Competition between electronic correlations and hybridization in CaMn$_2$Bi$_2$

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We study the interplay between electronic correlations and hybridization in the low-energy electronic structure of CaMn$_2$Bi$_2$, a candidate hybridization-gap semiconductor. Utilizing state-of-the-art advanced density functionals we find both the antiferromagnetic Néel order and band gap in good agreement with the corresponding experimental values. We further find that, under hydrostatic pressure, the band gap is mainly governed by magnetic correlations, whereas hybridization has a greater impact on states at higher band energies. This result suggests that CaMn$_2$Bi$_2$ is more closely related to the high-temperature superconducting cuprates and iron pnictides than the heavy fermion class of materials. Finally, we also find the antiferromagnetic CaMn$_2$Bi$_2$ to be topologically trivial for all pressures studied.

I. INTRODUCTION

The electronic structure of fermionic correlated systems is driven by the competition between the tendencies of the electron to spread out as a wave and to localize as a particle, the latter usually accompanied with magnetism. That is, the interplay of the spin and charge degrees of freedom is a central issue. Layered two-dimensional (2D) materials provide a unique platform for studying this dual nature of the electronic states which produces rich phase diagrams including high temperature superconductivity, non-trivial topological insulating and semimetallic phases, and quantum spin liquid states.

In particular, the iron-based superconductors have been under vigorous experimental and theoretical study since the discovery of unconventional high-temperature superconductivity in La[O$_{1-x}$F$_x$]FeAs in 2008. Since then a family of compounds with related layered crystal structures and chemical compositions were discovered including FeSe, LiFeAs, RFe$_2$As$_2$ (R=rare earth), AFe$_2$As$_2$ (A=Ca, Sr, Ba, Eu), termed the ‘11’, ‘111’, ‘1111’, and ‘122’ type structures, respectively. The highest superconducting transition temperature of 56 K has been found in the 1111-type compound Gd$_{0.8}$Th$_{0.2}$FeAsO. To enhance the superconducting transition temperature and search for new broken symmetry phases, Fe was substituted away and replaced by other transition metals such as Cr, Mn, Co, and Ni. These isostructural compounds form new ground states including metallic (Co-based), itinerant antiferromagnetic (Cr-based), superconducting (Ni-based), and semiconducting antiferromagnetic (Mn-based) behavior. The Mn-based pnictides garnered special interest due to their similarity to the phenomenology of the high-temperature cuprate superconductors. In particular, the Mn-based compounds exhibit insulator-metal transitions upon either doping or application of pressure, but superconductivity has yet to be reported. In general this suggests that the manganese pnictides possibly form a bridge between the pnictide and cuprate material families.

Recent experimental and theoretical studies find CaMn$_2$Bi$_2$ to host many intriguing properties including large anisotropic magnetoresistance and a plane-to-chain structural transition, but most curiously it has been suggested that CaMn$_2$Bi$_2$ may be a hybridization-gap semiconductor. In line with this claim, low-temperature electrical transport measurements find a slight increase of the gap under pressure. This type of behavior is akin to Ce$_3$Bi$_2$P$_3$ and other heavy fermion compounds. Therefore, CaMn$_2$Bi$_2$ could provide a link between the cuprates, pnictides, and heavy fermion systems.

In this article, we present a first-principle investigation of the electronic and magnetic structure of CaMn$_2$Bi$_2$. We find electronic correlations to dominate the band gap, with the effect of hybridization limited to energies 0.5 eV and higher. Under applied hydrostatic pressure we find an insulator-metal transition near 20 kbar along with reduced manganese magnetic moments as expected for a correlated system. Hybridization is seen to increase with pressure, but the energy scales at which it plays a role prevent it from influencing the band gap. Finally, we also find the antiferromagnetic CaMn$_2$Bi$_2$ to be topologically trivial for all studied pressures.

Ab initio calculations were carried out by using the pseudopotential projector-augmented wave method implemented in the Vienna ab initio simulation package (VASP) with an energy cutoff of 600 eV for the plane-wave basis set. Exchange-correlation effects were treated using the strongly-constrained-and-appropriately-normed (SCAN) meta-GGA scheme, where a 12 × 12 × 8 Γ-centered k-point mesh was used to sample the Brillouin zone. Spin-orbit coupling effects were included self-consistently. We used the low-temperature $P^3m1$ (164) crystal structure in accord with the experimental measurements. All sites in the unit cell along with the unit cell dimensions were relaxed using a conjugate gradient algorithm to minimize energy with an atomic force tolerance of 0.01 eV/Å and a total energy tolerance of $10^{-6}$ eV. The theoretically obtained
structural parameters are in good agreement with the corresponding experimental results.

