Correlated Topological Insulators with Mixed Valence

Feng Lu, JianZhou Zhao, Hongming Weng, Zhong Fang,* and Xi Dai†

Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China

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We propose the local density approximation + Gutzwiller method incorporating a Green's function scheme to study the topological physics of correlated materials from the first principles. Applying this method to typical mixed valence materials SmB_6, we find its nontrivial Z_2 topology, indicating that SmB_6 is a strongly correlated topological insulator. The unique feature of this compound is that its surface states contain three Dirac cones in contrast to most known topological insulators.

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Most Z_2 topological insulators (TIs) [1–5] discovered up to now are semiconductors which are free of strong correlation effects and their topological nature can thus be predicted quite reliably by first principles calculations based on density functional theory [6]. The Z_2 classification of band insulators has been generalized to interacting systems by looking at its response to external electric magnetic field, namely the topological magnetoelectric effect (TME) [7]. A correlated insulator is a TI if the θ angle defined in the TME is π. Given the TME theory and several simplifications [8], however, its application to realistic materials is still absent due to (1) the lack of suitable compounds, and (2) the difficulty in compute reliably correlated electronic structures from the first principles. In this Letter, we study a special class of materials, the mixed valence (MV) compounds, which contain rare-earth elements with *non-integer chemical valence*. By combining the Gutzwiller variational approach from the first principles and the Green's function method for the TME, we found SmB_6, a typical MV compound, is a 3D correlated TI. Interestingly, it has three Dirac cones on the surface, in contrast to most of the known TIs.

Classic MV compounds, such as SmB_6 and YbB_{12} [9], share the following common features. (i) The x-ray photoelectron spectroscopy and x-ray absorption spectra contain peaks from both divalent and trivalent multiplets with comparable spectral weight [10–12], indicating the valence of Sm or Yb to be close to 2.5. (ii) A small semiconducting gap opens at least in part of the Brillouin zone (BZ) at low temperature [13]. Previous electronic structure studies indicate that the electrons transfer from Sm (or Yb) $4f$ orbitals to $5d$ orbitals, which leads to fractional occupation in $4f$ orbitals [14,15]. From the band structure point of view, the electron transfer between $4f$ and $5d$ orbitals indicates possible band inversion between them, which is a crucial ingredient to realize TI (if it happens an odd number of times in the entire BZ). In the mean while, SmB_6 has been recently suggested to be among the possible candidates of the interesting topological Kondo insulators [16–19]. Although the analytical studies of MV compounds have been conducted by several groups, the reliable first principle calculation, which is crucial to identify the possible topological phases, is still lacking, due to the strong correlation nature of these materials [20,21]. Here, we report that the local density approximation (LDA)+Gutzwiller method, a newly developed first-principles tool for correlated electron systems, enables us to search for the topological phases in correlated matters. By taking the MV compound SmB_6 as an example, we will focus on two key issues: (i) how to compute the Z_2 topological index with (LDA)+Gutzwiller; (ii) what is the topological nature of SmB_6 with the strong correlation effects among the f electrons?

The LDA+Gutzwiller method combines the density functional theory within LDA with the Gutzwiller type trial wave function, which takes care of the strong atomic features in the ground state. Here we just sketch the most important aspects, and leave the details to Refs. [22–24]. We start from the common Hamiltonian (used for most of the LDA++ schemes),

$$H_{\mathrm{Total}} = H_{\mathrm{LDA}} + H_{\mathrm{int}} + H_{\mathrm{DC}}, \tag{1}$$

where H_{LDA} is the single particle Hamiltonian obtained by LDA and H_{int} is the local interaction term for the $4f$ electrons described by the Slater integrals F_0, F_2, F_4, F_6. In the present Letter, for the Sm atom we choose $F_0 = 5.8$ eV and $F_2 = 9.89$ eV, $F_4 = 7.08$ eV, $F_6 = 4.99$ eV to be their atomic values [25,26]. H_{DC} is the double counting term representing the interaction energy already considered at the LDA level. In the present Letter, we compute the double counting energy using the scheme described in Ref. [27]. We then use the following Gutzwiller trial wave function, $|G\rangle = P_G|0\rangle = \prod_i P_i|0\rangle$, where $|0\rangle$ is a noninteracting state (obtained from LDA), $P_i = \sum_{\Gamma_i} \lambda_{\Gamma_i} |\Gamma_i\rangle\langle\Gamma_i|$ is the Gutzwiller projector at the ith site with $|\Gamma_i\rangle$ being the atomic eigenstates and λ_Γ being the variational parameters to be determined by minimizing the ground state total energy (under the Gutzwiller approximation) [23,28,29], $E_G = \langle 0|H_{\mathrm{eff}}|0\rangle + \sum_\Gamma \lambda_\Gamma E_\Gamma$. Here $H_{\mathrm{eff}} = P_G H_{\mathrm{LDA}} P_G$ is called the renormalized effective single particle

