High Temperature Superconductivity in Transition Metal Oxypnictides: a Rare-Earth Puzzle?

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We have performed an extensive *ab initio* LDA and LSDA+U calculations of electronic structure of newly discovered high-temperature superconducting series $ReO_{1-x}F_xFeAs$ (Re=La,Ce, Pr, Nd, Sm and hypothetical case of Re=Y). In all cases we obtain almost identical electronic spectrum (both energy dispersions and the densities of states) in rather wide energy interval (about 2 eV) around the Fermi level. We also debate that this fact is unlikely to be changed by the account of strong correlations. It leads inevitably to the same critical temperature T_c of superconducting transition in any theoretical BCS-like mechanism of Cooper pair formation. We argue that the experimentally observed variations of T_c for different rare-earth substitutions are either due to disorder effects or less probably because of possible changes in spin-fluctuation spectrum of FeAs layers caused by magnetic interactions with rare-earth spins in ReO layers.

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The recent discovery of the new superconductor $LaO_{1-x}F_xFeAs$ with the transition temperature T_c up to 26K [1, 2, 3, 4] has been immediately followed by the reports of even higher T_c =41K in $CeO_{1-x}F_xFeAs$ [5], T_c =43K in $SmO_{1-x}F_xFeAs$ [6] and T_c =52K in $NdO_{1-x}F_xFeAs$ and $PrO_{1-x}F_xFeAs$ [7, 8]. A number of other element substitutions were studied producing compounds with rather wide interval of T_c values [9]. These discoveries of the whole new class of superconductors, based on doped layered oxypnictides ReOMPn (Re=La,Ce,Pr,Nd,Sm,Gd; M=Mn,Fe,Co,Ni,; Pn=P,As), open the new chapter in studies of high-temperature superconductivity outside the well-known domain of copper oxides. Of course, at the moment, the microscopic nature of superconductivity in these compunds remains unclear, though a number of aspects of this has already been discussed [10, 11, 12, 13, 14, 15].

The LDA electronic structure and phonon spectrum of LaFeAsO were first calculated in Ref. [16] (see also [10]). These were extended to an account of strong electronic correlations on Fe via LDA+DMFT in Ref. [17]. Spin polarized LDA calculations for LaFeAsO with antiferromagnetic ordering in the ground state were done in Refs. [18, 19]. First principles (FLAPW) calculations of the doping dependent phase diagram of LaO-MAs (M=V-Cu) were performed in Ref. [20].

Here we present the results of an extensive *ab initio* calculations of electronic structure of newly discovered high-temperature superconducting series $ReO_{1-x}F_xFeAs$ (Re=La, Ce, Nd, Pr, Sm and hypo-

thetical case of Re=Y) within LDA and LSDA+U frameworks.

Table 1. Combined list of experimental and calculated parameters for ReOFeAs systems.

ReOFeAs	La	Ce	Pr	Nd
T_c, K	26	41	52	51.9
a, Å	4.035334	3.996	3.9853	3.940
c, Å	8.740909	8.648	8.595	8.496
Source	Ref. [1]	Ref. [5]	Ref. [8]	Ref. [6]
LDA N_{E_f}, states/Ry/cell	56.19	56.51	52.1	54.21

According to the experimental data all ReOFeAs (Re=La, Ce, Pr, Nd, Sm) compounds have (at room temperature) well defined tetragonal ZrCuSiAs-type crystal structure with the P4/nmm space group. The structure of iron oxypnictides is formed by FeAs layers sandwitched between LaO layers. These two layers are separated by a distance of 1.8 Å. The nearest neighbors of Fe ions are four As ions which form a tetrahedron. The crystal structure of LaOFeAs is shown in Fig. 1. The values of experimentally obtained lattice constants for different known rare-earth substitutions are presented in Table 1. As the atomic number of rare-earth element increases the lattice constants decrease indicating the contraction of the cell due to the lanthanoid compression effect. The systematic decrease of the lattice constants was also observed for F$^-$ substitution to the site of O^{2-} ions [1].
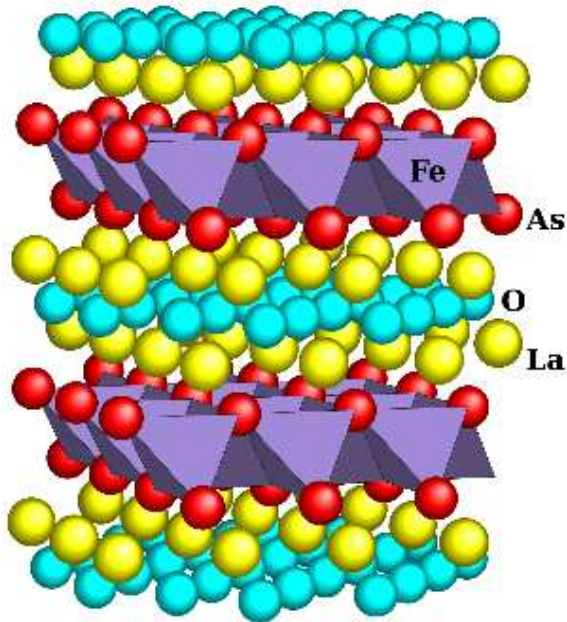
Fig. 1. Tetragonal crystal structure of LaOFeAs compound. FeAs layers are formed by Fe ions tetrahedraly surrounded by As ions.

