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The semiconductor-to-ferromagnetic-metal transition in $FeSb_2$

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Abstract. We propose $FeSb_2$ to be a nearly ferromagnetic small gap semiconductor, hence a direct analog of FeSi. We find that despite different compositions and crystal structures, in the local density approximation with on-site Coulomb repulsion correction (LDA+U) method magnetic and semiconducting solutions for U=2.6 eV are energetically degenerate similar to the case of FeSi. For both $FeSb_2$ and FeSi ($FeSi_{1-x}Ge_x$ alloys) the underlying transition mechanism allows one to switch from a small gap semiconductor to a ferromagnetic metal with magnetic moment $\approx 1\mu_B$ per Fe ion with external magnetic field.

PACS. 71.27.+a Strongly correlated electron systems; heavy fermions – 71.30.+h Metal-insulator transitions and other electronic transitions

The unusual crossover from a small gap semiconductor at low temperatures to a metallic state with enhanced magnetic fluctuations above room temperature observed in FeSi has long been a subject of great interest [1–5]. Two different models have been proposed to explain this anomaly. One proposal is that FeSi is a Kondo insulator [2]. The second is that FeSi is a nearly ferromagnetic semiconductor [3,4]. This latter proposal is supported by ab initio electronic structure calculations using the LDA+U method [6] which found that a ferromagnetic metallic state was very close by in energy [3]. Further support for this second model comes from the direct observation of this semiconductor-metal transition as the lattice is expanded by the isoelectronic substitution of Ge for Si [7]. In order to determine critical magnetic field a minimal two-band model with interband interaction was suggested. Even in the mean field approximation the model nicely describes the full phase diagram of the $FeSi_xGe_{1-x}$ alloy series [7].

Recently, a second Fe-compound, $FeSb_2$, was found to have a similar crossover as FeSi from a small gap semiconductor to a metallic state with strong magnetic fluctuations [8,9]. This raises immediately the question whether ab initio calculations confirm the close analogy between the two Fe compounds. This is a nontrivial question since these electronic structure calculations show strong hybridi zation between the Fe-3d orbitals and the s-p electrons of the close Si or Sb neighbors. This strong hybridization clashes with the assumption of weak hybridization between localized and itinerant electrons that underlies a Kondo insulator description and makes it difficult to relate the Kondo insulator model to the ab initio electronic structure. However in view of the differing compositions and crystal structures of FeSi and $FeSb_2$ it is by no means obvious that closely similar models can be derived from ab initio electronic structure calculations for both compounds. For this reason it is clearly important to examine $FeSb_2$ closely.

$FeSb_2$ crystallizes in the marcasite crystal structure [10]. Each Fe atom is surrounded by a slightly distorted octahedron of Sb neighbors with 2 neighbors at 2.57 Å and 4 at 2.59 Å. The octahedra are corner sharing in the ab plane and edge sharing along the c-axis.

The results of density functional calculations using a local density approximation (LDA) [11] within TB-LMTO-ASA program [12] are shown in Figures 1 and 2 (the calculations were performed without spin-polarization). Atomic spheres radii were chosen as R(Fe) = 2.67 a.u. and R(Sb) = 2.99 a.u., in ASA approximation to fulfil the volume 6 classes of empty spheres were inserted with radii from 1.56 to 0.81 a.u. The overall bandwidth is ≈10 eV with strong Fe-Sb hybridization due to the short Fe-Sb bonds. The density of states (DOS) is shown in Figure 1. The Fermi energy lies in a small band gap similar to the case of FeSi. Also in Figure 1 the DOS broken down in Fe-3d(t_{2g}) and Sb-4p states is displayed. Narrow bands appear above and below the band gap with predominantly 3d character – again similar to the case of FeSi. There is however a substantial contribution of the Sb-4p states to valence band peak just below the Fermi