Hamiltonian and E_Γ is the eigenenergy of the Γth atomic eigenstate. The scheme preserves the nice aspect of being variational; however, it is beyond LDA (and also LDA+U) because the total energy E_G now relies on the balance between the renormalized kinetic energy of quasiparticle motion and the local interaction energy, which is configuration dependent. We note that including the complete form of all the Slater integrals (F_0 to F_6) in the local interaction is essential to obtain the correct electronic structure for these materials.

The linear response theory for the coefficient of the TME has been developed and simplified by Z. Wang *et al.* [8]. For interacting systems, when the self-energy contains no singularity along the imaginary axis, the formula for the TME coefficient only requires the single particle Green's function at zero frequency, $\hat{g}(k, 0)$. Because the singular point for the self-energy along the imaginary axis only appears for a Mott insulator with completely localized f orbitals, which is not the case for SmB_6, we can safely apply the above method here. Therefore, the way to determine the Z_2 invariance is just by diagonalizing the Hermite matrix $-\hat{g}(k, 0)^{-1} = \hat{H}_0 - \mu_f + \hat{\Sigma}(0)$ and treating the eigenstates with the negative eigenvalues as the "occupied states." If the system also has a spatial inversion center, the Z_2 invariance can simply be determined by counting the parities of these "occupied states" on the time reversal invariant momenta (TRIM) points, the same as that done for the noninteracting topological band insulators [1,2].

In the Gutzwiller approximation (or the equivalent slave boson mean field approach), the low energy single particle Green's function of an interacting system can be expressed by the quasiparticle effective Hamiltonian and the quasiparticle weight $\hat{z}$ (which in general is a matrix) as,

$$\hat{g}(k, i\omega) = \frac{\hat{z}}{i\omega - \hat{H}_{\text{eff}} + \mu_f} + \hat{g}_{ic}(k, i\omega), \qquad (2)$$

where the second term describes the incoherent part of the Green's function, which is ignorable for low frequency. Therefore, by applying the Green's function method described above, we reach the conclusion that the Z_2 invariance in the LDA+Gutzwiller method is determined by the occupied eigenstates of the Gutzwiller effective Hamiltonian H_{eff}, which can be interpreted as the band structure of the quasiparticles.

We now focus on SmB_6, which is crystallized in the CsCl-type structure with Sm ions and B_6 clusters being located at the corner and body center of the cubic lattice, respectively (see Fig. 1). The LDA part of the calculations has been done by full potential linearized augmented plane wave method implemented in the WIEN2K package [30]. BZ integration was performed on a regular mesh of $12 \times 12 \times 12$ k points. The muffin-tin radii (R_{MT}) of 2.50 and 1.65 bohr were chosen for Sm and B atoms, respectively. The largest plane-wave vector K_{max} was give by $R_{\text{MT}}K_{\text{max}} = 8.5$. The spin-orbit coupling is included in all calculations.

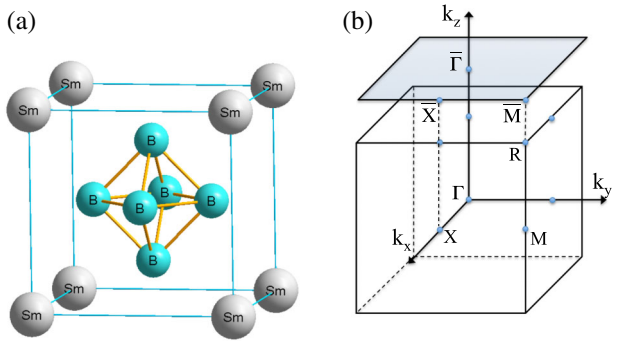

FIG. 1 (color online). (a) The CsCl-type structure of SmB_6 with $Pm3m$ space group. Sm ions and B_6 octahedron are located at the corner and center of the cubic lattice respectively. (b) The bulk and surface BZ for SmB_6.

