

Comparative Study of Electronic structure of New Superconductors (Sr,Ca)Pd₂As₂ and related compound BaPd₂As₂.

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This paper presents the comparative study of LDA calculated electronic structure of new isostructural to iron based systems superconductors (Sr,Ca)Pd₂As₂ with T_c about 1K and similar but structurally different system BaPd₂As₂. Despite chemical formula looks similar to iron superconductors and even main structural motif is the same - layers of Fe square lattices, electronic structure of (Sr,Ca)Pd₂As₂ and BaPd₂As₂ differs from Fe(As,Se)-HTSC completely. All these systems have essentially three dimensional Fermi surfaces in contrast to Fe(As,Se) materials. The Fermi level is crossed by low intensive tails of Pd-4d and As-4p states. However (Sr,Ca)Pd₂As₂ and BaPd₂As₂ materials have rather well developed peaks of Pd-4d($x^2 - y^2$) band. Thus by doping of about 2 holes per unit cell one can increase density of states at the Fermi level by a factor about 2.5. Since experimentally these compounds were found to be simple BCS superconductors the hole doping may considerably increase T_c. LDA calculated total densities of states at the Fermi level for stoichiometric systems perfectly agree with experimental estimates signifying rather small role of electronic correlations.

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Novel noncuprate HTSC FeAs based systems after their discovery in 2008 [1] stimulated an avalanche of experimental and theoretical investigations [2, 3, 4]. Moreover long series of related perspective compounds was synthesized.

Electronic structure of many FeAs systems was investigated by us [5, 6, 7, 8, 9] and other groups [10, 11]. Also we made some effort to investigate FeSe based superconductors (chalcogenides) [12, 13, 14, 15] and to compare them with pnictides [16]. Electronic structures of some related systems were studied during recent years: APt₃P [17], BaFe₂Se₃ [18], SrPt₂As₂ [19].

This work was motivated by recent detailed work of Anand *et al.* [20] on superconducting and normal state properties of (Sr,Ca)Pd₂As₂ and BaPd₂As₂ single crystals. SrPd₂As₂ and CaPd₂As₂ systems were found to be superconductors with T_c 0.92K and 1.27K correspondingly, while the BaPd₂As₂ showed only traces of superconductivity. These Pd systems can be considered as a physically interesting end-point compounds of A(Fe_{1-x}M_x)₂As₂ with M=Cr,Mn,Co,Ni,Cu,Ru,Rh and A=Ca,Sr,Ba series with respect to maximal number of charge carriers in such systems. Changes of magnetic and superconducting properties of A(Fe_{1-x}M_x)₂As₂ series are quite non trivial. Detailed overview of electronic properties of these compounds is presented in the paper

by Anand *et al.* [20]. However theoretical band structures of SrPd₂As₂, CaPd₂As₂ and BaPd₂As₂ materials were not investigated yet to our knowledge.

Here we present the detailed comparison of band structures of SrPd₂As₂, CaPd₂As₂ and BaPd₂As₂ materials with respect to each other and also to isovalent (Sr,Ba)Ni₂As₂ compounds [21, 22, 23] and iron pnictides and chalcogenides in general.

For our band structure calculations within the local density approximation (LDA) we used refined crystal structure data of Ref. [20]. SrPd₂As₂ and CaPd₂As₂ have tetragonal body centred crystal structure with the space group $I/4mmm$ the same as typical pnictide representative BaFe₂As₂ [24] where two mirrored FeAs₄ tetrahedra layers are contained in the elementary cell [6] (see also Fig. 1 on the left side). Although in most cases 122-pnictide systems belong to the space group $P4/nmm$ [9]. The lattice parameters are $a=4.2824\text{\AA}$ and 4.3759\AA and $c=10.088\text{\AA}$ and 10.1671\AA for Ca and Sr systems respectively. As compared to Ba122 pnictide the Ca and Sr systems have larger a and smaller c parameters. Wyckoff positions of ions are identical to 122 systems: Ca,Sr – 2a(0,0,0); Pd – 4d(0,0.5,0.25); As – 4e (0,0,0.3763) for Ca and (0,0,0.3768) for Sr systems.

