

Electronic Structure of New AFeAs Prototype of Iron Arsenide Superconductors

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This work is provoked by recent discovery of new class prototype systems AFeAs (A=Sr,Ca) of novel layered ironpnictide High- T_c superconductors ($T_c = 36$ K). Here we report *ab initio* LDA results for electronic structure of the AFeAs systems. We provide detailed comparison between electronic properties of both new systems and reference LaOFeAs (La111) compound. In the vicinity of the Fermi level all three systems have essentially the same band dispersions. However for iron fluoride systems F($2p$) states were found to be separated in energy from As($4p$) ones in contrast to La111, where O($2p$) states strongly overlaps with As($4p$). Thus it should be more plausible to include only Fe($3d$) and As($4p$) orbitals into a realistic noninteracting model than for La111. Moreover Sr substitution with smaller ionic radius Ca in AFeAs materials leads to a lattice contraction and stronger Fe($3d$)-As($4p$) hybridization resulting in smaller value of the density of states at the Fermi level in the case of Ca compound. So to some extent Ca system reminds RE111 with later Rare Earths. However Fermi surface of new fluorides is found to be nearly perfect two-dimensional. Also we do not expect strong dependence of superconducting properties with respect to different types of A substitutes.

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At the beginning of 2008 new layered ironpnictide High- T_c superconductors were found. Up to now there are known several classes of such systems. Following the order of discoveries: 1. Re111 (Re=La,Ce,Pr,Nd,Sm) with parent compound $\text{LaO}_{1-x}\text{F}_x\text{FeAs}$ and T_c about 40–55 K [1–8]; 2. A122 (A=Ba, Sr) with parent system $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$ [9–12] and T_c about 38 K; 3. $\text{Li}_{1-x}\text{FeAs}$ with $T_c = 18$ K [13, 14]. Recently a new prototype material SrFeAs was reported [15, 16]. This system has characteristic for ironarsenides SDW anomaly at about 175 K. Later on this system doped with Co showed superconductivity at $T_c \sim 5$ K [17]. Finally for the system $\text{Sr}_{1-x}\text{La}_x\text{FeAs}$ superconductivity with $T_c = 36$ K was obtained by Zhu et al. [18]. Also Zhu et al. [18] provide some crystallographic and resistivity data on CaFeAs and EuFeAs compounds. Inspired by this new step of ironpnictides developments we continue our work on these materials [19–21] and propose here first principle investigation of electronic structure of fluoride compounds.

LDA (local density approximation) calculated electronic structure of La111 was addressed in Refs. [22–24] and is related with one for LaOFeP [25]. Investigation of RE111 series showed band structure to be insensitive to the type of a Rare Earth [19]. Comparative study of electronic properties of other prototype systems BaFe_2As_2 [26, 27] and LiFeAs is presented in Refs. [20, 21].

The manuscript is organized as follows: first we describe crystal structure of (Sr,Ca)FeAs compounds and computational details. Then we provide circumstantial comparison between La111 [19] and both Sr and Ca compounds with respect to the LDA computed band dispersions, total, partial and orbitally resolved densities of states. Short summary finalize our paper.

1. Crystallographic and computational details. First crystal structure data for SrFeAs were reported by Tegel et al. [15]. As well as other FeAs-systems [1, 28, 13] SrFeAs has tetragonal structure with the space group $P4/nmm$. Lattice parameters are $a = 3.9930(1)$ Å and $c = 8.9546(1)$ Å [15]. Atoms occupy following Wyckhoff positions [15, 29]: F(2a) (0.75,0.25,0), Fe(2b) (0.75, 0.25, 0.5) and Sr(2c) (0.25,0.25,0.1598), As(2c) (0.25,0.25,0.6527). This crystal structure was confirmed by several groups [16–18]. Also Zhu et al. [18] determined lattice parameters of CaFeAs as $a = 3.879$ Å, $c = 8.601$ Å. In Ref. [18] no analysis of atomic positions for Ca system was given. Thus for the time being in our calculations for Ca compound we use the same atomic positions as for Sr one. General appearance of the Sr(Ca)FeAs crystal structure is similar to one of La111 and so we refer reader to the Refs. [19, 20].

Main building blocks of new Sr and Ca systems are AF and FeAs tetrahedra layers with combined cation state “+1” and “-1” correspondingly. To this end AF

layer is equivalent to the REO layer of RE111 systems [1]. However larger ionic radius of Sr in comparison with, for example, La, gives sizeable expansion along c -axis of SrFFeAs structure, while a and b are almost not affected. Smaller ionic radii of Ca results in lattice contraction of CaFFeAs relative to Sr one. Nevertheless c lattice parameter of CaFFeAs is of the same size as for PrOFeAs compound [8]. Physically important interatomic distances within FeAs₄ tetrahedron layer Fe-Fe and Fe-As are practically identical to those of La111.

