Prediction of a Surface State and a Related Surface Insulator-Metal Transition for the (100) Surface of Stochiometric EuO

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We calculate the temperature and layer-dependent electronic structure of a 20-layer EuO(100) film using a combination of first-principles and model calculation based on the ferromagnetic Kondo-lattice model. The results suggest the existence of a EuO(100) surface state which can lead to a surface insulator-metal transition.

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In the recent past many theoretical and experimental research works have focused on the intriguing properties of rare-earth metals and their compounds. Among others, the extraordinary surface magnetic properties of the lanthanides [1], as, e.g., an enhanced Curie temperature of the Gd(0001) surface compared to that of bulk Gd [2], have provoked numerous research activities. Concerning the interplay between electronic structure and exceptional magnetic properties at the gadolinium surface a Gd(0001) surface state [3,4] is believed to play a crucial role and its temperature dependent behavior has been discussed intensely, e.g., [5].

Rare-earth materials are so-called local-moment systems; i.e., the magnetic moment stems from the partially filled $4f$ shell of the rare-earth atom being strictly localized at the ion site. Thus the magnetic properties of these materials are determined by the localized magnetic moments. On the other hand, the electronic properties like electrical conductivity are borne by itinerant electrons in rather broad conduction bands, e.g., $6s$, $5d$ for Gd. Many of the characteristics of local-moment systems can be attributed to a correlation between the localized moments and the itinerant conduction electrons. For this situation the ferromagnetic Kondo-lattice model (FKLM) which is also referred to as the s-f model has been proven to be an adequate description. In this model, the correlation between localized moments and conduction electrons is represented by an intra-atomic exchange interaction.

In this Letter we introduce a multiband FKLM and use it to calculate the temperature and layer-dependent band structure of EuO films. For all the calculations, the surfaces of the films are parallel to the fcc(100) crystal plane and the films are referred to as EuO(100) films. These films consist of n equivalent parallel layers. The lattice sites within the film are indicated by a greek letter α, β, γ, ..., denoting the layer, and by a latin letter i, j, k, ..., numbering the sites within a given layer. The different subbands of the conduction bands of EuO will be denoted by the indices m, m'.

The Hamiltonian for the multiband FKLM,

$$\mathcal{H} = \mathcal{H}_s + \mathcal{H}_f + \mathcal{H}_{sf}\,, \tag{1}$$

consists of three parts. The first,

$$\mathcal{H}_s = \sum_{ij\alpha\beta\sigma} T_{ij\alpha\beta}^{mm'} c_{i\alpha m\sigma}^{+} c_{j\beta m'\sigma}\,, \tag{2}$$

contains the kinetic energy of the conduction band electrons. $c_{i\alpha m\sigma}^{+}$ ($c_{i\alpha m\sigma}$) is the creation (annihilation) operator of an electron with spin σ from the mth subband at the lattice site $\mathbf{R}_{i\alpha}$. The $T_{ij\alpha\beta}^{mm'}$ describe the hopping between the mth subband at the lattice site $\mathbf{R}_{i\alpha}$ and the m'th subband at the lattice site $\mathbf{R}_{j\beta}$. These hopping integrals have to be determined within a first-principles band-structure calculation.

The second part of the Hamiltonian represents the system of the localized f moments and consists itself of two parts,

$$\mathcal{H}_f = -\sum_{ij\alpha\beta} J_{ij}^{\alpha\beta} \mathbf{S}_{i\alpha}\mathbf{S}_{j\beta} - D_0 \sum_{i\alpha} (S_{i\alpha}^{z})^2, \tag{3}$$

where the first is the well-known Heisenberg interaction. Here the $\mathbf{S}_{i\alpha}$ are the spin operators of the localized magnetic moments, which are coupled by the exchange integrals, $J_{ij}^{\alpha\beta}$. The second contribution is a single-ion anisotropy term which arises from the necessity of having a collective magnetic order at finite temperatures, $T > 0$ [6]. The according anisotropy constant D_0 is typically smaller by some orders of magnitude than the Heisenberg exchange integrals, $D_0 \ll J_{ij}^{\alpha\beta}$.