The electronic structure of ReOFeAs (Re=La, Ce, Pr, Nd, Sm and Y) compounds was calculated in the local (spin) density approximation (L(S)DA) and LSDA+U [21] method by using linearized muffin-tin orbitals (LMTO) [22]. The details of the atomic spheres radii and LMTO basis set used in the calculation are given in the Table 2. Since the experimental data for atomic coordinates are limited, in the case of Ce, Pr, Nd, Sm and Y systems we used the same z_{Re} and z_{As} as for the LaOFeAs compound: z_{La}=0.141545, z_{As}=0.65122 [1].To our knowledge there is no experimental data for the lattice parameters and atomic coordinates for SmOFeAs. Thus for SmOFeAs we use the same lattice parameters and atomic positions as for Nd system. The hypothetical compound with yttrium is not synthesized yet and for its electronic structure calculation we exploit the data for La compound from Ref. [1]. We also keep fixed the radii of atomic spheres of Fe, As and O across the series. The f-states of rare-earths were treated as a pseudocore states. The Brillouin zone was sampled using 20 irreducible **k** points.

The obtained LDA bands along high symmetry lines of the Brillouin zone and density of states (DOS) for pure LaOFeAs and PrOFeAs superposed with each other are shown in Fig. 2 and Fig. 3, correspondingly. Both density of states and band structure are in good agreement with the more accurate calculation within full potential linearized augmented planewave (LAPW)

Table 2. Details of LMTO calculations for ReOFeAs (Re=La, Ce, Pr, Nd, Sm, Y).

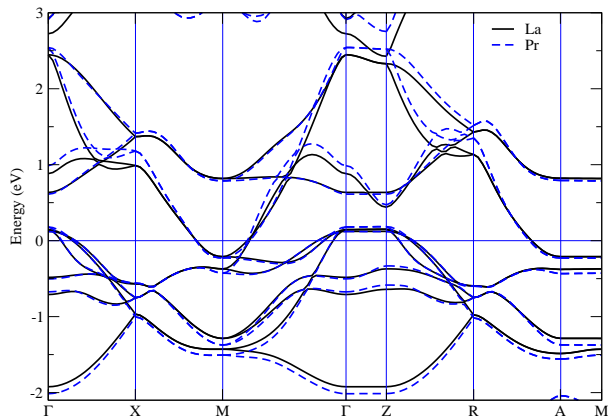| type of atom	LMTO basis	R_{AS}, Å
La	$6s5d4f$	1.63
Ce	$6s5d4f$	1.61
Sm	$6s5d4f$	1.59
Nd	$6s5d4f$	1.62
Pr	$6s5d4f$	1.625
Y	$5s4d$	1.637
Fe	$4s4p3d$	1.377
As	$4s4p$	1.42
O	$3s2p$	1.09

Fig. 2. LDA energy bands for LaOFeAs (solid lines) and PrOFeAs (dashed lines) compounds. The Fermi level corresponds to zero.

method using WIEN2k package [23, 24]. The only significant change in spectra to a substitution of different rare-earths reduces to the increase of the size of tetrahedral splitting because of lattice contraction. One can see these effects at about -1.5 eV for Fe-d states, -3 eV for As-p (Figs. 3, 4).

