Electronic structure of new oxygen-free 38 K superconductor Ba$_{1-x}$K$_x$Fe$_2$As$_2$ in comparison with BaFe$_2$As$_2$ from first principles

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Based on first-principles FLAPW-GGA calculations, we have investigated the electronic structure of the newly discovered oxygen-free 38 K superconductor Ba$_{1-x}$K$_x$Fe$_2$As$_2$ in comparison with a parent phase – the tetragonal ternary iron arsenide BaFe$_2$As$_2$. The density of states, magnetic properties, near-Fermi bands compositions, together with Sommerfeld coefficients $\gamma$ and molar Pauli paramagnetic susceptibility $\chi$ have been evaluated. The results obtained allow us to classify these systems as quasi-two-dimensional ionic metals, where conduction is strongly anisotropic, happening only in the (Fe-As) layers. According to our calculations, in the case of hole doping of BaFe$_2$As$_2$, the density of states at the Fermi level grows, which, possibly, may be a factor promoting the occurrence of superconductivity for Ba$_{1-x}$K$_x$Fe$_2$As$_2$. On the other hand, Ba$_{1-x}$K$_x$Fe$_2$As$_2$ lies at the border of magnetic instability and pairing interactions might involve magnetic or orbital fluctuations.

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Since the discovery (in February 2008 [1]) of superconductivity with $T_C \sim 26$ K in the fluorine-doped quaternary La-Fe oxyselenide LaO$_{1-x}$F$_x$FeAs, further promising developments [2, 3] in search for related oxynitride-based superconductors (SCs) have been achieved, in particular with replacing La atoms by other rare-earth metals (Ln = Gd [4], Ce [5], Sm [6], Pr and Nd [7, 8]), resulting in $T_C \sim 41-55$ K. Moreover, comparable values of $T_C$ have been reported for replacing of rare-earth atoms by Th (Gd$_{1-x}$Th$_x$OFeAs) [9] or Sr (La$_{1-x}$Sr$_x$OFeAs, where $x \sim 0.09-0.20$) [10], as well as for undoped oxygen-deficient samples LnO$_{1-x}$FeAs (Ln = Sm, Nd, Pr, Ce, La) [11].

These unusual materials attract now considerable interest because they are the first non-Cu-based layered superconductors adopting a comparably high critical temperature and the upper critical field, are located on the border of magnetic instability, and should have an unconventional mechanism of superconductivity, which may be connected with magnetic fluctuations and a spin density wave (SDW) anomaly.

The parent phase – oxyselenide LaOFeAs adopts the tetragonal ZrCuSiAs-type structure (space group $P4/nmm$) [12], where positively charged (La-O)$^+$ layers alternate with negatively charged (Fe-As)$^-$ layers along the c axis; the bonding between these layers is mostly ionic. On the other hand, though the chemical bonding in the (La-O) layers is also ionic, strong covalent interactions occur inside the (Fe-As) layers. According to the available experimental and theoretical data [13–19] for LaOFeAs, the electronic bands in a window around the Fermi level are formed mainly by the states of the (Fe-As) layers, whereas the bands of the (La-O) layers are rather far from the Fermi level. Thus, superconductivity in LaFeAsO is determined mainly by structural and electronic states of the (Fe-As) layers.

Recently, a related system – the ternary iron arsenide BaFe$_2$As$_2$ was investigated and a SDW anomaly similar to that in LaFeAsO was found at 140 K [20]. Moreover, this phase with a tetragonal ThCr$_2$Si$_2$-type structure (space group $I4/mmm$) [21] contains identical (Fe-As) layers formed of [FeAs$_4$] tetrahedra, which are separated by barium sheets instead of (La-O) layers in LaFeAsO. In both phases, one electron is transferred to the (Fe-As) layer according to the ionic picture: Ba$^{2+} \rightarrow 0.5$(FeAs)$^-$ and (LaO)$^+$ $\rightarrow$(FeAs)$^-$. The authors of [20] assumed that BaFe$_2$As$_2$ may be a suitable parent phase in the search for a new family of oxygen-free SCs. Really, quite recently [22] a superconducting transition at $T_C \sim 3$ K was observed for BaNi$_2$P$_2$, which belongs to the same ThCr$_2$Si$_2$-like structural type. Moreover, it was found [23] that the ternary iron arsenide BaFe$_2$As$_2$ with partial substitution K $\rightarrow$ Ba becomes superconducting to $T_C \sim 38$ K for Ba$_{0.6}$K$_{0.4}$Fe$_2$As$_2$.

