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First-Principles Study of Kondo Insulator SmB_6

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We applied the Perdew-Burke-Ernzerhof hybrid functional (PBE0) within the density functional theory (DFT) to study electronic properties of the heavy fermion Kondo semiconductor SmB_6. The calculation of the Hartee-Fock exchange contribution to the exact-exchange within the atomic sphere approximation for bulk SmB_6 represents a computationally efficient, parameter-free method that provides good qualitative and quantitative agreement with photoemission experiments. Specifically, we found an energy difference of 7 eV between the occupied and unoccupied correlated Sm f states. Furthermore, the spin-orbit coupling yields a splitting of the occupied Sm f states of about 1 eV in agreement with recent angular resolved photoemission spectroscopy. The electronic spectrum in the vicinity of the X point shows a hybridization between the Sm $5d$ conduction band and the localized Sm $4f$ states at the Fermi level. This might lead to a transport gap opening.

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SmB_6 is a typical mixed valence heavy fermion Kondo semiconductor belonging to the class of rare-earth hexaborides. Its electronic properties at high temperatures can be viewed as independent localized moments (f–electrons) interacting with a sea of conduction electrons. At low temperature the periodic arrangement of the spins creates a Kondo lattice and the hybridization between localized f-electrons and conduction bands leads to a narrow hybridization gap opening.

Pioneering electronic band structure calculations by Yanase and Harima [1], using the local spin-density approximation (LSDA) with spin-orbit interaction, yield a narrow energy gap of about 14 meV at the Fermi level, but the splitting of 0.7 eV between Sm $f_{5/2}$ and $f_{7/2}$ states is inadequately described due to improper treatment of the correlation effects within LSDA. The splitting between the filled and empty f bands is expected to be about 7 eV according to photoemission experiments [2, 3]. A more proper treatment of the correlated f states within the LSDA+U method showed a reasonable splitting of the occupied and empty f bands [4]. Although the LSDA+U provides reasonably correct average positions for the occupied Sm f states (useful for further atomic multiplet positioning in energy) when comparing to the XPS spectra [4], it improperly describes the density of states (DOS) for the occupied Sm f states in the energy window of 5 eV below the Fermi level, namely the Sm^{2+} ^{6}H, ^{6}F and ^{6}P multiplets. Recently a Green function scheme based on the Gutzwiller method was used to predict a topological Kondo insulating phase in SmB_6 [5]. Although this technique captures the low energy hybridization around the Fermi level, it leads to a strong localization of the Sm f states and can not describe properly the experimentally observed splitting of about 1 eV of ^{6}H and ^{6}F multiplets. On the other hand, the density functional mean-field theory within the Hubbard-I approximation provides good agreement between the partial DOS of the Sm f-electrons and the ^{6}H and ^{6}F peak positions [6]. Despite the satisfactory agreement, the previous approaches rely on a priory unknown Hubbard and exchange parameters and, in addition, suffer from the double counting problem. A parameter-free alternative to the calculations of correlated systems is the use of hybrid functionals.

Here we present calculations based on the Perdew-Burke-Ernzerhof hybrid functional (PBE0) [7–9], considered for correlated Sm f-electrons within the on-site approximation [10], as implemented in the WIEN2k package [11]. The on-site approximation considers the Hartree-Fock method only inside the atomic spheres. This provides a significant reduction of the computational cost [12], eluding difficulties due to the strong nonlocal nature of the exchange potential. The approximation is, therefore, less suitable in a weakly correlated regime and does not improve gaps in semiconductors. However, it allows orbital resolved healing for the strongly correlated electrons which are poorly described by the LSDA.