In addition to the contribution of the itinerant-electron system and the contribution of the localized f moments we have a third contribution to account for an intra-atomic interaction between the conduction electrons and the localized f spins. The form of that contribution in the case of multiple conduction bands can be derived from the general form of the on-site Coulomb interaction between electrons of different subbands, with the restriction that electron scattering processes caused by the Coulomb interaction are restricted to two involved subbands [7]. By distinguishing between bands of localized and itinerant electrons, respectively, one gets the on-site Coulomb interaction between both groups of electrons. For the special situation of europium with an exactly half-filled localized $4f$ shell and by assuming the interband exchange to be independent on the different subbands, one eventually gets the multiband s-f interaction:

$$\mathcal{H}_{sf} = -\frac{J}{\hbar}\sum_{i\alpha m} \boldsymbol{\sigma}_{i\alpha m} \cdot \mathbf{S}_{i\alpha}\,, \tag{4}$$

where $\mathbf{S}_{i\alpha}$ is the local moment originating from the Hund's rule coupling of the localized f electrons, $\boldsymbol{\sigma}_{i\alpha m}$ is the Pauli spin operator of an electron from the mth band of itinerant electrons, both at the lattice site $\mathbf{R}_{i\alpha}$, and J is the intra-atomic s-f exchange interaction.

The many-body problem that arises with the Hamiltonian (1) is far from being trivial and a full solution is lacking even for the case of the bulk. In a previous paper we have presented an approximate treatment of the special case of a single electron in an otherwise empty conduction band [8]. The presented approach applies to the situation in a model-type ferromagnetic semiconductor film containing a single-nondegenerated s-like band. However, the approach as well as the obtained results are directly transferrable to the case of the multiband Kondo-lattice model applicable to a real ferromagnetic semiconductor film such as EuO.

Because of the empty conduction bands we are considering throughout the whole paper, the Hamiltonian (1) can be split into an electronic part, $\mathcal{H}_s + \mathcal{H}_{sf}$, and a magnetic part, $\mathcal{H}_f$, which can be solved separately [8]. For the magnetic subsystem $\mathcal{H}_f$ we employ an approach based on the random phase approximation (RPA) which has been described in detail in [6]. As the result one gets the layer- and temperature-dependent magnetizations of the local-moment system. These are depicted for EuO(100) films of various thicknesses in Fig. 1. For the respective calculations, the Heisenberg interactions have been approximated within the tight-binding approximation, taking into account the nearest and the next nearest neighbor interactions, with values for EuO of $J_1/k_B = 0.625$ K and $J_2/k_B = 0.125$ K, respectively [9]. The calculated Curie temperature converges as a function of film thickness in a manner similar to that found experimentally for Gd(0001) films [10]. Moreover, the calculated Curie temperature of a 20-layer EuO(100) film of 66.7 K approximates very well the experimental value of T_C for bulk EuO of 69.33 K [11].

For the electronic part a moment-conserving decoupling approximation (MCDA) for suitably defined Green functions is employed [8]. In the set of equations which constitute the solution for the electronic subsystem, there appear f-spin correlation functions which have to be evaluated within the magnetic subsystem [Eq. (3)]. These f-spin correlation functions mediate the temperature dependence of the electronic structure of the system.

For the limiting case of ferromagnetic saturation of the localized f-spin system ($T = 0$), there exists an *exact* solution for the FKLM with empty conduction band ($n = 0$) [12]. While the spin-↓ spectrum exhibits strong correlation effects, the spectrum of the spin-↑ electron is only rigidly shifted compared to the free solution obtained for the case of vanishing s-f interaction, $J = 0$. This means that the spin-↑ spectra obtained within a ferromagnetic band-structure calculation provide the single-particle input

