Electronic structure of the pyrochlore metals Cd$_2$Os$_2$O$_7$ and Cd$_2$Re$_2$O$_7$

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First principles density functional calculations within the local spin density approximation (LSDA) and the generalized gradient approximation (GGA) are reported for pyrochlore Cd$_2$Os$_2$O$_7$ and Cd$_2$Re$_2$O$_7$. 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 semi-metallic band structures, in which the $E_F$ lies in an pseudogap. The band structure of Cd$_2$Os$_2$O$_7$ near $E_F$ is dominated by very heavy hole and electron bands, though at $E_F$ the electron sections are lighter. Cd$_2$Re$_2$O$_7$ 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.

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 magnetoelasttic 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$_2$Os$_2$O$_7$ is metallic at room temperature, but undergoes a metal-insulator transition at 226 K. Upon cooling through the transition, the resistivity, $\rho(T)$, crosses over from a metallic temperature dependence to an insulating ($\rho$ strongly increasing as $T$ is reduced) shape, though it does not fit a standard activated form. Instead, Sleight and co-workers 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 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/mole K$^2$ in the range 2K to 4K and the low $T$ susceptibility is high for an ordered antiferromagnetic insulating phase. The thermopower above the transition is hole-like and small. Just below the transition, the thermopower increases to $+40 \mu V/K$, but then decreases and crosses zero. A very large electron-like thermopower, up to $S = -300 \mu V/K$ is seen well below the transition. 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$_2$Re$_2$O$_7$, which differs from Cd$_2$Os$_2$O$_7$ by one electron per transition metal, was recently reported to be superconducting at $\sim$1K with a substantial diamagnetic signature. It displays metallic properties up to 200K where an apparently isothermal transition of unknown character occurs. Like Cd$_2$Os$_2$O$_7$, this transition shows signatures in electrical transport and susceptibility, though the details differ. Interestingly, the low temperature linear specific heat coefficient for Cd$_2$Re$_2$O$_7$, $\gamma=30$ mJ/molK$^2$ (Ref. 3) is similar to the value $\gamma \sim 20$mJ/molK$^2$ estimated for the high temperature phase of Cd$_2$Os$_2$O$_7$ (Ref. 3) 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 ap-
proximation (LDA) and the generalized gradient approximation (GGA), using the general potential linearized augmented planewave (LAPW) method including spin-orbit, which we find important. The calculations were done with well converged zone mappings and basis sets (including local orbitals to relax linearization errors and treat semi-core states). The experimental crystal structure at 180K of Mandrus and co-workers, \( \text{a} = 10.1598 \text{Å} \) and \( x(O1) = 0.319 \) was used throughout for Cd\(_2\)Os\(_2\)O\(_7\). 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 \( x(O1) = 0.3198 \). Donohue and co-workers refined the crystal structure of Cd\(_2\)Re\(_2\)O\(_7\) obtaining \( a = 10.219 \text{Å} \) and \( x(O1) = 0.309 \). 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 \( x(O1) = 0.316 \) in this way. The energy of this relaxed structure was 0.35 eV / cell (4 Re atoms) lower in energy than with the reported value of \( x(O1) = 0.309 \), 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\(_2\)Os\(_2\)O\(_7\), also calculated in the LDA is almost the same, \( \omega = 459 \text{ cm}^{-1} \), 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\(_2\)Os\(_2\)O\(_7\). 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\(_2\)Os\(_2\)O\(_7\), which we investigated using self-consistent unconstrained and fixed spin moment calculations. These were done by the method described in Ref. Not surprisingly, our calculated non-spin-polarized band structure for Cd\(_2\)Os\(_2\)O\(_7\) 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\(_2\)Os\(_2\)O\(_7\) features Os ions (nominally Os\(^{15+}, 5d^3\)) at the center of O octahedra. Cd\(_2\)Re\(_2\)O\(_7\) 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\(_2\)Os\(_2\)O\(_7\) is shown in Fig. while that of Cd\(_2\)Re\(_2\)O\(_7\) is in Fig. The corresponding non-spin-polarized densities of states (DOS) near \( E_F \) are shown in Fig. and . 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 4 Os ions per unit cell). The \( t_{2g} \) band width 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\(_2\)Os\(_2\)O\(_7\) 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.