The band structure obtained by LDA is shown in Figs. 2(a) and 2(b), where we can find three major features. (i) The Sm-4f orbitals, which split into the $j = 5/2$ and $j = 7/2$ manifolds due to the spin-orbit coupling, form narrow bands, respectively, with width around 0.5 eV near the Fermi level. (ii) The low energy band structure is semiconductorlike with a minimum gap of about 15 meV along the Γ-X direction. (iii) There are clear band inversion features at the X points, where one 5d band goes below the

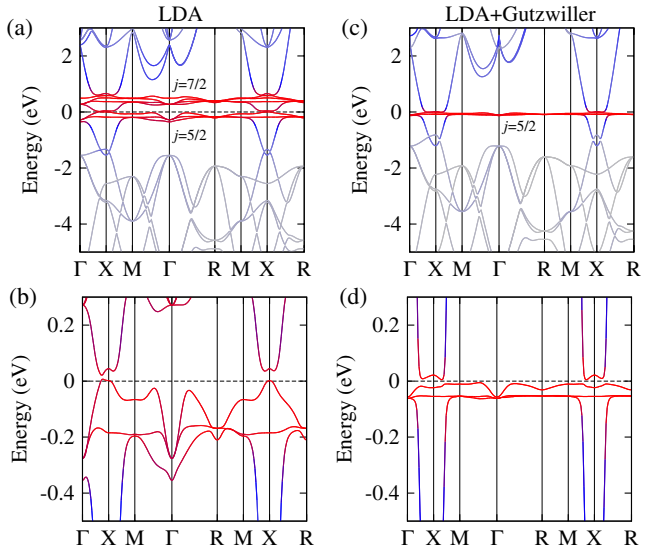

FIG. 2 (color online). The calculated band structure for SmB_6 in different energy scales by LDA [(a),(b)] and LDA+Gutzwiller [(c),(d)]. The (b) and (d) are just the zoom in of (a) and (b) respectively, around the fermi level. Compared to the LDA results, the 4f $j = 7/2$ bands in LDA+Gutzwiller have been pushed up to be about 4.0 eV above the fermi level, leaving the band structure near the fermi level being dominated by 4f $j = 5/2$ and 5d states. The blue, red and grey colors represent the weight of the orbital character for 5d, 4f, and 2p, respectively.

f bands, which reduces the occupation number of the f states to be around 5.5.

The first two features of the LDA band structures are not consistent with the experimental observations. First, the x-ray photoelectron spectroscopy measurements find quite strong $4f$ multiplet peaks, indicating the strong atomic nature of $4f$ electrons in SmB_6 (in other words, most of the $4f$ electrons are not involved in the formation of energy bands) [10,11]. Second, both transport [31–33] and optical [34–37] measurements reveal the formation of a small gap only for temperatures below 50 K. The above two features imply that the f electrons in SmB_6 have both localized and itinerant natures and the correct description of its electronic structure should include both of them. The qualitative physical picture can be ascribed to Kondo physics, which involves both itinerant and localized electronic states [17]. At high temperatures, these localized orbitals ($4f$ states) are completely decoupled from the itinerant energy bands, forming atomic multiplet states. While at low temperatures, the coherent hybridization between localized and itinerant states is gradually developed leading to the formation of "heavy quasiparticle" bands. The insulating behavior appears when the chemical potential falls into the "hybridization gap" between the heavy quasiparticle and the conduction bands, which is mainly of the $5d$ orbital character in SmB_6.

