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Electronic structure of $BaCu_2As_2$ and $SrCu_2As_2$: *sp*-band metals

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The electronic structures of $ThCr_2Si_2$ structure $BaCu_2As_2$ and $SrCu_2As_2$ are investigated using density-functional calculations. The Cu *d* orbitals are located at 3 eV and higher binding energy and are therefore chemically inert with little contribution near the Fermi energy. These materials are moderate density of states, *sp*-band metals with large Fermi surfaces and low anisotropy.

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Recent results, motivated by the discovery of high-temperature Fe-based superconductivity,[1] have shown that 3*d* pnictides in the $ThCr_2As_2$ structure show a remarkable range of properties. This includes the itinerant spin density wave and high-temperature superconductivity characteristic of the Fe-based superconductors for $BaFe_2As_2$, $SrFe_2As_2$, and $CaFe_2As_2$.[2–9] Remarkably, in contrast to cuprates, superconductivity can be induced by doping on the Fe site, using Co and Ni as electron dopants.[10–13] $BaCo_2As_2$ and $BaNi_2As_2$ show very different properties, namely, those of a material very close to ferromagnetism,[14] and a low-temperature electron-phonon superconductor, respectively.[15–17]

The electronic structures of $BaFe_2As_2$, $BaCo_2As_2$, and $BaNi_2As_2$ are, however, closely related,[14,17–20] with Fe *d* bands near E_F, modest hybridization with As, and a similar shaped density of states with a pseudogap at an electron count of six *d* electrons as in the Fe-based oxyarsenides and FeSe.[21,22] The very different properties of these three compounds arise because of the different electron counts of the transition elements, which lead to different placements of the Fermi level. This provides an explanation for the ability to dope $BaFe_2As_2$ with Co or Ni and obtain a coherent superconducting alloy.[10,11]

The Mn and Cr compounds, $BaMn_2As_2$ and $BaCr_2As_2$, show rather different electronic structures from $BaFe_2As_2$, with strong spin-dependent hybridization between the transition element *d* states and As *p* states. $BaMn_2As_2$ is an antiferromagnetic semiconductor,[23,24] while $BaCr_2As_2$ is an antiferromagnetic metal with itinerant character.[25] It is interesting to note that although the electronic structures and properties of the Fe compounds, FeSe and $BaFe_2As_2$ are similar, the trends with transition element substitution in the $ThCr_2Si_2$ structure pnictides are very different from those in the α-PbO structure selenides, presumably reflecting the different chemistry of pnictogens and chalcogens.[26] Synthesis of $BaCu_2As_2$ and $SrCu_2As_2$ was reported by Pfisterer and Nagorsen,[27] but little is known about their electronic structure or physical properties.

Here we investigate the properties of the Cu compounds $BaCu_2As_2$ and $SrCu_2As_2$ using density-functional calculations. We show that in contrast to the Fe, Co, and Ni compounds, where the transition element is divalent, nominal d^6 Fe^{2+}, d^7 Co^{2+} and d^8 Ni^{2+}, and also in contrast to the cuprate superconductors, which are based on divalent d^9 Cu^{2+} ions, the Cu in $BaCu_2As_2$ has a fully occupied stable d^{10} shell at high binding energy.

The present first-principles calculations were done within the local-density approximation (LDA) using the general potential linearized augmented plane-wave (LAPW) method,[28] similar to prior calculations for $BaFe_2As_2$.[20] We used the reported experimental lattice parameters,[27] $a = 4.446$ Å, $c = 10.007$ Å, for $BaCu_2As_2$ and $a = 4.271$ Å, $c = 10.018$ Å, for $SrCu_2As_2$. The internal parameter z_{As} was determined by energy minimization. The resulting values were $z_{As} = 0.3657$ for $BaCu_2As_2$ and $z_{As} = 0.3697$ for $SrCu_2As_2$. We used well converged basis sets including local orbitals to treat the semicore states and relax the Cu *d* state linearization.[29] Relativistic effects were included at the scalar relativistic level. The LAPW sphere radii were 2.2 Bohr for Ba and Sr and 2.1 Bohr for Cu and As.