II. MAGNETIC AND ELECTRONIC STRUCTURE

Figure 1 shows the three possible antiferromagnetic ground state configurations within the crystal structure of CaMn$_2$Bi$_2$. The magnetic moments (green and gold arrows) are stabilized on the manganese sites within the plane oriented along the $b$-axis in accord with experimental observations. Our first principles total energy calculations find the Néel-type order to be the ground state consistent with neutron diffraction, with the other candidate magnetic states lying at least 40 meV above in energy. The magnitude of the magnetic moments along with the band gap and relative total energy of the various magnetic configurations are given in Table I.

| Order    | Magnetic Orbital (µB) | Total Gap (meV) | Relative Energy (meV/Mn) |
|----------|-----------------------|-----------------|--------------------------|
| Neel     | 4.125 0.053           | 4.18 291        | 0                        |
| Stripy   | 4.116 0.045           | 4.161 0.437     | 48                       |
| Zig-Zag  | 4.139 0.045           | 4.184 291       | 109                      |

Experimentally, the Néel phase exhibits a magnetic moment of 3.85 µB and a band gap between 31 - 62 meV, depending on the report. Additional recent transport studies find a small activation gap between 2 - 4 meV. Our calculations yield a larger magnetic moment and energy gap, however our results improve upon those obtained using the HSE06 hybrid functional. Previous studies on transition metal solids, including Fe, Co, Ni, and Mn, where SCAN was employed yielded the complex charge and noncollinear magnetic ordering that occurs at low temperatures, but with a slight enhancement of the magnetization. The enhancement is attributed to an oversensitivity of the iso-orbital indicator, $\alpha$, used to discern various chemical bonding environments and is currently being amended. Curiously, this oversensitivity was not found in studies of the cuprates and 3d perovskite oxides in general. To remedy the overestimation, we introduce an effective Hund’s coupling $J$ on the Mn-d states within the scheme of Dudarev et al. to dampen the electronic correlations captured by SCAN. Physically, $J$ has also been shown to play a key role in the Mn-based pnictides. Figure 2 shows the change in the density of states (DOS) near the Fermi level as a function of $J$, along with an inset of the magnetic moment (red solid line) and band gap (blue solid line) overlaid with the average experimental values (dashed lines). Increasing $J$ from 0.0 to 2.0 eV pushes the leading edge of the conduction band towards the Fermi energy, decreasing the band gap. Simultaneously, the density of valence (conduction) states grows (narrows). The band gap and magnetic moment monotonically decrease with increasing $J$, with the gap closing for a $J$ of 2.0 eV. A $J$ of 1.3 eV is found to reproduce the experimental parameters, as indicated by the green dashed line.

Figure 3 shows the site-resolved density of states (DOS) for various atomic orbitals including Mn-d and...
FIG. 3. (color online) Site-resolved partial density of states for the same phase for various values of $J$. Shading and lines of various colors (see legend) give the contributions from manganese-$d$, and bismuth-$s$ and -$p$ orbitals. The green (blue) dashed lines follow the shift in manganese (bismuth) states with increasing $J$. Black dashed line marks the Fermi Energy.

Bi-$s,p$ as a function of the effective $J$. On tuning $J$ from 0 to 2 eV the gap in the magnetically split Mn-$d$ states (centered at -4.5 eV and 1.0 eV) clearly contracts, marking a reduction of the Mn-$d$ on-site correlations. Below the Fermi energy, the overlap between Bi-$p$ and Mn-$d$ orbitals is enhanced, due to the increase in Mn-$d$ weight, while the bands move towards the Fermi energy. Above the Fermi level, the center-of-gravity of the Mn-$d$ states shifts towards the Fermi energy with increasing $J$; however the bandwidth stays relatively the same, which implies no significant change in Bi/Mn hybridization. The Bi-$s$ dominated band stays centered about 2.5 eV above the Fermi energy for all $J$, illustrating that $J$ is just influencing the correlation strength of the Mn levels. Additionally, we find calcium to have negligible weight within the energy range discussed, and therefore it is not a factor.

III. EFFECT OF PRESSURE

Applied external pressure provides a direct means to gauge the relative ratio between hybridization and correlation strengths in a material. If the band gap is driven by correlations, pressure squeezes the lattice sites of the crystal closer together forcing the wave functions of neighboring atomic sites to overlap. Electrons then tend to become more delocalized in the material, yielding a metal. In contrast, if the band gap is governed by hybridization, pressure further separates bonding and anti-bonding states, thus increasing the band gap. When both hybridization and correlations are present, the gap can undergo non-monotonic behavior under pressure as a result of their competition.

Figure 5 (left panel) shows the site-resolved partial density of states in the Neel type antiferromagnetic phase of CaMn$_2$Bi$_2$ under hydrostatic pressures from 0 to 100 kbar. At zero pressure the AFM order opens a gap in the Mn-$d$ states of 42 meV, consistent with the average reported experimental value, along with the majority bismuth states centered at 2.5 and -5.0 eV, respectively. As pressure is applied, the energy separation between the bismuth states increase, as indicated by the blue dashed lines, due to the enhanced hybridization. The motion of the manganese states is not as clear-cut. The manganese dominated levels below $E_F$ move to towards higher energies, reducing the band gap. There is also a concomitant broadening of the states and a strengthening of Mn-$d$ and Bi-$p$ overlap.