Such a Kondo picture can be nicely captured by our LDA+Gutzwiller calculations, which provide equal-footing descriptions of both the itinerant $5d$ bands and those heavy quasiparticle states formed by $4f$ orbitals. The quasiparticle band structures obtained by LDA +Gutzwiller are shown in Figs. 2(c) and 2(d). Compared with the LDA results, there are three major differences induced by the strong correlation effects. (i) The $4f$ $j = 7/2$ bands are pushed up to around 4.0 eV above the fermi level, leaving the band structure near the fermi level being dominated by $4f$ $j = 5/2$ and $5d$ bands. (ii) The band width of those heavy quasiparticle bands formed by $4f$ orbitals are much reduced to be less than 0.1 eV. The quasiparticle weight z of these heavy quasiparticle bands is about 0.18, indicating that the quasiparticles are formed by less than 20% of the $4f$ spectral weight and the remaining weight is attributed to the atomic multiplets (or the Hubbard bands). (iii) A hybridization gap between $4f$ quasiparticle bands and the itinerant $5d$ bands appears along the Γ to X direction. The detailed hybridization process is illustrated in Fig. 3. Along the Γ to X direction, the point group symmetry is lowered to be C_{4v}, whose double group contains two irreducible two-dimensional representations, Γ_6 and Γ_7. Along Γ to X, the original $4f$ $j = 5/2$ orbitals split into two Γ_7 and one Γ_6 bands, which cross with another Γ_7 band formed by $5d$ orbitals. The hybridization terms among the three Γ_7 bands are allowed and generate the hybridization gap, which is around 10 meV now. We note that in contrast to the LDA results, the semiconductor gap obtained by LDA+Gutzwiller is indirect, which is quite consistent with the transport measurements [37].

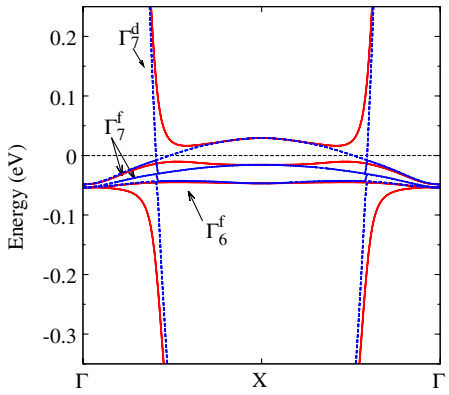

FIG. 3 (color online). Band hybridizations between $4f$ and $5d$ along Γ to X direction. The original $4f$ $j = 5/2$ orbitals split into two Γ_7^f and one Γ_6^f bands. The Γ_7^f bands cross and hybridize with another Γ_7^d band formed by $5d$ orbitals.

We would emphasize that by LDA+Gutzwiller, we can only obtain the quasiparticle part in the spectral function, but not the Hubbard bands containing the atomic multiplet structure [15,21]. While the Gutzwiller type wave function can well capture the multiplet features in the ground state [23,28,38]. The Gutzwiller variational parameter λ_Γ determines nothing but the probability of each atomic configuration Γ in the ground state (which is defined as $\langle G|\Gamma\rangle\langle\Gamma|G\rangle$). In Fig. 4, we plot the corresponding probabilities for SmB_6 obtained by LDA+Gutzwiller together with that obtained by the LDA wave function ($\langle 0|\Gamma\rangle\langle\Gamma|0\rangle$). The LDA ground state is dominated by the atomic

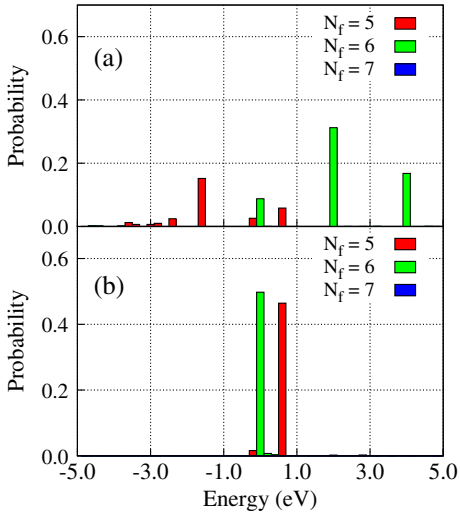

FIG. 4 (color online). The probability of atomic eigenstates in the ground state obtained by (a) LDA alone and (b) LDA+Gutzwiller. N_f is the total number of f electrons for the corresponding atomic eigenstates. The horizontal axis denotes the corresponding atomic eigenenergy.

TABLE I. The products of parity eigenvalues of the occupied states for TRIM points, Γ, X, R, and M in the BZ.

Γ	$3X$	R	$3M$
+	−	+	+

configurations with the number of f electrons $N_f = 6$; on the other hand, however, the distribution of the probability of atomic states obtained by LDA+Gutzwiller is almost equally concentrated on two atomic multiplet states with five and six f electrons, respectively, leading to approximately +2.5 valence of Sm.