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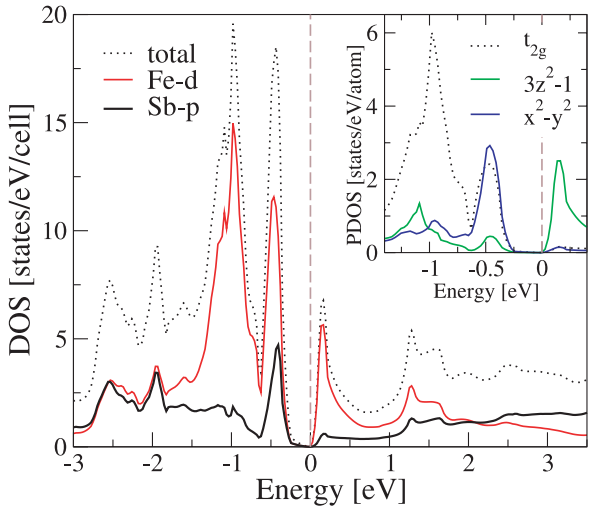

Fig. 1. Total and partial densities of states for $FeSb_2$ from the LDA calculation. Inset shows partial t_{2g}-DOS and $3z^2 - r^2$, $x^2 - y^2$ orbitals DOS of Fe-3d states. The Fermi energy corresponds to zero.

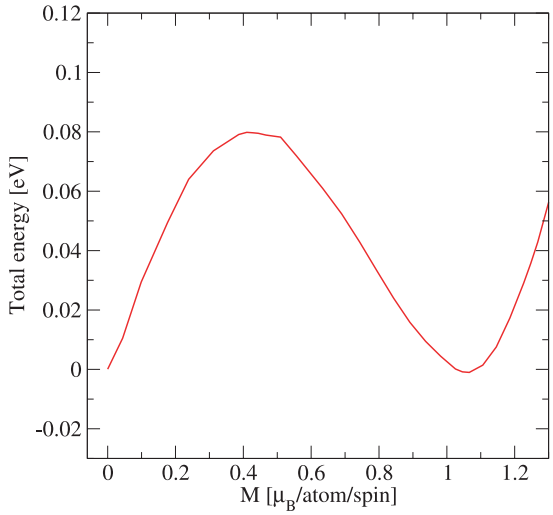

Fig. 3. Total energy dependence on magnetization value for $FeSb_2$. From the LDA+U calculation with $U = 2.6$ eV and $J_H = 0.88$ eV. Energy is related to the energy of nonmagnetic state.

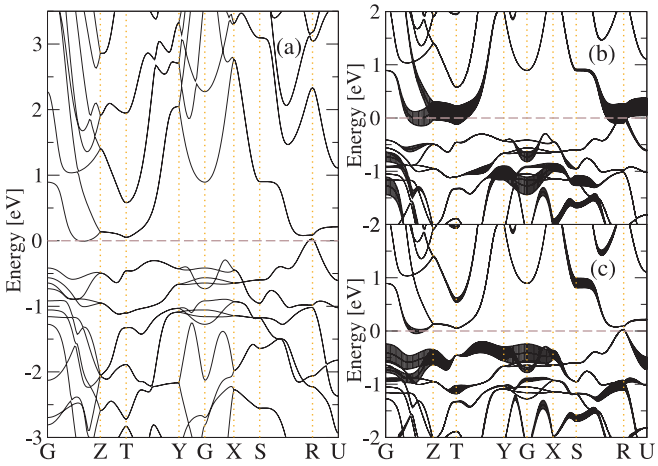

Fig. 2. (a) Band structure of $FeSb_2$ from the LDA calculation. Right panels show partial contributions of (b) $3z^2 - r^2$ and (c) $x^2 - y^2$ orbitals to the total band structure. Additional broadening of the bands corresponds to the contribution of the orbital. The Fermi energy corresponds to zero.

energy but in the interval from the Fermi energy to ≈1 eV Sb-4p states are presented very weakly.

