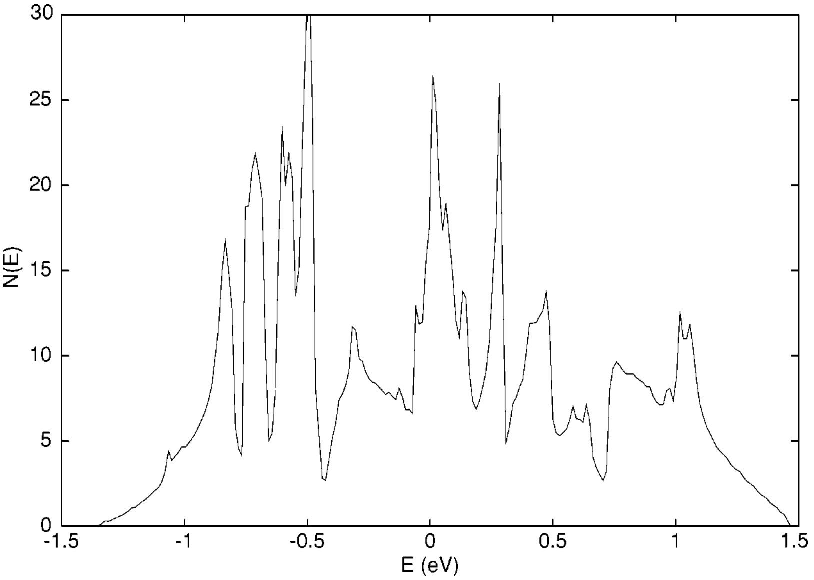

FIG. 3. LDA paramagnetic electronic density of states of $Cd_2Os_2O_7$ for the t_{2g} manifold on a per unit cell (four Os atoms) basis. Spin orbit is included.

$\times 10^{-7}$ emu/g, which yields a Stoner enhancement of $(1-NI)^{-1}\sim 2.2$. The GGA, which sometimes overestimates the tendency towards magnetism in $4d$ and $5d$ oxides, places $Cd_2Os_2O_7$ closer to a magnetic instability, with $\chi = 2.4\times 10^{-6}$ emu/g and $\chi/\chi_B = (1-NI)^{-1}\sim 6$. Taking into account the difference in the LDA and GGA values of $N(E_F)$, the GGA value of the effective Stoner I is 50% higher than the corresponding LDA value. This is reminiscent of the situation for Sr_2RuO_4, where LSDA calculations correctly produce a paramagnetic state, while the GGA produces an incorrect ferromagnetic ground state,[17,18] due to an overestimated I. In any case, Stoner ferromagnetism would rigidly exchange split the band structure, at least for small moments; as can be seen from the band structure, this would not result in an insulating electronic structure.

The band structure is quite isotropic (note, e.g., the similar dispersions around E_F along Γ-X and Γ-L in Fig. 1) and does not display strong nesting. Thus there is no obvious preferred wave vector to check in searching for a magnetic instability. However, noting that there are four Os atoms in the unit cell, we checked for a Γ point antiferromagnetic instability, in which two of the four Os atoms are spin up and two are spin down. In principle, a state like this could produce an insulating band structure. This is because the site dependent on-site exchange splittings reduce hopping between opposite spin Os atoms, thus potentially narrowing the bands enough to open the pseudogap between the sixth and seventh bands producing a full band gap. While we find that $Cd_2Os_2O_7$ is unstable against such an antiferromagnetic ordering in the GGA without spin orbit, we find that spin orbit favors the paramagnetic state. In the LSDA an antiferromagnetic ordering of this type does not occur.

Within the GGA, including spin orbit, we find that the material is on the borderline of an instability against this antiferromagnetic order. The resulting antiferromagnetic state, with spin moments of $\approx 0.3\mu_B$/Os, has the same energy as the paramagnetic state to within the precision of our calculations. Furthermore, with this size of moments, the