Moreover, the Gutzwiller wave function provides correct description of the intermixing between $j = 7/2$ and $j = 5/2$ orbitals, which can not be captured by the LDA only calculation and manifests itself in the average occupancy of the f orbitals. The occupancy of $j = 5/2$ and $j = 7/2$ orbitals are 5.31 and 0.22, respectively, using the LDA type wave function ($|0\rangle$), while the f orbital occupancy is modified to be 3.64 for $j = 5/2$ and 1.89 for $j = 7/2$ orbitals using the Gutzwiller type wave function ($|G\rangle$). The dramatic increment of the occupancy for $j = 7/2$ orbitals is the important consequence of the F_2-F_6 terms in the atomic interactions, which can not be expressed by a pure "density-density" form in any single particle basis and generates a strong multiconfiguration nature for the ground state wave function.

The band inversion feature around the X points persists in the LDA+Gutzwiller quasiparticle bands. As discussed in previous paragraphs, the topological nature of this interacting system is fully determined by the Gutzwiller effective Hamiltonian H_{eff}. Since the spatial inversion symmetry is present for SmB_6, we are now able to determine its topological nature by simply counting the parities of those occupied quasiparticle states at 8 TRIM points. As listed in Table I, the parities are all positive except the X points. Because there are totally three equivalent X points in the whole BZ, the Z_2 topological index for SmB_6 has to be odd, resulting in strongly correlated topological insulators with topological indices (1; 111).

To see the topological surface states, we construct a tight binding model using the projected Wannier functions [39–41], which can reproduce the LDA band dispersion quite precisely. The surface states of the (001) surface are then obtained by combining the above tight binding Hamiltonian and the same rotational invariant Gutzwiller approach on a 40-layer slab. The obtained quasiparticle bands of the slab are plotted in Fig. 5. It is clearly seen that the surface states contain three Dirac cones: one cone is located at $\bar{\Gamma}$ and the other two are at two $\bar{X}$ points of the surface BZ. The interesting multi-Dirac-cones behavior is quite unique among the existing TIs and is a natural consequence of the band inversion at the bulk X points, which are projected onto $\bar{\Gamma}$ and two $\bar{X}$ points of the (001) surface BZ. The multiple Dirac cones on the surface of

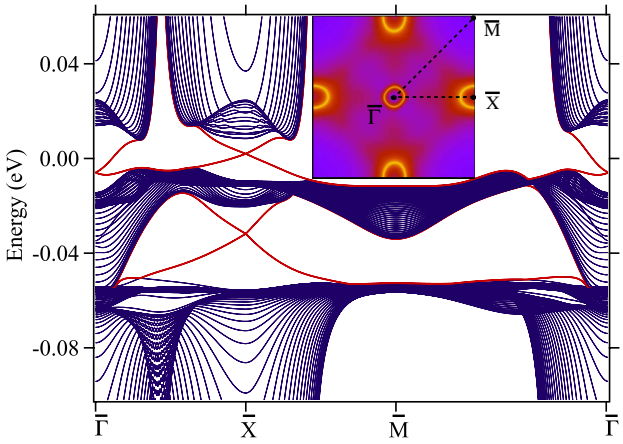

FIG. 5 (color online). The surface states of SmB_6 on the (001) surface. The surface states are obtained by LDA+Gutzwiller with a 40 layer slab on the basis of projected Wannier functions. (Inset) The fermi surfaces for surface states on (001) surface.

SmB_6 may generate interesting physical phenomena, such as the unique quasiparticle interference pattern in the scanning tunneling microscope, which will be studied in our further publications.

In summary, we have developed the LDA+Gutzwiller method incorporating the Green's function scheme to study the topological phases of strongly correlated materials from the first-principles (beyond LDA and LDA+U). This method is systematically applicable to all correlated compounds as long as the quasiparticle weight is not reaching zero. Both quasiparticle bands and atomic multiplet structures can be captured well in the present technique. Applying this method onto the typical mixed valence compound SmB_6, we demonstrate that it is a strongly correlated 3D TI with unique surface states containing three Dirac cones on the (001) surface. The strong interaction among the f electrons reduces both the band width and the quasiparticle weight for almost one order, but the topological feature remains.

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*Corresponding author.
zfang@aphy.iphy.ac.cn
†Corresponding author.
daix@aphy.iphy.ac.cn

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