Being chemically similar to Ba122 pnictide the BaPd₂As₂ system has very different crystal structure. According to Ref. [20] the space group of BaPd₂As₂ is $P/4mmm$. Ions positions are: Ba – 1a(0,0,0); Pd – 2e(0,0.5,0.5); As – 2h(0.5,0.5,0.2505). This crystal

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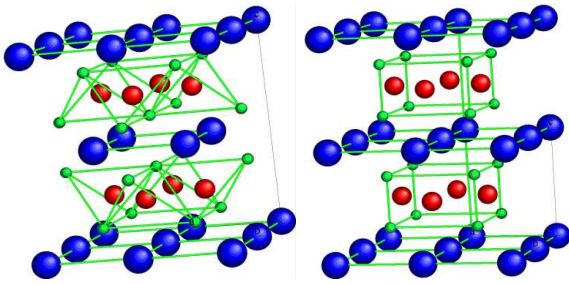


Fig. 1. Crystal structure of $(\text{Sr,Ca})\text{Pd}_2\text{As}_2$ (left) and BaPd_2As_2 (right). Blue balls are Sr,Ba ions, green – As and red – Pd.

structure is drawn in Fig. 1 on the right side. The crystal structure also consists from layers. But in contrast to Ba122 and other Fe-pnictides and chalcogenides Fe ions here (which form square lattice) are surrounded by As rectangles (see the right panel of Fig. 1) and not tetrahedrons (e.g. see Fig. 1, left panel).

Electronic structure calculations were performed within the linearized muffin-tin orbitals method (LMTO) [25] with default settings. LDA calculated band dispersions plotted along high-symmetry Brillouin zone directions are shown in Fig. 2 for SrPd_2As_2 (top panel) and BaPd_2As_2 (bottom panel) on the right sides. Since band structure of CaPd_2As_2 obtained by us is only slightly different from that of SrPd_2As_2 below we present only theoretical data for SrPd_2As_2 system.

For the Sr system our band dispersions are quite similar to those obtained in Ref. [23] for isovalent SrNi_2As_2 compound except a little bit shifted up in energy part of As-4p states within X-P direction. This leads to a slightly simpler than in Ni case Fermi surface, which is plotted in Fig. 4 (upper row) and described below. Around Γ we observe small hole pocket while around X-point we see large electronic pocket. Close to N-point there is another electronic pocket of the Fermi surface. Fermi level is crossed by bands containing many contributions of different states without any dominant orbital.

It is interesting that band dispersions and Fermi surfaces of isovalent BaNi_2As_2 compound reported in Refs. [21, 22] are quite different from those of SrNi_2As_2 and SrPd_2As_2 . Which agrees with our calculations. This is rather puzzling since BaNi_2As_2 crystal structure is very much similar to SrNi_2As_2 and SrPd_2As_2 compounds. At the same time densities of states of BaNi_2As_2 are rather close to those plotted on the right side of upper panel of Fig. 2 for SrPd_2As_2 .

From SrPd_2As_2 density of states one can see that most of the spectral weight is formed by Pd-4d and As-4p states. Pd-4d states are located between -4 and -0.5

eV (see also the upper panel of Fig. 3), As-4p states belong to the interval (-6;-4) eV. Significant hybridization between Pd-4d and As-4p states is also evident. Comparing this Sr system to e.g. Ba122 Fe-pnictide we see that Pd-4d states are obviously more extended in energy than Fe-3d. Overall shape of the SrPd_2As_2 total DOS as expected is similar to that of SrNi_2As_2 and to Ba122 Fe-pnictide. However the value of total DOS at the Fermi level $N(E_F)=1.93$ states/eV/f.u. is more than twice lower than for Ba122 Fe-pnictide because additional electron doping moves the Fermi level up into lower DOS region. Indirect estimates of $N(E_F)$ from experiments gives 1.89 states/eV/f.u. [20] which agrees well with our calculated value, signifying that correlation effects are more or less not important in the SrPd_2As_2 . This can be due to more extended in energy Pd-4d states in contrast to Fe-3d states e.g. in Ba122 Fe-pnictide.