Linearized muffin-tin orbitals method (LMTO) [30] was employed to calculate electronic structure of Sr(Ca)FFeAs compounds.

2. Results and discussion. Upper panel of Fig.1 shows comparison of band dispersions obtained within LDA for new SrFFeAs (black lines) compound with one recently published for La111 [19] (gray lines). Bands crossing Fermi level are essentially identical for both compounds and belong to Fe(3d) states (from -2 eV to 2.5 eV). Main difference comes in the region of As(4p) states (-5.5 eV to -2 eV). Here for La111 As(4p) and O(2p) states are essentially overlapped. For SrFFeAs As(4p) states stay still in interval $(-5.5; -2)$ eV but F(2p) states are completely separated from them in energy and are located below between -7.5 and -6 eV.

In the lower panel of Fig.1 we compare band dispersions of Ca (gray lines) and Sr (black lines) iron fluorides. Band structure of both systems reminds each other. Again bands crossing Fermi level for Ca compound do not change much from those of Sr one. However because of lattice contraction and thus stronger hybridization effects Fe(3d) band for CaFFeAs is slightly wider. For the same reason As(4p) bands are slightly lower in energy than for Sr material. The F(2p) bands are most affected by both lattice contraction and Sr to Ca substitution. First one leads to about 1 eV broadening second one to the energy elevation. So after all F(2p) bands somewhat intersect with As(4p) bands. One can note that to some extent difference between Sr and Ca iron fluorides resembles very much difference between La111 and Pr111 iron arsenides (see Ref. [19]) although former one is larger and not that uniform.

Fig.2 displays direct matching of LDA calculated DOS of Sr (solid black line) and Ca (dashed black line) iron fluorides with La111 (gray line) [19]. Upper panel contains total DOS of all three systems. The values of total DOS on the Fermi level are 3.65 state/eV/cell for CaFFeAs, 4.27 state/eV/cell for SrFFeAs and 4.01 state/eV/cell for reference La111 system, i.e. are only slightly different from each other.

In the energy interval of Fe(3d) states DOSes of all compounds are rather repetitive (see also next from top