These results clearly show that electronic structure of ReOFeAs compounds (e.g. DOS around the Fermi level, see Table 1) practically does not depend on the kind of rare-earth ion (Re) used in a wide energy interval around the Fermi level, which is relevant for superconductivity in FeAs layers. This simply follows from the fact that electronic states of ReO layers are rather far from the Fermi level. Thus there is almost negligible hybridization between Fe-d and O-p electronic states as illustrated by partial DOS contributions shown in Fig. 3. Within FeAs layers however there is quite sizeable hybridization between Fe-d and As-p. Smaller but still
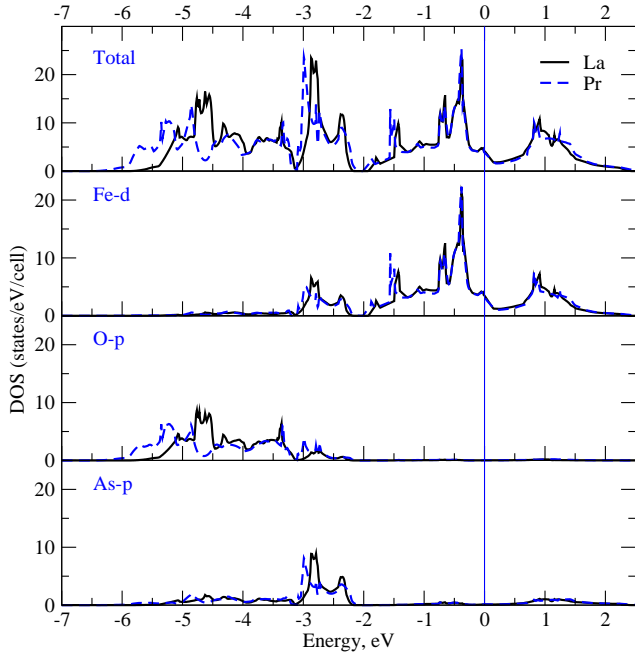
Fig. 3. Total and partial LDA DOS for LaOFeAs (solid lines) and PrOFeAs (dashed lines) compounds. The Fermi level corresponds to zero.
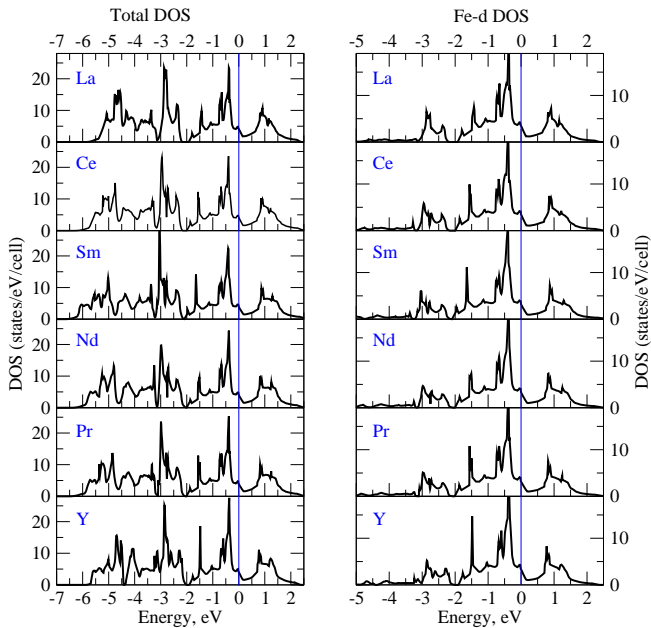

Fig. 4. Total (left) and partial Fe-d (right) LDA DOS for series ReOFeAs systems. The Fermi level corresponds to zero.

finite hybridization between O-p and As-p is obtained. Therefore the ReOFeAs systems can be considered as

quasi-two-dimensional which is similar to the case of conventional high-T_c cuprates.

Similarity of compounds within ReOFeAs series is unlikely to be changed by the account of strong electronic correlations on Fe, along the lines of Ref. [17], since only bare Fe bands are important in such type of calculations. In Fig. 4 we show that no substantial modifications of Fe-d electronic states close to the Fermi level are found due to rare-earths substiutions. But one can in principle expect that interplay of orbital degrees of freedom within Fe-d shell because of different tetrahedral splitting might affect DOS value on the Fermi level within multi-orbital Hubbard model. However no such effects has been reported in Ref. [17].
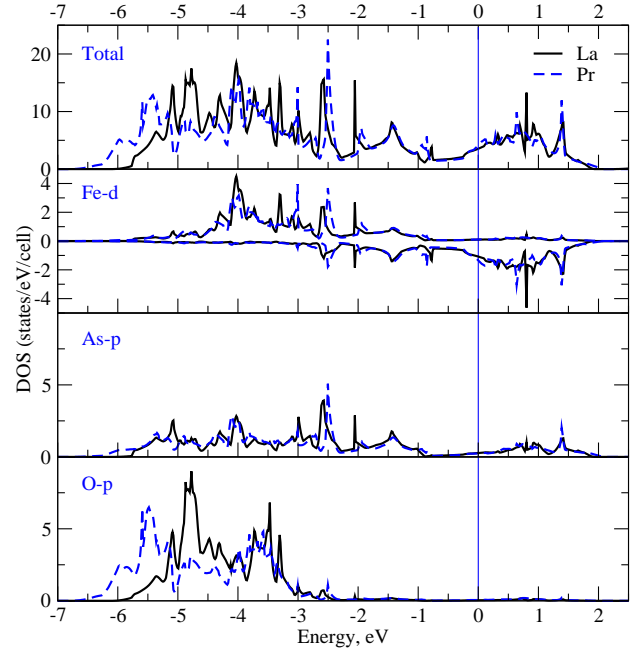