In contrast, the manganese levels above $E_F$ exhibit anomalous non-monotonic behavior. For pressures less than 20 kbar, the peaks in the DOS stay relatively constant in energy, only showing a slight shift to the left (green dashed lines). For pressures greater than 20 kbar, the motion of peaks in the DOS appears to be propor-
FIG. 5. (color online) (left panel) Site-resolved partial density of states in the Neel type antiferromagnetic phase of CaMn$_2$Bi$_2$ under various values of pressure. Shading and lines of various colors (see legend) give the contributions from manganese-d, and bismuth-s and -p orbitals. The green (blue) dashed lines follow the shift in manganese (bismuth) states with increasing pressure. Red solid line tracks the leading edge of the conduction states as the system passes through a metal-insulator transition. Black dashed line marks the Fermi Energy.

(right panel) The spin and orbital components of the total magnetic moment, along with the band gap as a function of pressure.

Figure 5 (right panel) shows the total magnetic moment along with its spin and orbital components and the band gap as a function of pressure. The total magnetic moment is dominated by spin magnetization both displaying a monotonic linear decrease with pressure. On the other hand, the orbital contribution increases in a power law fashion, with a slight plateau upon the gap closing. Here, the competition between hybridization and correlation with pressure can be readily observed. The spin magnetization provides a direct indicator of the strength of correlations, while the orbital component tracks the overlap of Bi and Mn atomic wave functions, which in turn induce an effective spin-orbit coupling on the Mn sites. Additionally, we also found the Mn moments to slightly ($\approx 1^\circ$) tilt out-of-plane with applied pressure.

In the original analysis performed by Gibson et al.\textsuperscript{18} it was claimed that the gap behaves as a hybridization gap. This was justified by tracking the changes in position of the Bi-\(p\) and \(s\) levels with expanding and contracting the unit cell volume by 1%. However, this claim is made by disregarding the Mn-\(d\) bands which sit in between the bismuth levels forming the band gap and follow the trend of a correlation gap. Additionally, the pressure study by some of us\textsuperscript{20} reports an increase in activation energy of 20 K to 40 K (2 - 4 meV) with pressure using electrical transport measurements. The small gap values could possibly be driven by impurity states within the gap, making the sample sensitive to slight perturbations in pressure. However, to fully compare our first-principle calculations to the experimental resistivity measurements, a more rigorous modeling of the transport process is required.

IV. TOPOLOGICAL CHARACTER

Originally, CaMn$_2$Bi$_2$ was thought to be a possible magnetic 3D Dirac semimetal, where the Mn-\(d\) states...
were assumed to behave as core electrons.\textsuperscript{38} This then allows for a clean band inversion of Bi-$s$ and Bi-$p$ levels. However, Gibson et al.\textsuperscript{18} found that the Mn-$d$ orbitals play a significant role at the Fermi level, hybridized with the manifold of bismuth states. This ultimately disrupts the Bi-$s$ and Bi-$p$ level, avoiding a topological non-trivial ground state.

To confirm the topological nature of CaMn$_2$Bi$_2$ we used the vasp2trace code\textsuperscript{40} in conjunction with the Check Topological Material module\textsuperscript{40–42} provided on the Bilbao Crystallographic Server.\textsuperscript{43–45} CaMn$_2$Bi$_2$ is indeed found to be topological trivial for all pressures up to 100 kbar, due to the fact that the Mn-$d$ levels dominate the low energy electronic structure and preventing the Bi-$s$ and $p$ states to overlap and invert. However, if the on-site energy of the manganese bands were to be tuned away from the Fermi level or the Bi-$s$ state brought closer to the Fermi level, the bismuth $s$ and $p$ level could be inverted, making the ground state topologically non-trivial.

V. CONCLUDING REMARKS

By examining the ground state electronic structure of CaMn$_2$Bi$_2$ as a function of pressure, we find the low energy electronic structure to follow the characteristic behavior of a correlation gap. This behavior implies CaMn$_2$Bi$_2$ is more closely related to the cuprate high-temperature superconductors than the Ce$_3$Bi$_4$Pt$_3$ heavy fermion compounds. To fully elucidate its connection to the cuprate compounds and to what extent they are similar, i.e. exhibiting charge/spin density waves and superconductivity, further doping dependent studies are needed to uncover its full phase diagram. Moreover, the addition of holes should produce an interesting interplay between itinerant antiferromagnetic carriers and those on the strongly spin-orbit coupled Bi-$p$ orbitals, creating a ripe environment for new exotic phases of matter.

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