Mott state and quantum critical points in rare-earth oxypnictides RO$_{1-x}$F$_x$FeAs (R = La, Sm, Nd, Pr, Ce)

Gianluca Giovannetti [a,b], Sanjeev Kumar [a,b], Jeroen van den Brink [a,c,*]

[a] *Institute Lorentz for Theoretical Physics, Leiden University, P.O. Box 9506, 2300 RA Leiden, The Netherlands*
[b] *Faculty of Science and Technology and MESA + Research Institute, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands*
[c] *Institute for Molecules and Materials, Radboud Universiteit Nijmegen, P.O. Box 9010, 6500 GL Nijmegen, The Netherlands*

ARTICLE INFO

ABSTRACT

We investigate the magnetic phase diagram of the newly discovered iron-based high temperature oxypnictide superconductors of the type RO$_{1-x}$F$_x$FeAs, with rare earths R = La, Sm, Nd, Pr and Ce by means of *ab initio* SGGA and SGGA + U density functional computations. We find undoped LaOFeAs to be a Mott insulator when incorporating electronic correlations via SGGA + U for any physically relevant value of U. The doped compounds are according to SGGA conductors with a transition from an antiferromagnetic to a nonmagnetic state at a hole doping of concentration $x_c = 0.075$ for R = Nd, Pr and at electron doping $x_c = 0.25$ for Ce and 0.6 for Sm. Superconductivity in these rare-earth oxypnictides thus appears in the vicinity of a magnetic quantum critical point where electronic correlations are expected to play an important role because of the vicinity of a Mott insulating state at zero doping.

© 2008 Elsevier B.V. All rights reserved.

0. Introduction

Very recently, more than two decades after the discovery of high temperature superconductivity in the cuprates [1], a new class of iron-based superconductors was discovered in the family of rare-earth oxypnictides [2,3]. The highest superconducting temperatures reported so far are for doped oxypnictides of the type RO$_{1-x}$F$_x$FeAs with R = Sm, Nd, Pr and Ce with the transition temperatures of T_c = 43, 52, 52 and 41 K, respectively [4–7]. The Sm compound synthesized under high pressure was recently reported [8] to have a T_c of 55 K. The lanthanum compound [2] has a significantly lower T_c of 26 K.

The electronic structure of these type of oxypnictides was first studied with density functional bandstructure methods by Lebègue [9], who investigated the related phosphide LaOFeP, a material with the same crystallographic structure as the iron arsenides. Even if this compound is build from layers containing formally Fe^{2+} ions, Lebègue showed that this oxypnictide is characterized by large intralayer Fe–P covalency. It was subsequently established that also the electronic bands of the arsenide materials are very similar to the ones in the phosphide [10,11]. The observed large iron 3d bandwidth ($\sim$4 eV) strongly reduces the tendency for Fe^{2+} to develop a magnetic moment. In the case of

LaOFeP this leads to the stabilization of a nonmagnetic metallic groundstate [9]. This result contrasts with recent first principles calculations on the arsenide compound LaOFeAs. This material was found to be an antiferromagnetic conductor. It was put forward that in the arsenide a spin density wave groundstate forms due to the presence of Fermi surface nesting [12–15]. Here we show that electronic correlations, incorporated within SGGA + U drastically change this picture: for physically relevant values of U LaOFeAs is a magnetic Mott insulator.

The fact that the closely related iron–phosphide and arsenide have different magnetic groundstates, suggests that at zero temperature these materials could be close to an antiferromagnetic—paramagnetic phase transition of the iron 3d moments—a quantum critical point. Our SGGA *ab initio* density functional calculations confirm that indeed in the rare-earth oxypnictides with a high superconducting transition temperature, RO$_{1-x}$F$_x$FeAs with R = Pr, Nd, Sm and Ce, such a quantum critical point is present. In the doped compounds superconductivity appears in the vicinity of this quantum critical point.
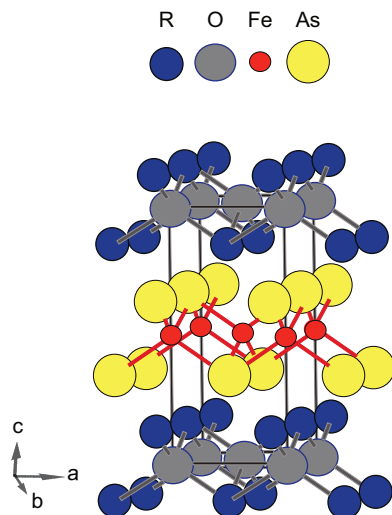
1. Crystal structure

The ROFeAs compounds have a ZrCuSiAs type structure, characterized by the presence of Fe–As layers, where Fe is in the center of corner sharing As tetrahedra, see Fig. 1. We compute the relaxed atomic positions, the electronic and the magnetic

* Corresponding author at: Institute Lorentz for Theoretical Physics, Leiden University, P.O. Box 9506, 2300 RA Leiden, The Netherlands.
E-mail address: brink@ilorentz.org (J. van den Brink).

structure of these systems within the framework of the density functional theory [16,17] using the Vienna *ab initio* simulation package (VASP) [18]. The Kohn–Sham equations in the self-consistent calculations were solved within a spin generalized gradient approximation (SGGA) for the electronic exchange-correlation potential (PW91 functional [19]). For the undoped material electronic correlations in the Fe 3d-shell were accounted for within SGGA + U [20,21]. The electronic structure is computed using the projector augmented wave method (PAW [22,23]), and the valence pseudo-wave functions are expanded in a plane wave basis set with a cutoff energy of 500 eV. All the integrations in the Brillouin zone are performed with a tetrahedron scheme [24] using a sampling grid of $12 \times 12 \times 6$ k-points and convergency was checked by performing a number of calculations also with a denser grid of k-points.