To understand the structure of Pd-4d DOS of the SrPd_2As_2 we present (on the upper panel of Fig. 3) the orbitally resolved DOSes. Here we see that about 0.8eV below the Fermi level there is peak formed by Pd-4d($x^2 - y^2$). Thus by doping of about 2 holes per unit cell one can increase $N(E_F)$ more than twice. Consequently one can expect increase of the T_c since this system was experimentally found to be a simple BCS like superconductor [20].

Lower panel of Fig. 2 demonstrates LDA electronic band dispersions and densities of states of BaPd_2As_2 . Since its crystal structure is totally different from all other Fe pnictides and chalcogenides no wonder that its electronic structure is different too. Around Γ and R points we found large and small hole-like pockets and around M point there are two electron-like pockets (see also lower line of the Fig. 4). Similar to the Sr material in case of Ba compound Fermi level is also crossed by bands containing many contributions of different states without any dominant orbital contribution and finally giving quite low DOS.

Despite different band dispersions, the shape of total and partial DOSes for Ba compound is somewhat similar to Sr ones. Pd-4d states are located between -3 eV and -0.5 eV, while As-4p states are situated right below Pd-4d states and continue down to -6 eV. Considerable admixture (hybridisation) between Pd-4d and As-4p states is observed. The LDA calculated value of total density of states at the Fermi level $N(E_F)$ for BaPd_2As_2 is 2.29 states/eV/f.u. (taking into account the fact that there is only one f.u. in the unit cell for Ba material). This value agrees well with experimental estimates of Ref. [20] giving 2.03 states/eV/f.u.. However one can guess that electron-phonon coupling constant

obtained experimentally in Ref. [20] is slightly overestimated or some other rather weak interactions should be taken into account.

Similar to the Sr system in BaPd₂As₂ about 0.7eV below the Fermi level there is peak in the Pd-4d DOS due to the band of $x^2 - y^2$ symmetry which is clearly seen at this energy within dispersions. Thus we also can expect here that hole doping can lead to appearance of superconductivity (its traces were actually observed experimentally in Ref. [20]).

In Fig. 4 we present Fermi surfaces of SrPd₂As₂ (upper row) and BaPd₂As₂ (lower row) obtained within LDA calculations. For both compounds panels (a) give general view of the Fermi surfaces in corresponding first Brillouin zone. Fermi surface of the Sr system is essentially three-dimensional in contrast to e.g. 122 Fe-pnictides (see Ref. [6]). The structure of the Fermi surface is quite complicated and consists of three sheets. On the panel (b) (upper row of Fig. 4) there is hole-like sheet in according to performed above band structure analysis but this sheet does not cross $k_z = 0$ plane. On panels (c) and (d) hole and electronic sheets are presented. The latter one cross the $k_z = 0$ plane forming the Fermi surface presented on the panel (e).

LDA calculated Fermi surface for the Ba system is quite simple with respect to the shape of different sheets. That can be seen on the panel (a) of lower row of the Fig. 4. Again the Fermi surface is essentially three-dimensional and also has three sheets. In the centre there is large hole-like Fermi surface sheet (see panel (b) in the lower line of Fig. 4) while in the corners there are two electron-like sheets.