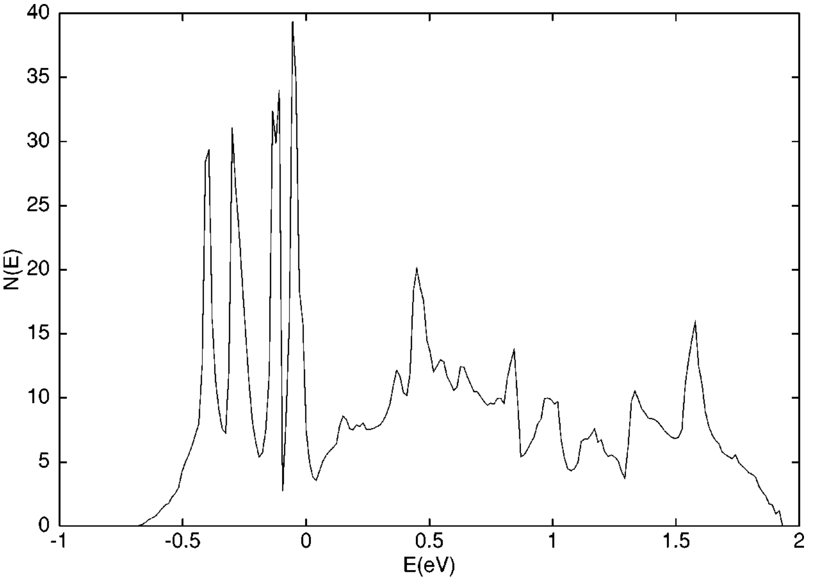

FIG. 4. LDA paramagnetic electronic density of states of $Cd_2Re_2O_7$ for the t_{2g} manifold on a per unit cell (four Re atoms) basis. Spin orbit is included.

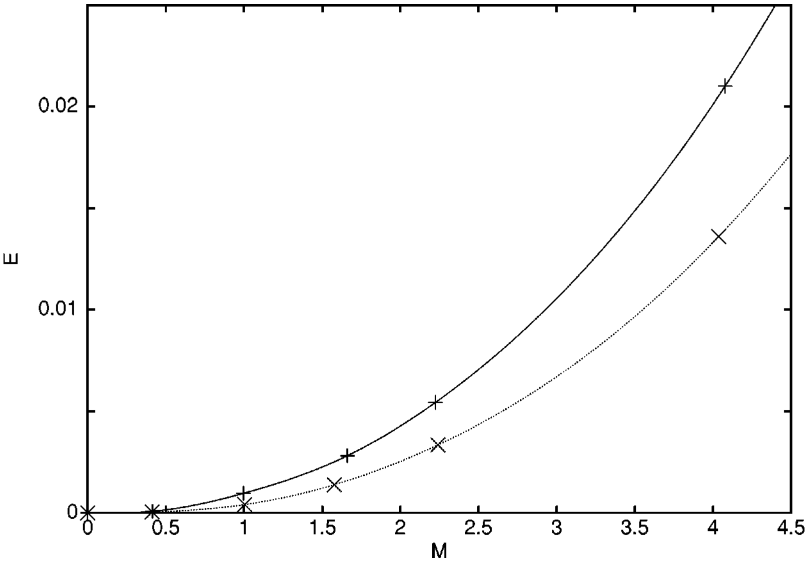

FIG. 5. Energy (Ry/cell) as a function of magnetization (μ_B/cell) for $Cd_2Os_2O_7$ from fixed spin moment calculations including spin orbit. The solid (dotted) lines are for the LSDA (GGA).

band narrowing is insufficient to destroy the metallic state. The Os sublattice consists of corner sharing tetrahedra, with the Os atoms at the corners. As a result it is not possible to find a structure in which all nearest-neighbor Os bonds are antiferromagnetic, and additionally, the lattice is strongly geometrically frustrated for nearest-neighbor spin Hamiltonians. However, based on our band-structure results, the proximity of $Cd_2Os_2O_7$ to magnetism is itinerant in nature, and therefore cannot be described in terms of simple nearest-neighbor spin Hamiltonians. In fact, the experimental low thermodynamic data do not show any evidence of a large near ground-state degeneracy. However, it is still the case that the simple collinear antiferromagnetic state we considered is favored relative to a ferromagnetic state, and so one may speculate that more complicated arrangements that would better fulfill a tendency for antiferromagnetic neighbors may be lower in energy. In particular, even though small moment itinerant magnets are generally collinear, as may be understood from arguments based on band kinetic energy considerations, here for want of a better alternative, one might postulate that a noncollinear ground state may occur. One example of such a state would be an arrangement in which the Os moments are directed either towards or away from the center of the tetrahedra. Such a state could be at the Γ point or could have the character of a spin-density wave (SDW), with modulation at a nonzero wave vector. Even so, because of the multiple Fermi surfaces, including some that are more or less isotropic, it is unclear that a simple SDW would produce a fully gapped state.