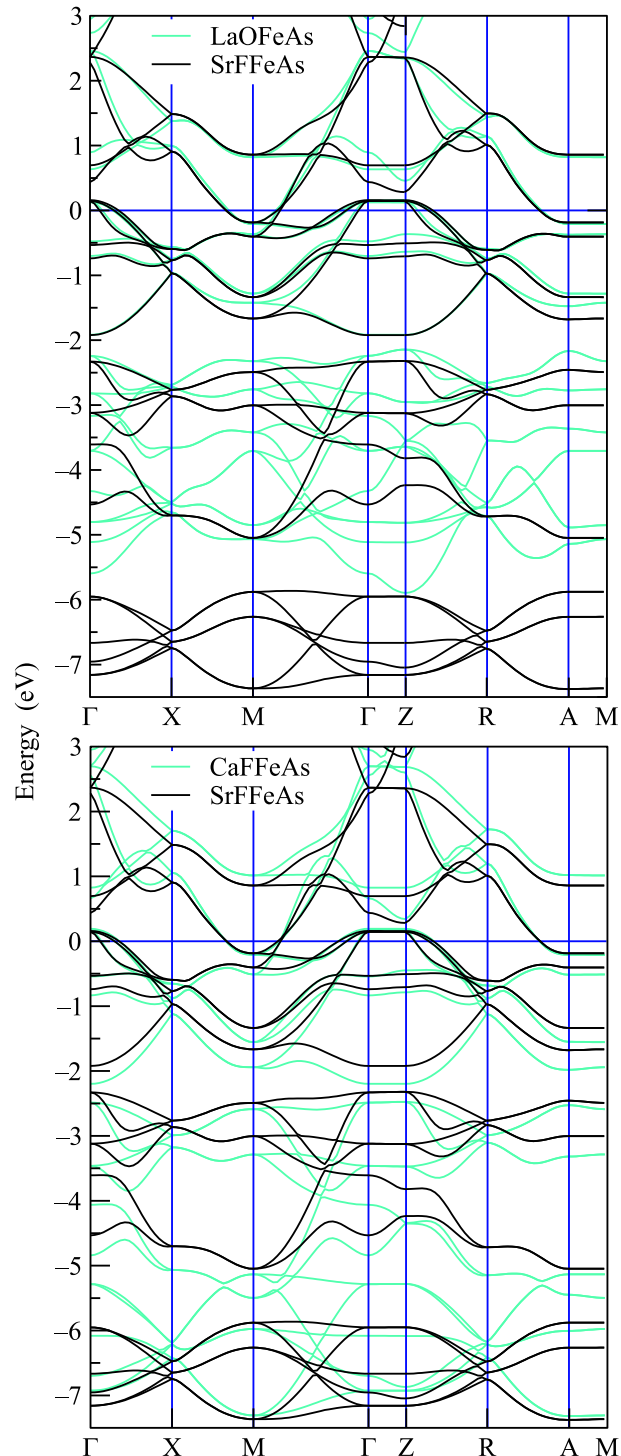


Fig.1. Comparison of LDA band dispersions for La111 (wide gray lines) and SrFFeAs (black lines) on the upper panel and for CaFFeAs (wide gray lines) and SrFFeAs (black lines) on the lower panel. The Fermi level corresponds to zero

panel of Fig.2). Moderate hybridization is observed between Fe(3d) and As(4p) states for both fluorides and practically no hybridization between Fe(3d) and F(2p)

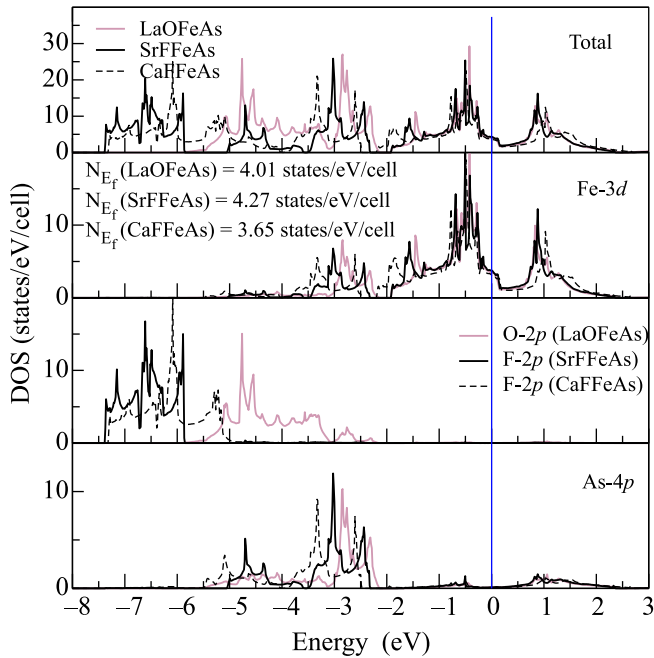


Fig.2. Comparison of LDA calculated total and partial DOS for SrFeFeAs (solid black line), CaFeFeAs (dashed black line) and La111 [19] (gray line). Panels from top to bottom: total DOS, Fe(3d), O(2p) and F(2p), As(4p). The Fermi level corresponds to zero

as well as between As(4p) and F(2p) states (see next from bottom panel of Fig.2). For the Sr compound fluorine 2p states are observed to be separated from all Fe(3d) and As(4p) states. And for the case of Ca system F(2p) state touch As(4p) ones.

Finally we present orbitally resolved Fe(3d) DOS for Sr and Ca iron arsenide-fluorides in Fig.3. Bird eye picture looks like the one for La111 (see Ref. [20]): Fermi level is crossed by bands of predominantly t_{2g} symmetry $-xz, yz, x^2-y^2$ (later because of $\pi/4$ rotation of local coordinate system around c -axis). Nevertheless there are several fine distinctions with La111. The x^2-y^2 orbital is strongly changed around 0.5 eV. Some changes can be seen also for $3z^2-r^2$ orbital around -0.5 eV and xz, yz orbitals around -1.5 eV (see also Fig.1, upper panel). The same is valid also for Ca system except some bands broadening. By looking on the Fig.3 one can also understand lowering of the total density of states for Ca system with respect to Sr one mentioned above. Largest contribution to the DOS at the Fermi level comes from the x^2-y^2 orbital for all of FeAs systems [19, 20, 21]. Because of stronger Fe-As hybridization it becomes wider and at the same time lower in intensity to keep normalization.