In conclusion we performed LDA calculations of electronic band structure for recently reported in Ref. [20] materials (Sr,Ca)Pd₂As₂ and BaPd₂As₂ related to the 122 Fe-pnictide systems. In general band structure of the Sr system is very similar to that of isovalent material SrNi₂As₂ reported elsewhere [23]. However the band structure of another isovalent system BaNi₂As₂ is surprisingly quite different to the SrPd₂As₂ compound though the crystal structure is very similar. The band structure of BaPd₂As₂ system is very dissimilar to any other 122 systems because of its different crystal structure. It is interesting that considered in this work Sr and Ba systems has one similarity within the band structure. Namely, in the DOS of both materials there is rather intensive peak formed by Pd-4d($x^2 - y^2$) states (about 0.7 eV below the Fermi level). Thus doping of about 2 holes per unit cell may lead to a considerable increase (by a factor 2.5) of the total DOS value at the Fermi level $N(E_F)$ giving rise to T_c for the Sr compound and perhaps appearing of superconductivity in the Ba com-

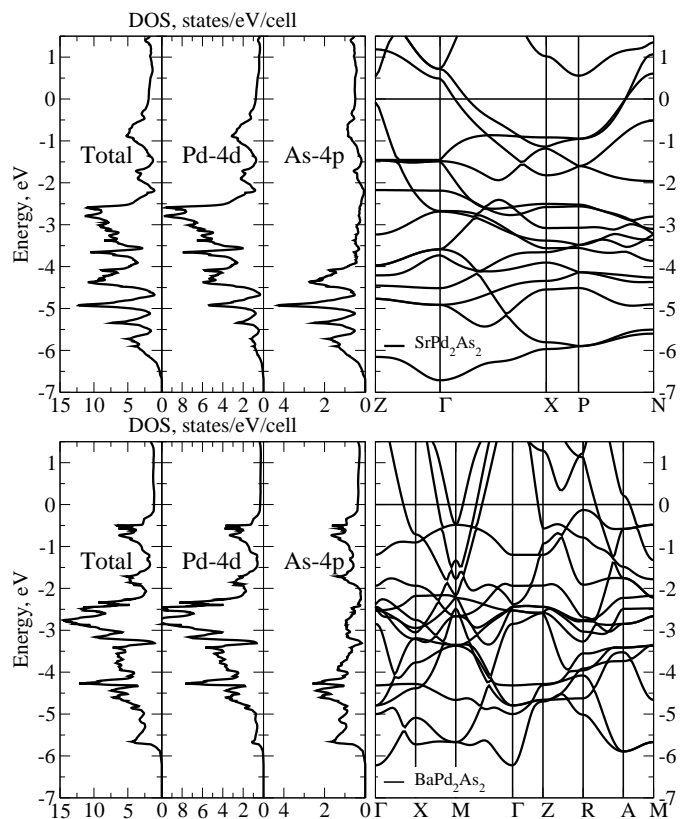


Fig. 2. LDA calculated band dispersions and densities of states of (SrPd₂As₂ (top) and BaPd₂As₂ (bottom). The Fermi level is zero.

pound (traces of superconductivity were observed here experimentally in Ref. [20]). Obtained in LDA calculations values of $N(E_F)$ for stoichiometric systems are in perfect agreement with experimental estimates [20] thus signifying minor role of correlation effects in these systems.