Fig. 5. Total and partial LSDA+U DOS for LaOFeAs (solid lines) and PrOFeAs (dashed lines) compounds. The Fermi level corresponds to zero.

Also we performed LSDA and LSDA+U calculation for collinear antiferromagnetically ordered Fe ions in FeAs plane. Spins were directed perpendicular to the FeAs plane. Values of Coulomb interaction U and Hund exchange J were taken 3 and 1 eV respectively. Corresponding LSDA+U DOS for LaOFeAs and PrOFeAs compounds are presented in Fig. 5. Here one can say that any kind of spin-polarized LSDA or LSDA+U type of calculations do not make these compounds remarkably different. Our results are in good agreement with Refs. [18, 19]. Also one can mention that for all systems we obtained half-metallic LSDA+U solution.

We also have done LSDA+U calculations with AFM ordered Re ions, while Fe ions were not magnetic. We have found that rather large magnetic moments of Re ions have alsmost no effect on FeAs layer. Namely no magnetization of FeAs layer induced by Re ions is observed.

Thus, situation with rare-earth ions in ReOFeAs system seems in many respects quite similar to that in $ReBa_2Cu_3O_{7-x}$ series of copper oxide superconductors, studied in the very early days of high-T_c research in cuprates [25, 26]. In this series, the electronic states of rare-earth ions also just do not overlap with electronic states of CuO_2 conducting planes. This leads to the well established fact of almost complete independence of superconducting $T_c \sim 92K$ on the type of the rare-earth ion for the case of Re=Y,Nd,Sm,Eu,Gd,Ho,Er,Tm,Yb,Lu,Dy [25], with only two exceptions – the much lower value of $T_c \sim 60K$ in the case of La and no superconductivity in the very special case of Pr [26].

Almost identical electronic structure of Fe oxypnictides ReOFeAs with different rare-earth substitutions in a wide energy range around Fermi level should inevitably lead to practically the same values of superconducting transition temperature T_c in any kind of BCS-like pairing mechanism. Rare-earths just do not influence electronic structure of FeAs layers due to a very small overlap of appropriate electronic states. Thus, no significant change of pairing interaction constant should be expected. There is no serious reason to expect any significant change of phonon's spectrum due to the rare-earth substitution either as well as spin fluctuation spectrum in FeAs layers.

Thus we have a kind of a rare-earth puzzle! In contrast to $ReBa_2Cu_3O_{7-x}$ series of copper oxides experimental data of Refs. [5, 6, 7, 8, 9] show that the rare-earth substitutions in ReOFeAs series lead to rather wide range of T_c - from about 10 K in case of Gd up to 52 K in case of Nd and Pr systems. Two possible explanations of this puzzle seem feasible at the moment:

(i) Different quality of samples (disorder effects) may lead to a wide range of T_c, as disorder usually leads to a strong suppression of exotic types of pairing (e.g. anisotropic p- or d-wave, triplet pairing, etc.), which are discussed now for ReOFeAs series [11, 12, 13, 14]. In general, situation here is qualitatively similar to the case of copper-oxides, where d-wave pairing is strongly suppressed by disorder (see e.g. [27]). Similar argument is usually used to explain typically lower values of T_c in $LaBa_2Cu_3O_{7-x}$ as due to disorder in La and Ba positions and oxygen vacancies [26]. This stresses the importance of systematic studies of disorder effects in the new class of ReOFeAs high-T_c superconductors.

(ii) Basically, spin-ordering effects of rare-earths (like Ce, Pr, Nd, Sm, Gd possessing localized spin moment) may, in principle, induce a change of spin fluctuation spectrum (and T_c) due to magnetic interaction between rare-earths and FeAs layers (in case of spin-fluctuation mechanism of pairing, as discussed e.g. in Refs. [11, 12]). However, these interactions are most probably rather weak, as illustrated by our LSDA+U calculations. Still, these effects are worth studying since the situation with rare-earth spins ordering is at present unclear from the experimental point of view.

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