The calculated electronic densities of states (DOS) and band structures are shown in Figs. 1 and 2. Both $BaCu_2As_2$ and $SrCu_2As_2$ are metallic. As may be seen, the Cu *d* bands are narrow and are located at high binding energy, more than

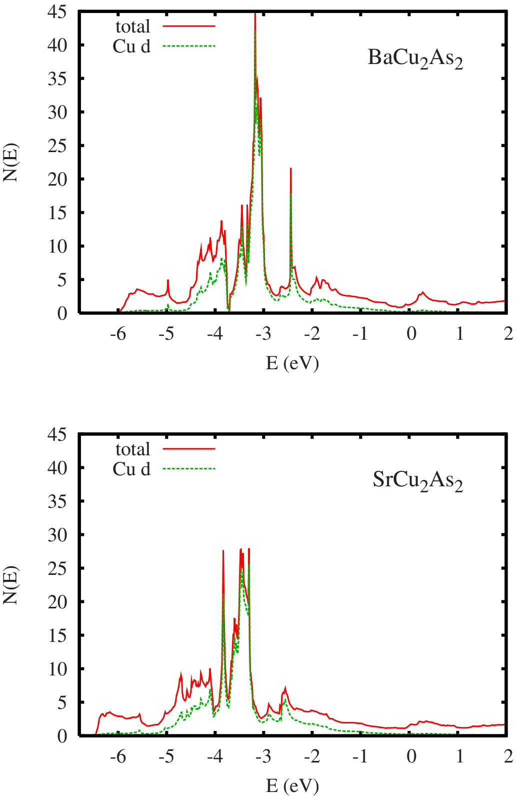

FIG. 1. (Color online) Electronic density of states and Cu *d* projection for $BaCu_2As_2$ (top) and $SrCu_2As_2$ (bottom).

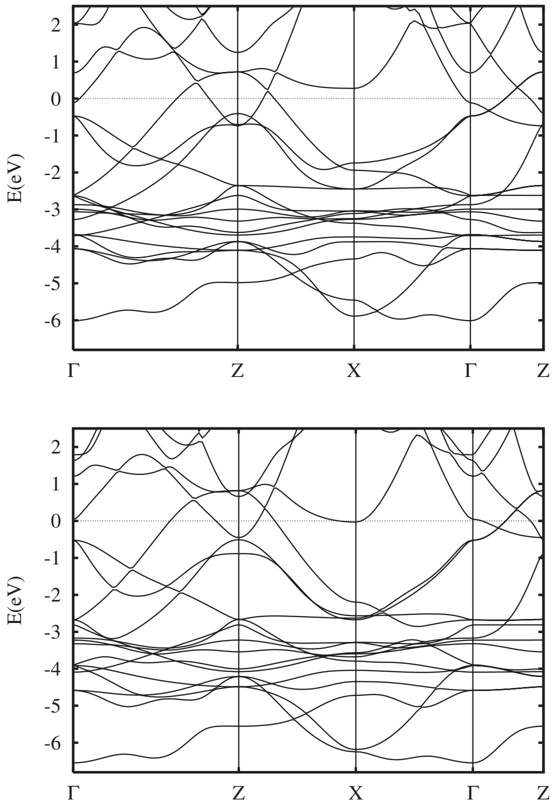

FIG. 2. Band structure of $BaCu_2As_2$ (top) and $SrCu_2As_2$ (bottom). The bands are plotted along lines in the basal plane and along the k_z direction. The body centered tetragonal reciprocal lattice vectors are $(2\pi/a,0,-2\pi/c)$, $(0,2\pi/a,-2\pi/c)$, and $(0,0,4\pi/c)$. In terms of these, the long Γ-Z direction is from (0,0,0) to (1,0,1/2) in the body centered tetragonal zone, while the short Γ-Z direction is from (0,0,0) to (0,0,1/2). X denotes the zone boundary (1/2,1/2,1/2) point. A two-dimensional band structure would show no dispersion along the short Γ-Z direction and would be symmetric about the midpoint of the long Γ-Z direction.

3 eV below the Fermi energy, E_F. Furthermore, there is very little Cu d contribution to the DOS near E_F. Therefore, the Cu d orbitals are fully occupied in these compounds and are chemically inert. However, it is interesting to note that the Cu bands are somewhat broader in $SrCu_2As_2$ than in $BaCu_2As_2$, reflecting the shorter Cu-Cu distance in the Sr compound (3.02 Å vs 3.14 Å). In any case, the Cu d bands lie on top of a background of broad pnictogen p and metal sp bands extending from −6 eV to above E_F. Therefore these compounds are sp metals. Turning to the band structure, which is plotted along lines either in the basal plane (constant k_z) or along k_z, it is clearly seen that there are strong dispersions in both the ab plane and along the c-axis (k_z) directions, showing three-dimensional character.

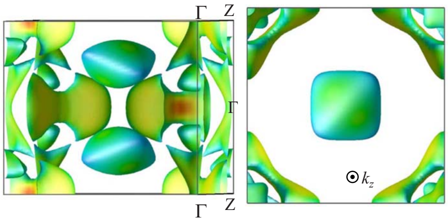

FIG. 3. (Color online) Fermi surface of $BaCu_2As_2$ shaded by velocity (light blue is low velocity). The left (right) panel shows a view perpendicular to (along) the c axis.