The band structure of $FeSb_2$ is presented in Figure 2a. There is a small indirect energy gap with the minimum in the conduction bands lying on the GZ-lines and the maximum of the valence band is at the R-point. The narrow peak in the DOS at the bottom of the conduction band arises from the flat bands that extend over roughly half of the Brillouin near the Z- and R-points. The orbital character of these flat bands is predominantly $3z^2 - r^2$ (in the global coordinate system) as illustrated in Figure 2b. These are 3d orbitals pointing away from the Sb-sites in the octahedra surrounding the Fe atoms. The top of the valence band lies mostly in the DOS peak ≈0.3 eV below the conduction band and has predominantly 3d $(x^2 - y^2)$-character. There is however a small density of states with mostly Sb-p character which is responsible for the small indirect band gap.

The main feature of the LDA band structure is this small gap (≈0.3 eV) between relatively flat bands of 3d character giving rise to sharp peaks in the DOS. But the Sb-4p band contributes small density of states in this gap with zero at the Fermi level. In reference [13] from measurements of optical reflectivity the semiconducting optical gap was estimated as $E_g = 0.035$ eV. This value is larger than that obtained from the resistivity measurements ≈0.02–0.025 eV (see reference [9]). This situation is similar to FeSi except that E_g does not show any dependence on temperature up to the crossover temperature.

The LDA approximation was extended to allow for spin and orbital polarization by Anisimov et al. [6] by introducing a local Coulomb repulsion, U. This LDA+U method when applied to FeSi found that there was a ferromagnetic metallic state very close by in energy to the small gap semiconducting state of the LDA. The exact energy difference between the two depends on the choice of U. This result of LDA+U is nicely confirmed by the fact that the isostructural-isoelectronic compound FeGe has the ferromagnetic metallic ground state. Actually if spin-orbit terms were included the ferromagnetism of FeGe would develop a long period spiral structure as observed in practice due to the presence of a Dzyaloshinskii-Moriya term in resulting from the absence of inversion about the Fe sites.

The phase diagram of the $FeSi_xGe_{1-x}$ alloys can be reproduced by choosing the reasonable value of U, an onsite Coulomb repulsion on the Fe sites of $U = 3.7$ eV [7].

We have applied the LDA+U method to $FeSb_2$. As in the case of FeSi a second local minimum appears in the energy vs. uniform magnetization at a value of 1 μ_B per Fe (see Fig. 3). In this set of calculations we performed fixed spin moment procedure [3]. Again the exact energy

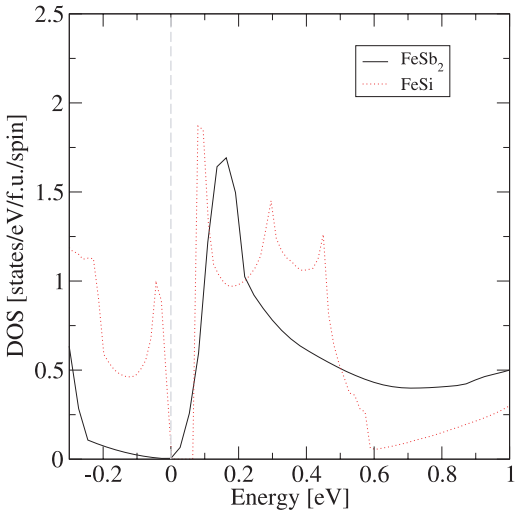

Fig. 4. Total densities of states of $FeSb_2$ and FeSi [3] from the LDA calculations near the Fermi energy.

difference between the two minima is dependent on the value of U.

In all our calculation we used the value J_H=0.88 eV for the exchange (Hund's) Coulomb parameter but varied the value of direct Coulomb parameter U. As a result, in $FeSb_2$ we found the critical value of the direct Coulomb parameter $U_c = 2.6$ eV. As in FeSi and $FeSi_xGe_{1-x}$ alloys, for any value of the U parameter less than U_c it is the nonmagnetic ground state that is lower in total energy. Otherwise for the U values above U_c ferromagnetic state is lower in energy. Only for U_c these two states have the same energy.

Comparison of the total $FeSb_2$ density of states near the Fermi energy to FeSi is shown in Figure 4.

The close similarity between the LDA+U results for FeSi and $FeSb_2$ agrees well with the close correspondence in their properties. It demonstrates the nearly ferromagnetic character of these small gap semiconductors.

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