In these Communications we present the first results of the ab initio calculations of the electronic properties for the above mentioned iron arsenide systems, namely, the newly discovered 38 K oxygen-free superconductor Ba$_{1-x}$K$_x$Fe$_2$As$_2$ in comparison with a parent phase – the tetragonal ternary iron arsenide BaFe$_2$As$_2$.

The positions of the atoms for the tetragonal arsenide BaFe$_2$As$_2$ are: Ba at 2a $(0, 0, 0)$, Fe at 4d $(0.5, 0, 0.25)$ and As at 4c $(0, 0, z)$. To explore the superconducting phase, one barium atom in the double $(a \times a \times c)$ unit
cell of BaFe$_2$As$_2$ was replaced by a K atom to simulate a hole-doped system with the nominal composition Ba$_{0.5}$K$_{0.5}$Fe$_2$As$_2$ and space group $C'mmm$, see Fig.1.

![Figure 1. Crystal structure of the ordered phase Ba$_{0.5}$K$_{0.5}$Fe$_2$As$_2$](image)

Our band-structure calculations were carried out by means of the full-potential method with mixed basis APW+lo (LAPW) implemented in the WIEN2k suite of programs [24]. The generalized gradient correction (GGA) to exchange-correlation potential in the PBE form [25] was applied. The experimentally determined lattice parameters and internal positions $z$ for BaFe$_2$As$_2$ and Ba$_{0.5}$K$_{0.5}$Fe$_2$As$_2$ (listed in Table 1) were used. Two series of calculations were performed: for the nonmagnetic (NM) and magnetic states — in the approximation of FM ordering.

The difference in the energy of magnetic and nonmagnetic states for LaOFeAs and BaFe$_2$As$_2$ is very small and does not exceed ~ 0.076 eV/form.unit for BaFe$_2$As$_2$ and ~ 0.046 eV/form.unit for Ba$_{0.5}$K$_{0.5}$Fe$_2$As$_2$, i.e. these materials lie at the border of their magnetic instability.

Let us discuss the main peculiarities of the electronic structure of BaFe$_2$As$_2$ versus Ba$_{0.5}$K$_{0.5}$Fe$_2$As$_2$ using paramagnetic densities of states (DOSs) as depicted in Fig.2.

For BaFe$_2$As$_2$, at high binding energies the quasi-core DOSs peaks are located from -14.3 eV to -12.9 eV with the Ba 5p states and from -12.0 eV to -10.2 eV with the As 4s states, as well as with some admixtures of the Fe 3d and Ba 5p states. The valence band (VB) extends from -5.4 eV up to the Fermi level $E_F = 0$ eV and includes three main subbands $A-C$, Fig.2. Among them the first subband $A$ ranging from the VB bottom to -3.8 eV is formed predominantly of comparable contributions of the As 4p and Fe 3d states. The next subband $B$ (in the region from -3.8 eV to -2.1 eV) contains the main contributions from the Fe 3d states, together with an admixture from the As 4p states. Thus, the above mentioned subbands $A$ and $B$ are derived from the Fe 3d states hybridized with the As 4p states and are responsible for covalent Fe-As bonding. Finally, the top of the VB (subband $C$, in the interval from -2.1 eV to $E_F$) is derived basically from the Fe 3d states. This Fe 3d-like band intersects the Fermi level and continues to +2.0 eV (unoccupied subband $D$); i.e. the near-Fermi region for BaFe$_2$As$_2$ is composed mainly of iron states with very small admixtures of As states.