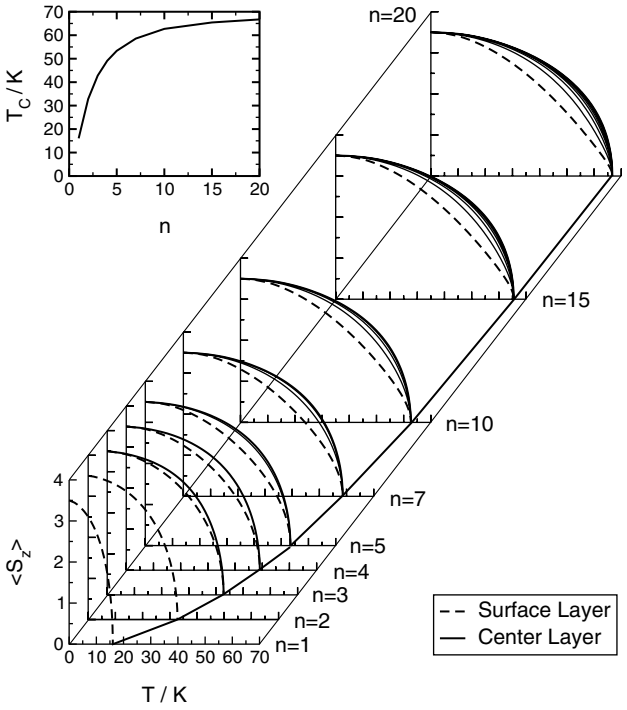

FIG. 1. Layer-dependent magnetizations, $\langle S_\alpha^z \rangle$, of EuO(100) films as a function of temperature for $J_1/k_B = 0.625$ K, $J_2/k_B = 0.125$ K, $D_0/k_B = 0.05$ K, for various thicknesses n of the films. Inset: Curie temperatures as a function of film thickness.

[cf. Eq. (2)] for the FKLM model calculation. Since the solution of the FKLM for $T = 0$ and $n = 0$ is exact, the problem of double counting of relevant interactions, which would normally occur when superimposing the results of a band-structure calculation with a model calculation, is elegantly avoided in the presented approach.

To obtain the temperature-dependent band structure of a EuO(100) film, the $T = 0$ band structures are needed as single-particle input for the model calculations. These have been calculated for the Eu-5d bands, which in EuO dominate the conduction band, using a standard tight-binding linear muffin-tin orbital program [13]. To account for the film geometry, we defined a supercell consisting of 20 EuO(100) layers followed by five layers of empty spheres, all equidistantly spaced. The lattice constant for the EuO(100) film has been chosen to be the lattice constant of bulk EuO, $a = 5.142$ Å [11]. In this approach we neglect surface relaxation and reconstruction, which might be present in EuO films.

Figure 2 shows the temperature- and spin-dependent local densities of states of the first, the second, and the center layer of a 20-layer EuO(100) film with an s-f exchange interaction of $J = 0.25$ eV. Here, as in Figs. 3 and 4 the energy zero refers to the Fermi energy of the system [14]. For $T = 0$, the spin-↑ and the spin-↓ spectra occupy the lowest and the highest energy range, respectively. With increasing temperature, the spectra for the two spin directions gradually approach each other until for $T = T_C$ ($\langle S_z \rangle / S = 0$, fat line) the spectra for both spin directions become the

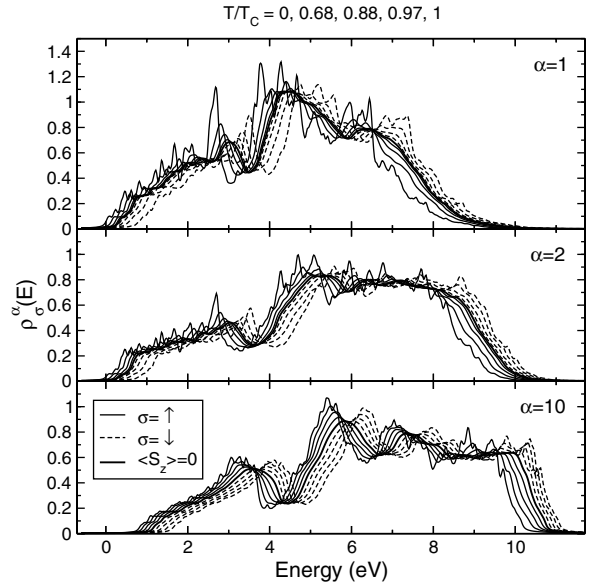

FIG. 2. Local densities of states of the empty Eu-5d bands of the first ($\alpha = 1$), second ($\alpha = 2$), and center ($\alpha = 10$) layers of a 20-layer EuO(100) film for different temperatures ($T_C = 66.7$ K). The energy zero refers to the Fermi energy [14].

same. As a result, the lower band edge of the spin-↑ bands is shifted towards lower energies when decreasing the temperature below T_C. This effect is known as the redshift of the optical absorption edge in bulk EuO [11]. The spin-↑ densities of state for $T = 0$ ($\langle S_z \rangle / S = 1$) are, except for constant energy shift, those obtained within the band-structure calculations, which is due to the lack of possibility for the spin-↑ electron to exchange its spin with the system of perfectly aligned local moments. However, the spin-↓ electron can flip its spin even for $T = 0$ by emitting a magnon and forming a polaronlike quasiparticle [8]. Hence, the spin-↓ spectra for $T = 0$ already exhibit correlation effects and differ from those of the band-structure calculations.