As mentioned, the \( t_{2g} \) manifold, which consists of 12 bands, is exactly half-filled. Unlike the scalar relativistic 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 electron-like Fermi surfaces. One, from the lowest conduction band is a shell around the \( \Gamma \) point, while the other consists of ellipsoids along the \( \Gamma-X \) 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: (1) by increasing the gap between the sixth and seventh bands or (2) by depressing the sixth band at the zone boundary and or raising the, degenerate at \( \Gamma \), 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 sur-
face are lighter (higher velocity) than the hole sections. For the paramagnetic metallic state, the calculated average Fermi velocity is low reflecting these heavy bands, $<v_{F}^{2}>^{1/2}=0.92<\gamma_{v}^{2}><v_{F}^{2}>^{1/2}=5.9 \times 10^{9} \text{ cm/s}$

The calculated electronic DOS, $N(E)$ for Cd$_2$Os$_2$O$_7$ has a large peak just above $E_F$ with $N(E_F)=9.24 \text{ eV}^{-1}$ on a per formula unit (2 Os atoms) basis. The GGA yields a somewhat higher value $N(E_F)=11.4 \text{ eV}^{-1}$. However, while these numbers are smaller than the scalar relativistic value of 12.7 eV$^{-1}$ reported by Mandrus and co-workers, our LDA specific heat coefficient $\gamma=22 \text{ mJ/molK}^2$ is still consistent within the range of electronic specific heats above the transition as estimated from experiment. This leaves little room for enhancement by electron phonon interactions or beyond density functional many body correlations.

The band structure and corresponding DOS for Cd$_2$Ru$_2$O$_7$ are shown in Figs. 3 and 4 respectively. As may be seen from the upper panel of Fig. 3, the large energy scale electronic structure is like that of Cd$_2$Os$_2$O$_7$, 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. 3) 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 semi-metallic. 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 $\Gamma$ 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$_2$Os$_2$O$_7$. However, because of the semi-metallic character, which places $E_F$ near the band edges, the velocity is still rather low, $<v_{F}^{2}>^{1/2}=7.5 \times 10^{9} \text{ cm/s}$. Jin and co-workers report that the Hall number is quite small, while these numbers are smaller than the scalar relativistic value of 17 eV$^{-1}$, our LDA specific heat coefficient $\gamma=5.4 \times 10^{-4} \text{ emu/mol}$, while Hanawa and co-workers obtain $3.0 \times 10^{-4} \text{ emu/mol}$ at low temperature, rising to $\approx 5 \times 10^{-4} \text{ emu/mol}$ above the 200K 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$_2$Os$_2$O$_7$

It should be noted that the high value of $(N_F)$ obtained in Cd$_2$Os$_2$O$_7$ 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 LSDA and GGA using fixed spin moment calculations, but found that Cd$_2$Os$_2$O$_7$ is predicted to be stable against ferromagnetism, so there is not such an instability. The calculated susceptibility is $\chi=9.0 \times 10^{-7} \text{ emu/g}$ in the LSDA. This was determined from a fourth order fit of the energy vs. moment for the small moment part of Fig. 3. The bare Pauli susceptibility from $N(E_F)$ is $\chi_B=4.2 \times 10^{-7} \text{ emu/g}$, 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$_2$Os$_2$O$_7$ closer to a magnetic instability, with $\chi=2.4 \times 10^{-6} \text{ emu/g}$ 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$_2$RuO$_4$, where LSDA calculations correctly produce a paramagnetic state, while the GGA produces an incorrect ferromagnetic ground state, 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 wavevector 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 ex-...
though 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 and reviewed by Halperin and Rice. 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 (1) heavy band masses (2) low carrier densities and (3) similar sizes and shapes of Fermi surfaces, although the latter condition can sometimes be relaxed as discussed in Ref. 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 or band ferromagnetic instability 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 a 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.

The general phenomenology of an excitonic insulator transition would seem to fit experimental knowledge and the above band structure results for Cd$_2$Os$_2$O$_7$, especially for triplet pairing. 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$_2$Re$_2$O$_7$ is similar. However, in this material the 200K transition is between two metallic states. Within the excitonic scenario the metallic conduction below 200K and the superconductivity depend on the existence of non-paired 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$_2$Os$_2$O$_7$ and Cd$_2$Re$_2$O$_7$ 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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The experimental observations (Ref. 2) of field induced magnetization and weak remnant magnetization suggest the presence of triplet paired excitons in the Os compound.

FIG. 1. LDA paramagnetic band structure of Cd$_2$Os$_2$O$_7$. Spin-orbit interactions were included via a second variational step. The horizontal reference denotes $E_F$. The bottom panel is a blow-up around $E_F$ showing the Os $t_{2g}$ manifold.

FIG. 2. LDA paramagnetic band structure of Cd$_2$Re$_2$O$_7$. Spin-orbit interactions were included via a second variational step. The horizontal reference denotes $E_F$. The bottom panel is a blow-up 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 non-rigid band behavior relative to Fig. 1.
FIG. 3. LDA paramagnetic electronic density of states of Cd$_2$Os$_2$O$_7$ for the $t_{2g}$ manifold on a per unit cell (4 Os atoms) basis. Spin-orbit is included.

FIG. 4. LDA paramagnetic electronic density of states of Cd$_2$Re$_2$O$_7$ for the $t_{2g}$ manifold on a per unit cell (4 Re atoms) basis. Spin-orbit is included.

FIG. 5. Energy (Ry/cell) as a function of magnetization ($\mu_B$/cell) for Cd$_2$Os$_2$O$_7$ from fixed spin moment calculations including spin orbit. The solid (dotted) lines are for the LSDA (GGA).