Besides, it is noteworthy that the contributions from the valence states of barium to the occupied subbands $A-C$ and the bottom of the conduction subband $D$ are negligible, i.e. in BaFe$_2$As$_2$ these atoms are in the form of cations Ba$^{2+}$. This means that the Ba sheets and the (Fe-As) layers are linked exclusively by ionic interactions, as distinct from the quaternary oxyarsenide LaOFeAs, where covalent bonding arises between the (La-O) and (Fe-As) layers owing to partial overlapping of the La and As states, see for example [15 — 18]. Thus,

<table>
<thead>
<tr>
<th>Phase/parameter</th>
<th>$a$ (Å)</th>
<th>$c$ (Å)</th>
<th>$z$ (Å)</th>
<th>$d$(Ba-As) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaFe$_2$As$_2$</td>
<td>3.999</td>
<td>13.016</td>
<td>0.3538</td>
<td>3.382</td>
</tr>
<tr>
<td>Ba$_{1-x}$K$_x$Fe$_2$As$_2$</td>
<td>3.999</td>
<td>13.016</td>
<td>0.3538</td>
<td>3.372</td>
</tr>
</tbody>
</table>

Table 1. The lattice parameters (a and c, in Å), internal coordinates ($z$), some interatomic distances ($d$, in Å) and bond angles As-Fe-As (in deg.) for BaFe$_2$As$_2$ and Ba$_{1-x}$K$_x$Fe$_2$As$_2$ [20, 23]
our results indicate that the iron arsenide BaFe$_2$As$_2$ consists of alternately stacked insulating Ba$^{2+}$ sheets and conductive (Fe-As)$^{1-}$ layers, and the bonding between them is of the ionic type, i.e. this system may be described as a quasi-two-dimensional ionic metal, where conduction is strongly anisotropic, happening only on the (Fe-As) layers.

In turn, the overall shape of the valence DOS for BaFe$_2$As$_2$ is very similar to that of the potassium doped system, except a new sharp quasi-core peak near $-14.3$ eV which is derived from K 3p states and narrowing of the Ba 5p peak, see Fig.2. In both compounds, the valence band which extends from $-5.4$ eV to the Fermi level (for BaFe$_2$As$_2$) and from $-4.9$ to $E_F$ (for Ba$_{0.5}$K$_{0.5}$Fe$_2$As$_2$) is derived basically from the Fe 3d states hybridized at the bottom of the VB with the As 4p states; some distinctions in DOSs profiles between BaFe$_2$As$_2$ and Ba$_{0.5}$K$_{0.5}$Fe$_2$As$_2$ (see Fig.2) are related with the deformations of [FeAs$_4$] tetrahedra building the (Fe-As) layers – as a result of partial replacement of barium by potassium, Table 1. In addition, for Ba$_{0.5}$K$_{0.5}$Fe$_2$As$_2$ the admixtures of Ba and K states in the VB are absent, i.e. this system remains a quasi-two-dimensional ionic metal.

The most remarkable difference in the DOS for BaFe$_2$As$_2$ versus Ba$_{0.5}$K$_{0.5}$Fe$_2$As$_2$ is the location of the Fermi level, see Fig.2. For the hole-doped Ba$_{0.5}$K$_{0.5}$Fe$_2$As$_2$, a decrease in the band filling leads to movement of the Fermi level in the region of higher binding energies. As a result, $E_F$ in Ba$_{0.5}$K$_{0.5}$Fe$_2$As$_2$ is shifted downwards and is located on a slope of the sharp peak $C$ in the region of enhanced DOS. Thus, the total density of states at the Fermi level $N(E_F)$ for Ba$_{0.5}$K$_{0.5}$Fe$_2$As$_2$ becomes almost 20% higher than the value of $N(E_F)$ for BaFe$_2$As$_2$, Table 2. Note that the growth of $N(E_F)$ is achieved exclusively due to the Fe 3d states, whereas the contribution from the As states remains less than 4%, Table 2.