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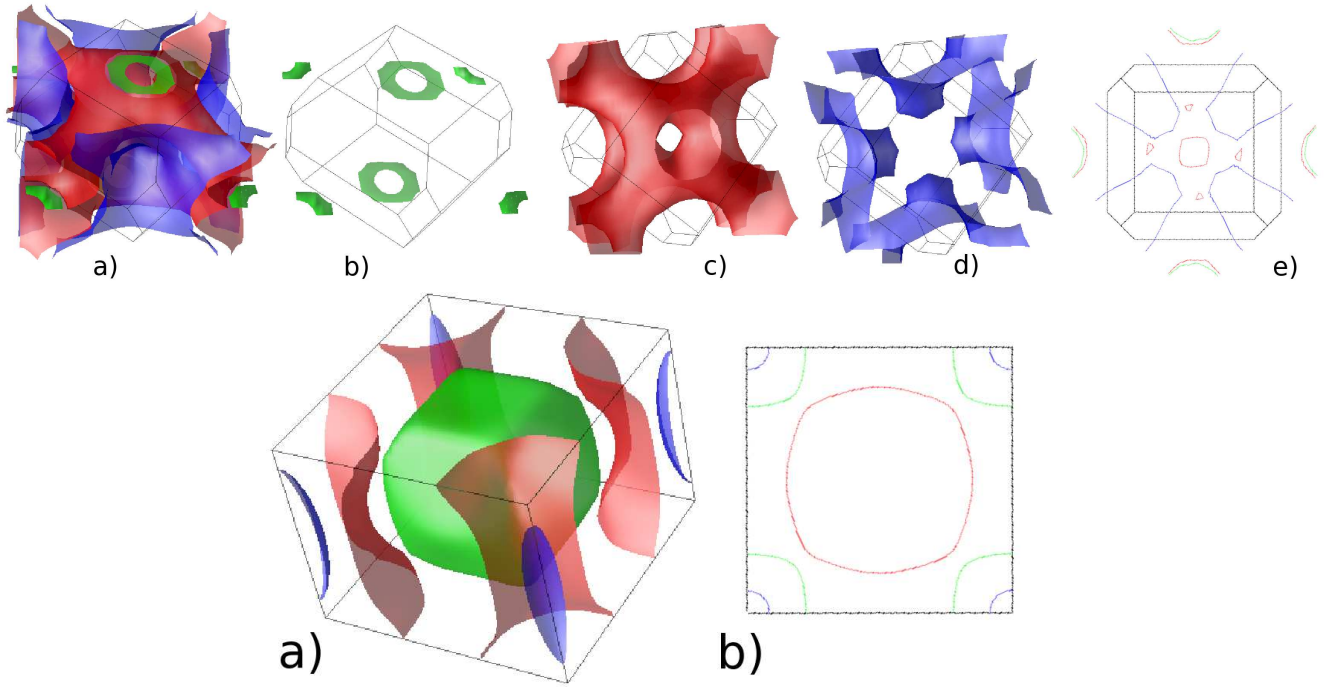


Fig. 4. LDA calculated FS for (Sr,Ca)Pd₂As₂ (top) and BaPd₂As₂ (bottom). a – all FS sheets together for both systems; b,c,d (top panel) – separate view of each of three FS sheets for (Sr,Ca)Pd₂As₂; e (top panel) and b (lower panel) – crosssection of FS at $k_z=0$ for (Sr,Ca)Pd₂As₂ and BaPd₂As₂ correspondingly.

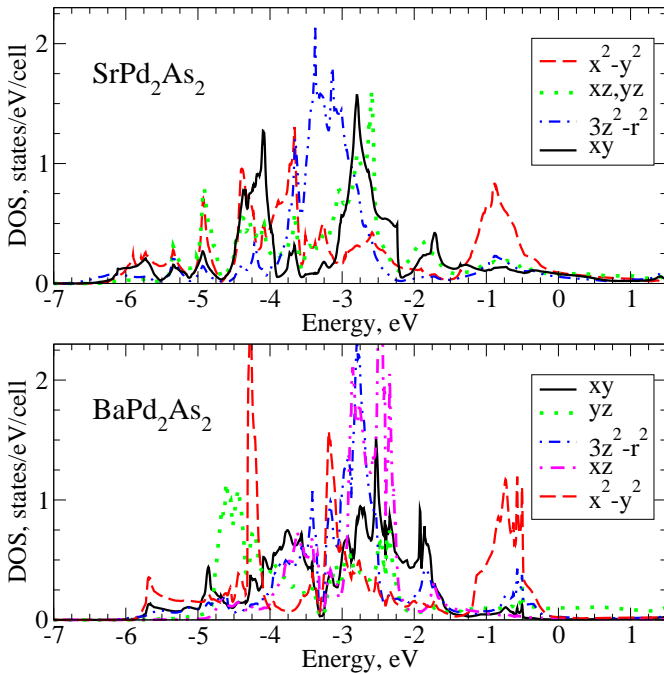


Fig. 3. Orbitally resolved densities of Pd-4d states from LDA calculations for (Sr,Ca)Pd₂As₂ (top) and BaPd₂As₂ (bottom). The Fermi level is zero.

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