In Fig. 1 we show the SmB_6 total DOS and the orbital resolved DOS for d states and relativistic $5/2$ and $7/2$ f states of the Sm atom. We found that the PBE0 separates six occupied Sm f states and eight unoccupied states of about 7 eV in agreement with photoemission experiments [2, 3]. The unoccupied $f_{7/2}$ states are broadened due to hybridization with the d states in the range of 3 eV. The occupied f states form two narrow peaks in the DOS, just below the Fermi level. The spin-orbit coupling contributes significantly to the splitting of the states of about 1 eV, as observed in recent angle-resolved photoemission spectroscopy (ARPES) measurements [13]. The peak in the vicinity of the Fermi level is dominated by

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the $f_{5/2}$ states, whereas the other peak is formed with both the $f_{5/2}$ and $f_{7/2}$ relativistic states.

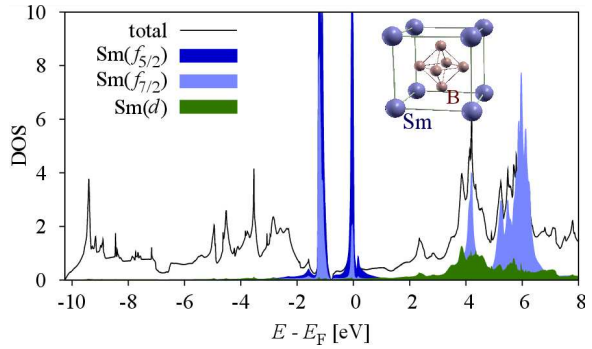

Fig. 1. Density of states (DOS) of SmB_6 calculated using PBE0 hybrid functional. The energy is measured with respect to the Fermi level E_F. The inset shows the crystal structure of SmB_6.

Despite the quasiparticle character of the quantum mechanical states in the system, we show in Fig. 2 the band structure along the high symmetry lines, with atomic and orbital resolved characters for the Sm atom. At the Fermi level there is apparent hybridization of the localized Sm f states with a wide dispersive valence band having Sm d-orbital character as well as contribution from the B atoms. The hybridization around the X point is, therefore, not entirely an on-site effect. Due to the spin-orbit coupling, the localized Sm f states split about 1 eV. This is also reported in ARPES experiments [13].

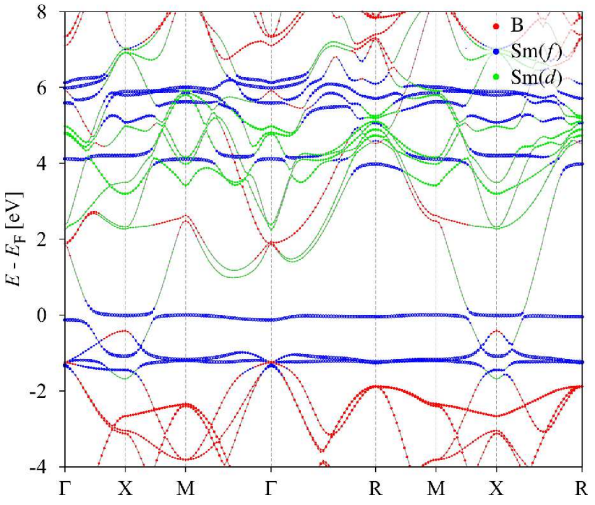

Fig. 2. Calculated band structure of SmB_6 along high symmetry lines using PBE0 hybrid functional. The circles' radii correspond to the atomic and orbital resolved character of the bands.

Performing similar calculations at the DFT+U level for both the fully localized limit [14] as well as the around mean field approximation [15] we have found that, in contrast to the hybrid functional approach, the DFT+U method is not able to reproduce correctly the 1 eV split of the valence Sm f states which is observed in ARPES experiments [13].

Although our calculations with PBE0 properly describe the localized Sm f states, they can not provide a conclusive prediction for the hybridization gap value. The localized band at the Fermi level is bended upward with a maximum at the M point, closing the transport gap. Therefore, the PBE0 functional is not well suitable for reproducing the specific Kondo induced transport physics in the system. For this further improvement in the description of the correlation effects is required.

In conclusion, we have applied the PBE0 hybrid functional to study the electronic properties of the SmB_6. We have found a well quantitative behaviour of the localized correlated Sm f states which is in agreement with spectroscopic experiments.

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