In Fig.4 the Fermi surface (FS) of the new Sr fluoride system is compared with that of LaOFeAs [20]. Most important contrast to La111 FS is nearly perfect

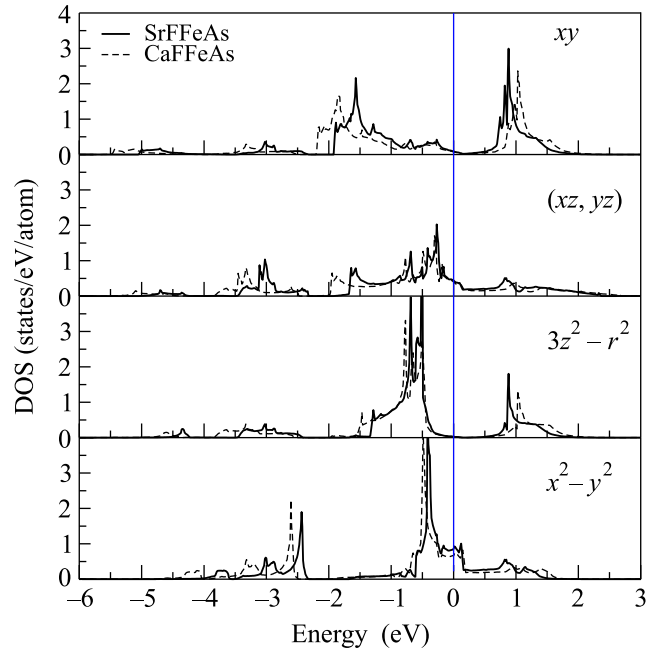


Fig.3. Comparison of LDA orbitally resolved Fe-3d DOS for SrFeFeAs (solid line) and CaFeFeAs (dashed line). The Fermi level corresponds to zero

two-dimensional character of the FS of SrFeFeAs. All cylinders are practically ideal especially two large ones around Γ -point. FS for Ca fluoride system is practically identical to that of Sr fluoride and we do not show it here.

3. Conclusion. LDA calculated electronic structure of new AFeAs (A=Sr,Ca) prototype of novel high- T_c ironpnitides superconductors is presented here in comparison with previously calculated [19, 20] for LaOFeAs material. Despite different chemical contents new systems and La111 have identical crystal structures. Thus in fluoride systems electronic properties are also determined by two-dimensional FeAs₄ layers as well. However LDA obtained Fermi surface of new fluorides is the most two-dimensional one among other known ironpnitides. Main distinction of fluoride systems from La111 is energy separation between F(2p) state and As(4p) states. Also practically no hybridization of F(2p) and As(4p) or Fe(3d) states is observed. It makes non interacting realistic model of fluorides including only As(4p) and Fe(3d) states well justified and easier to construct. The CaFeFeAs with contracted lattice (since Ca ion is smaller) to some extent reminds RE111 systems with later RE. In this work we do not observe any significant difference of electronic structure of new fluorides and La111 close to the Fermi level, thus we do not expect any remarkable changes of superconducting properties with respect to different A substitutes. Lower values of DOS at the

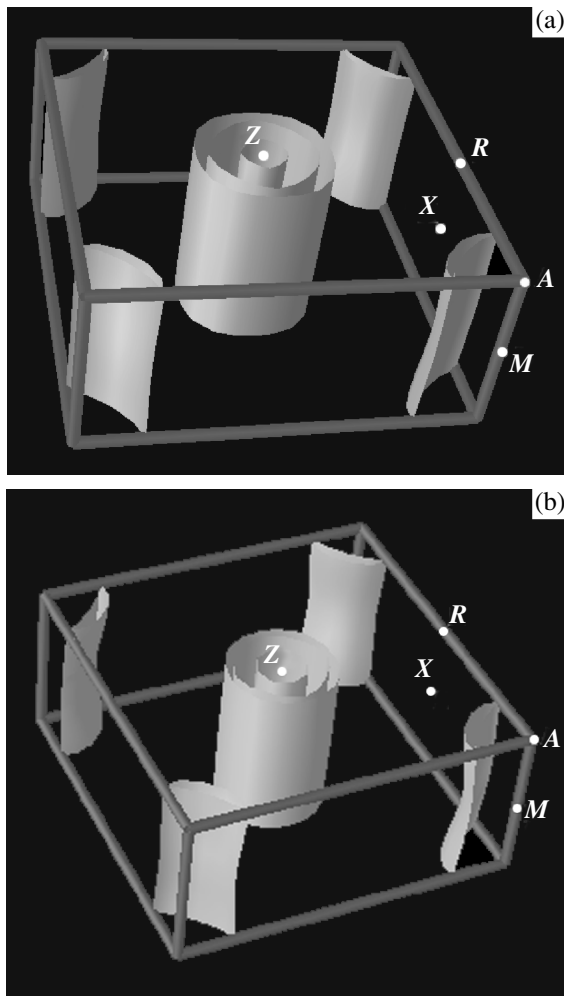


Fig.4. Comparison of LDA calculated Fermi surfaces for SrFFeAs (upper panel) and LaOFeAs (lower panel)

Fermi level for Ca compound probably makes it slightly less promising in this respect.

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