In Fig. 2 the lower band edges of the local densities of states of the surface layer ($\alpha = 1$) lie at lower energies than the respective local densities of state (LDOS) of the center layers and are even touching the Fermi energy, already indicating the existence of a surface state band at the lower edge of the Eu-5d bands and a possible surface insulator-metal transition. In the following, these interesting indicative observations are investigated in more detail.

In Fig. 3 the $T = 0$ local spectral density of the surface ($\alpha = 1$) and the center ($\alpha = 10$) layer of a 20-layer EuO(100) film can be seen for both spin directions. A surface state is a state which exists in the so-called forbidden region where no bulk states occur. For the bulk spectral density we take that of the center layer ($\alpha = 10$) of the 20-layer film (see Fig. 3). The forbidden regions lie below and above the bulk bands but also includes "white regions" right in the middle of the bulk bands. In this respect, in Fig. 3, clearly the lowest bands of the spin-↑ and of the spin-↓ spectral densities of the surface layer ($\alpha = 1$) around the Γ point and the M point constitute

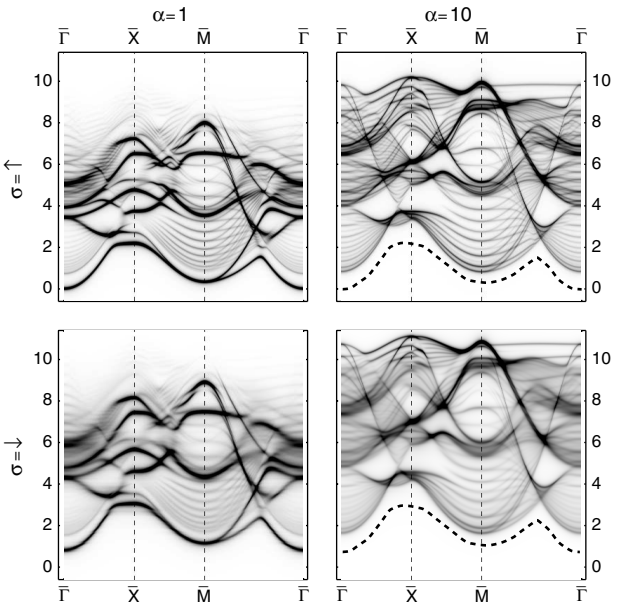

FIG. 3. Local spectral densities $S^{\alpha\alpha}_{\mathbf{k}\sigma}$ of the surface ($\alpha = 1$) and the center layer ($\alpha = 10$) of a 20-layer EuO(100) film for $T = 0$ and $J = 0.25$ eV. The dashed lines in the spectral densities for the center layers (right hand side) reproduce the positions of the lower band edges of the surface state bands as given by the spectral densities of the surface layers (left hand side). The energy zero refers to the Fermi energy.

surface state bands. These surface states originate from the local spin-density approximation calculation. With the s-f model calculation one can now investigate the temperature dependence of the surface state.