Each Os atom has two like spin and four opposite spin neighbors in the simple antiferromagnetic configuration we calculated. On the pyrochlore lattice, this leaves a fully connected 3D network of like spin nearest-neighbor atoms. One may speculate that a more complex arrangement that disrupts this fully connected network (as the noncollinear arrangement mentioned above would do) would narrow the bands enough to produce an insulating state. It is unclear whether such a state would be energetically favored here. However, the fact that we find the simple collinear antiferromagnetic state to be at least marginally stable in the GGA and favored with respect to ferromagnetism, may suggest that it is at least possible. In an itinerant magnetic state, like the one discussed above, the magnetic interactions in real space are inherently long range, so depression of the ordering temperature T_N due to geometric frustration is not to be expected. Still we emphasize that this scenario is not well supported by the current results for three reasons: (i) It is unclear that a purely magnetic instability exists in the LSDA, which may be a better approximation than the GGA for $5d$ compounds. An alternate scenario is a transition involving both charge and spin ordering, though there is not presently evidence for a charge-density wave in the experimental data. (ii) Noncollinear states, as mentioned, are generally not found or expected in itinerant low moment magnets. Finally, (iii) even if the system has magnetic instabilities it is unclear that they could be strong enough to produce a transition temperature above 200 K.

IV. SUMMARY, DISCUSSION, AND CONCLUSIONS

Band-structure calculations for $Cd_2Os_2O_7$ and $Cd_2Re_2O_7$ show a considerable sensitivity of the electronic structure near E_F to spin-orbit interactions. Both materials show semimetallic band structures with heavy bands near E_F. $Cd_2Re_2O_7$ has heavy-hole bands near the zone boundary and relatively light electron pockets around Γ, while the electronic structure of $Cd_2Os_2O_7$ is dominated by heavy bands for both the holes and electrons. Interestingly, because of the higher $N(E_F)$ in $Cd_2Os_2O_7$, the transport function Nv^2 differs by only 7%. However, the specific-heat enhancement in $Cd_2Os_2O_7$ is apparently quite small, while that in $Cd_2Re_2O_7$ is 2.4, leaving little room for electron-phonon interactions or simple many electron effects in the former. Furthermore, while $Cd_2Os_2O_7$ is at least near antiferromagnetism in the GGA, neither compound shows a clear proximity to magnetism in the LSDA, which may be a more reasonable approximation for $5d$ compounds. There are no clear nesting features in the band structures that would suggest spin- or charge-density wave Fermi-surface instabilities.

It is tempting to speculate that the metal-insulator transition in $Cd_2Os_2O_7$ and the 200-K transition in $Cd_2Re_2O_7$ are related to some common feature in their electronic structures. In this regard, we note that although they have different electron counts, both compounds have semimetallic band structures each with nominally equal numbers of holes and electrons dominated by very heavy bands. This is suggestive of a excitonic instability of the Fermi surface of the type proposed by Mott[19] and reviewed by Halperin and Rice.[20] The theory in its simplest form involves pairing between electrons on one sheet of Fermi surface and holes on another. Conditions that favor such a state are (i) heavy band masses (ii) low carrier densities, and (iii) similar sizes and shapes of Fermi surfaces, although the latter condition can sometimes be relaxed as discussed in Ref. 20. Such an instability is purely electronic, and in contrast to, e.g., a charge-density wave need not be coupled significantly to lattice degrees of freedom. The excitonic state may be either singlet, or triplet. Furthermore, it can coexist with superconductivity[21–23] or band ferromagnetism,[24–26] provided that there are excess carriers. While such a transition is due to electron correlations, it is not associated with an on-site Hubbard-like Coulomb repulsion, but rather **k**-dependent correlations near E_F. Importantly, the formation of an excitonic state involves weak thermodynamic signatures (it involves electrons only within a distance determined by the exciton binding energy from E_F) and is continuous. Hase and Nishihara have suggested that such a state may exist in the $4d$ oxide $CaPd_3O_4$.[27]

The general phenomenology of an excitonic metal-insulator transition would seem to fit experimental knowledge and the above band-structure results for $Cd_2Os_2O_7$, especially for triplet pairing.[28] The key parameters determining whether such a state can be formed are the exciton binding energy and the degree to which the size and shape of the electron and hole Fermi surfaces match in **k** as compared to the inverse size of an exciton. We cannot assess these as we do have the effective dielectric screening. However, we note that the very heavy bands should help to produce small excitons and favor this possibility. The situation in $Cd_2Re_2O_7$ is similar. However, in this material the 200-K transition is between two metallic states. Within the excitonic scenario the metallic conduction below 200 K and the superconductivity depend on the existence of nonpaired carriers below the transition. These could be provided by, e.g., slight off stoichiometry, which may perhaps be anticipated from the unusual Re valence. This doping could be sample dependent providing an explanation of the very different $\partial\rho/\partial T$ and the different T_c of the two reported samples discussed above.

We emphasize that the above discussion of excitonic states in $Cd_2Os_2O_7$ and $Cd_2Re_2O_7$ is speculative. However, if it is so, these materials will be interesting novel tests of many-body theories of excitonic phases, including superconductivity, possible triplet pairing, and the presence of strong spin-orbit interactions.

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