### Table 2

<table>
<thead>
<tr>
<th>Phase/parameter</th>
<th>$N^{Fe_{3d}}(E_F)$</th>
<th>$N^{As}(E_F)$</th>
<th>$N^{Total}(E_F)$</th>
<th>$\gamma$ (in $10^{-2}$ emu/mol)</th>
<th>$\chi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaFe$_2$As$_2$</td>
<td>1.860</td>
<td>0.071</td>
<td>4.553</td>
<td>10.73</td>
<td>1.47</td>
</tr>
<tr>
<td>Ba$<em>{0.5}$K$</em>{0.5}$Fe$_2$As$_2$</td>
<td>2.352</td>
<td>0.072</td>
<td>5.526</td>
<td>13.03</td>
<td>1.79</td>
</tr>
</tbody>
</table>
These data allow us also to estimate the Sommerfeld constants ($\gamma$) and the Pauli paramagnetic susceptibility ($\chi$) for iron arsenides $\text{Ba}_2\text{Fe}_2\text{As}_2$ and $\text{Ba}_{0.5}\text{K}_{0.5}\text{Fe}_2\text{As}_2$, assuming the free electron model, as: $\gamma = \left(\pi^2/3\right) N(E_F) k_B^2$, and $\chi = \mu_B^2 N(E_F)$. It is seen (Table 2) that both $\gamma$ and $\chi$ increase approximately by $20\%$ as going from $\text{Ba}_2\text{Fe}_2\text{As}_2$ to $\text{Ba}_{0.5}\text{K}_{0.5}\text{Fe}_2\text{As}_2$. These values are comparable with those obtained for Fe-containing oxypnictides (for example $\gamma = 12.5$ mJ/K$^{-2}$ mol$^{-1}$ for LaOFeP [26]).

In addition, the calculated Sommerfeld constant $\gamma_{\text{thor}}$ may be useful for simple estimations [27] of the average electron-phonon coupling constant $\lambda$ for $\text{Ba}_2\text{Fe}_2\text{As}_2$-based SCs, in the assumption of the conventional BCS phonon-mediated mechanism of superconductivity as $\gamma_{\text{thor}}(1 + \lambda)$. Within a crude estimate, using our $\gamma_{\text{thor}}$ for $\text{Ba}_2\text{Fe}_2\text{As}_2$ (Table 2) and the measured [20] $\gamma_{\exp} \approx 16$ mJ/mol-K$^2$ we obtain an empirical value of $\lambda$ of about 0.5, i.e. these materials should be within the weak coupling limit. For comparison, available experimental and theoretical estimates of $\lambda$ for other superconducting oxygen-free species with magnetic ions such as ACNi$_3$ anti-perovskites vary from 1.4 to 0.66, see [28].

On the other hand, the superconducting hole-doped iron arsenide $\text{Ba}_{0.5}\text{K}_{0.5}\text{Fe}_2\text{As}_2$ is very similar to the above mentioned layered oxypnictides, for which a set of unconventional superconductivity models was proposed, where, for example, pairing interactions might involve magnetic or orbital fluctuations [13–17]. Note that our results indicate that both $\text{Ba}_{0.5}\text{K}_{0.5}\text{Fe}_2\text{As}_2$ and $\text{Ba}_{0.5}\text{K}_{0.5}\text{Fe}_2\text{As}_2$ are at the border of magnetic instability, and the calculated magnetic moments for their FM states are about $1.90 \mu_B$/Fe for $\text{Ba}_2\text{Fe}_2\text{As}_2$ and about $0.74 \mu_B$/Fe for $\text{Ba}_{0.5}\text{K}_{0.5}\text{Fe}_2\text{As}_2$.

In summary, we studied the electronic structure of the newly discovered 38K oxygen-free superconductor $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$ in comparison with a parent phase – the tetragonal ternary iron arsenide $\text{BaFe}_2\text{As}_2$.

The density functional theory predicts that $\text{BaFe}_2\text{As}_2$ may be described as a quasi-two-dimensional ionic metal consisting of insulating $\text{Ba}$ sheets and conductive (Fe-As) layers; the bonding between them is ionic, whereas the conduction is strongly anisotropic and happens only in the (Fe-As) layers.

According to our calculations, the density of states at the Fermi level increases by about 25% as a result of hole doping through barium ions substitution. This may be a factor, which favors the occurrence of superconductivity in $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$. On the other hand, this system lies at the border of magnetic instability and, possibly, hole doping suppresses the SDW anomaly to induce superconductivity [23]. Thus, further in-depth studies are necessary to understand possible scenarios of superconducting coupling mechanisms for these systems, which may be of interest as a new material platform for further exploration of the relationships between magnetism and superconductivity for oxygen-free SCs.