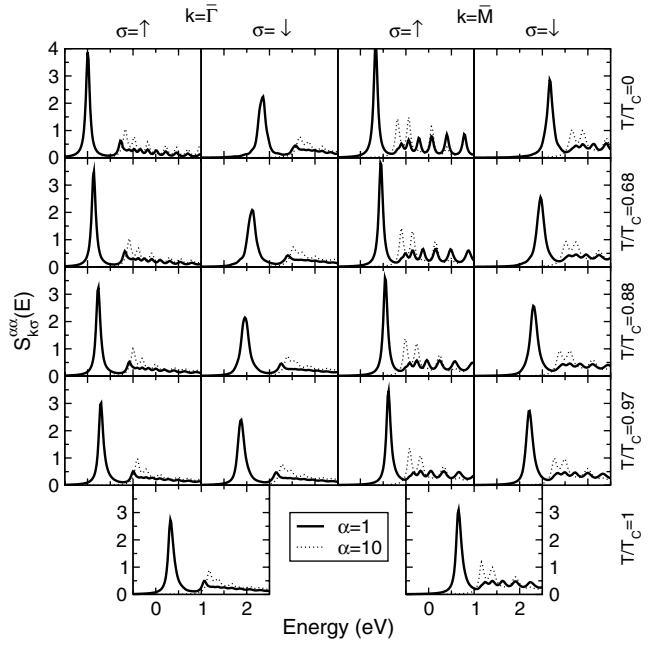

FIG. 4. Local spectral densities $S^{\alpha\alpha}_{\mathbf{k}\sigma}$ of the surface ($\alpha = 1$, solid lines) and the center layer ($\alpha = 10$, dotted lines) of a 20-layer EuO(100) film at the Γ point and the M point for $J = 0.25$ eV and for different temperatures ($T_C = 66.7$ K). The energy zero refers to the Fermi energy.

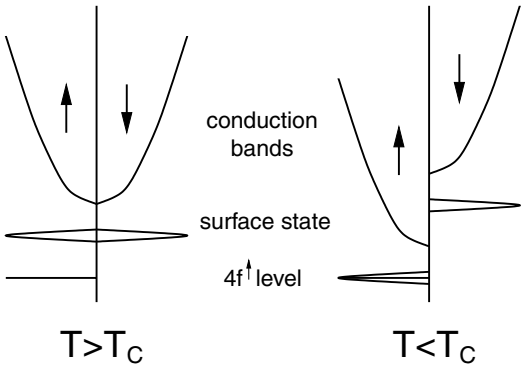

FIG. 5. Schematics of the surface (half)metal-insulator transition. For $T > T_C$ the Fermi energy (E_F) lies between the $4f^{\uparrow}$ levels and the surface state. For $T < T_C$ E_F lies within the spin-↑ surface state.

Figure 4 shows the spectral density of the surface layer of a 20-layer film at $\mathbf{k} = \bar{\Gamma}$ and $\mathbf{k} = \bar{M}$ for different temperatures. For comparison, the respective spectral densities of the center layer of the 20-layer films are plotted. The plotted spectral densities clearly indicate surface state bands. For $T = 0$ ($\langle S_z \rangle / S = 1$) the lower band edge of these surface state bands lies at the Γ point about 0.8 eV and at the $\bar{M}$ point about 0.45 eV below the lower conduction-band edge of the "bulk" bands of the central layer (cf. dashed line in Fig. 4). These splittings between the surface states and the lower edges of the bulk band are almost independent on the temperature. With increasing temperature both the surface states and the lower band edges of the bulk bands for the two spin directions converge Stoner-like.

As a result, the surface state does not change the down-shift of the lower band edge upon cooling below T_C (redshift) of the system. However, the lower band edge of the LDOS at the surface is lowered by about 0.8 eV compared to the bulklike LDOS in the center of the film. Thus, for the 20-layer EuO(100) film, the band gap between the occupied $4f^{\uparrow}$ bands and the unoccupied $5d_{t_{2g}}$ bands will be reduced by the same 0.8 eV. When decreasing the temperature to $T = 0$ the redshift will reduce the band gap further: by 0.35 eV according to our calculations and by 0.27 eV according to the experimental results [11]. The overall reduction of the $4f$-$5d_{t_{2g}}$ gap will amount to 1.15 eV and 1.07 eV, respectively. These values are exactly in the range of the experimental $4f$-$5d_{t_{2g}}$ gap of bulk EuO at 300 K of 1.12 eV [11]. These results indicate a possible surface insulator-metal transition in EuO(100) films as a function of decreasing temperature, $T \rightarrow 0$ (cf. Fig. 5). Because of the exchange splitting of the conduction bands into the lower-energetic spin-↑ band and the higher-energetic spin-↓ band the respective phase for $T \rightarrow 0$ would be a half-metal. As a result, the resistivity of the EuO(100) films should be highly dependent on an applied magnetic field and a colossal magnetoresistance effect would be observed.

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[14] The Fermi energy level has been determined by subtracting the experimental $4f$-$5d_{t_{2g}}$ gap of bulk EuO at 300 K of 1.12 eV [11] from the lower band edge of the center layer ($\alpha = 10$) of the 20-layer film at $T = T_c$.