The calculations for ROFeAs (R = La, Sm, Nd, Pr, and Ce) were performed using the experimental lattice parameters [25]. In cases for which experimental values for the atomic positions within the unit cell are not available, we computed those by minimizing the total energy of the paramagnetic state until the relative changes in energy were less than 10^{-7}. The combined results are summarized in Table 1. We also computed the relaxed structure in the antiferromagnetic state and within the numerical accuracy we find no differences in atomic positions. The electronic bandstructures of these systems that we calculated are very similar to the one of LaOFeAs [10–14]. Besides the magnetism caused by the iron 3d moments that is present in all the FeAs systems that we have studied, there is another contribution to the magnetism from the open 4f-shells of the rare-earth ions, except for lanthanum. A magnetic interplay between those subsystems can certainly occur, although probably only at very low tempera-

tures as the rare-earth magnetism is generally much weaker than the 3d one. Here we wish to focus on the magnetism of the Fe–As subsystem and therefore treat the rare-earth 4f electrons in the computations as core electrons, so that they fulfill their role as electron donors but preempting their contribution to magnetism.
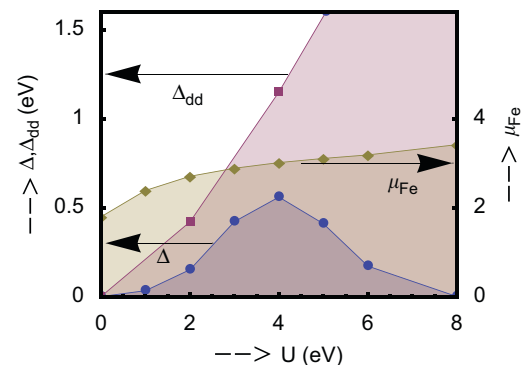
2. Electronic and magnetic structure of LaOFeAs

For the undoped ROFeAs compounds we find with SGGA that R = Nd and Pr are nonmagnetic, while Sm, Ce and La are antiferromagnetic, with iron moments of 1.08, 0.66 and $1.62\mu_B$, respectively. We also established the validity of the premise of earlier computations that the related iron phosphide LaOFeP is nonmagnetic [9]. However, it is well known that in materials containing transition metal ions with open 3d-shells electronic correlations play an important role. We therefore also compute the electronic structure for LaOFeAs with SGGA + U. In recently studied iron compounds the physical relevant values of U are between 4 and 6 eV; examples are Fe_3O_4 (5 eV [28]), Fe_2OBO_3 (5.5 eV [29]), FeO (4.3 eV, [30]) and Fe_2SiO_4 (4.6 and 4.9 eV, [30]).

The "striped" magnetic state (with ordering vector $(\pi, 0)$ on the squared lattice of iron atoms within the FeAs plane) we find in all cases to be the groundstate, in agreement with experimental observations [14,26,27]. In this magnetic phase already for very small values of U the system develops a Mott gap, see Fig. 2. We find for instance for U = 1 eV that $\Delta = 33$ meV. In the range of U between 4 and 6 eV, the Mott gap is around 400–550 meV.

A remarkable feature is that the gap closes for large values of U, around 8 eV. This contrast with our finding that with increasing U the splitting of the iron d-bands increases, as is clear from the value of the splitting between the occupied and empty Fe 3d-bands Δ_{dd} shown in Fig. 2. We obtain Δ_{dd} by computing the dominant character of the bands. From this one can estimate Δ_{dd}, but as bands by definition have a mixed character it is not rigorously defined. This analysis clearly shows that the reason for the closing of the gap Δ for large U is that arsenic bands are pushed out of the conduction and valence bands when U increases. It is evident in the bandstructure and densities of states that these As bands, hybridized with the Fe 3d states, start filling up the d–d gap.

The bandstructure for U = 0 and 4 eV is plotted in Fig. 3. The bands and the densities of states (DOS) in Fig. 4 reveal that the Hubbard U splits the 3d states into three sets of bands: a set of bands (I) below 4 eV, a set of bands, (II) at the top of the valence band and (III) at the bottom of the conduction band. We note that there is an anomalously large splitting between sets I and III of

Fig. 1. Schematic view of the crystal structure of ROFeAs consisting of layers of corner connected $FeAs_4$ tetrahedra (red/yellow) and RO_4 tetrahedra (blue/gray).

Table 1
Lattice constants and unit cell parameters of ROFeAs [25,7], with the experimental z_R and z_{As} for La [2] and values computed by relaxation otherwise

	a (Å)	c (Å)	z_R	z_{As}
SmOFeAs	3.940	8.496	0.1299	0.6402
NdOFeAs	3.965	8.575	0.1427	0.6437
PrOFeAs	3.985	8.595	0.1444	0.6417
CeOFeAs	3.996	8.648	0.1462	0.6426
LaOFeAs	4.038	8.753	0.1415	0.6512

Fig. 2. Gaps Δ and Δ_{dd} of LaOFeAs in the magnetic "stripe" phase from SGGA + U as a function of U. Δ is the gap between top of the valence and bottom of the conduction band. For large values of U, arsenic bands appear in the gap and closes it. Δ_{dd} is the splitting between the occupied and empty Fe 3d-bands. Also the local iron moment is shown.