The calculated Fermi surfaces for $BaCu_2As_2$ and $SrCu_2As_2$ are shown in Figs. 3 and 4, respectively. The Fermi surfaces are large and quite three dimensional. The Fermi surface of $BaCu_2As_2$ shows electron pockets along the $(1/2,1/2,k_z)$ direction (the center of the right panel of Fig. 3), and large complex sheets around $(0,0,k_z)$. In $SrCu_2As_2$, the electron pockets are larger and touch forming a large strongly corrugated electron cylinder running along the zone corner, again accompanied by complex large Fermi surfaces around the zone center. These are characteristic of a good metal reflecting the sp character of the electronic structure.

The calculated densities of states at the Fermi energy are $N(E_F)=1.26\ \mathrm{eV}^{-1}$ for $BaCu_2As_2$ and $N(E_F)=1.53\ \mathrm{eV}^{-1}$ for $SrCu_2As_2$ on a per formula unit basis. The corresponding Fermi velocities are $\langle v_x^2\rangle^{1/2}=2.8\times10^5$ m/s and $\langle v_z^2\rangle^{1/2}=2.6\times10^5$ m/s for $BaCu_2As_2$ and $\langle v_x^2\rangle^{1/2}=2.8\times10^5$ m/s and $\langle v_z^2\rangle^{1/2}=2.5\times10^5$ m/s for $SrCu_2As_2$, consistent with weakly anisotropic three-dimensional transport in both compounds. The high Fermi velocities reflect the dispersive nature of the sp bands near E_F, in contrast to the Fe, Co, and Ni compounds, which are d band metals. The values of $N(E_F)$ are high for an sp metal, but considering the extended nature of As p orbitals they are far from sufficient to yield Stoner magnetism. This was confirmed by fixed spin moment calculations of the energy as a function of constrained spin magnetization as shown in Fig. 5. As may be seen (note the very high energy scale), these compounds are very far from magnetism. This is as may be expected considering the absence of d bands near the Fermi energy. In fact, considering the high binding energy of the Cu d states it is unlikely that mild perturbations such as moderate pressures or alkaline earth substitutions can bring them to the Fermi energy and produce magnetism.

The general features of the electronic structures of $ThCr_2Si_2$ structure pnictides have been discussed by Hoffmann and Zheng[30,31] in terms of an interplay between pnictogen-pnictogen and pnictogen-metal bonding. Such an interplay has also been emphasized for the high pressure structure of $CaFe_2As_2$.[32] With the additional ingredient of direct metal-metal interactions, which are important in the middle of the series (Fe, Co, and Ni),[21] this allows a classification of the compounds. According to our calculations the Cu d states are well below the Fermi energy and therefore chemically inert in $BaCu_2As_2$ and $SrCu_2As_2$ and the bonding

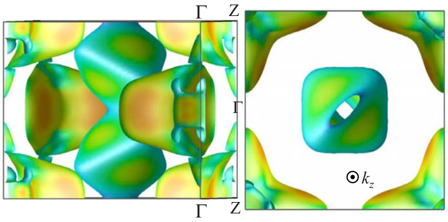

FIG. 4. (Color online) Fermi surface of $SrCu_2As_2$ shaded by velocity (light blue is low velocity). The left (right) panel shows a view perpendicular to (along) the c axis.

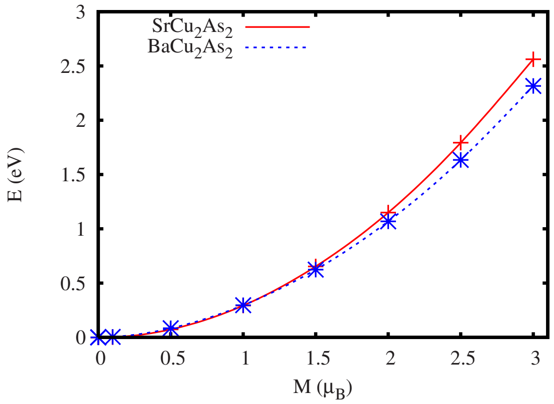

FIG. 5. (Color online) Fixed spin moment energy as a function of constrained spin magnetization, shown on a per formula unit basis for $BaCu_2As_2$ and $SrCu_2As_2$.

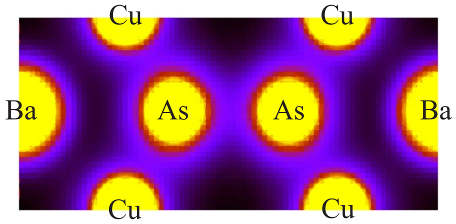

FIG. 6. (Color online) Charge density plot for $BaCu_2As_2$ in a (010) plane showing *sp* electron bonding between the As atoms and between As and Cu. The bright (yellow) denotes 0.2 e/Bohr^3 or higher, while the dark (black) is for charge densities below 0.02 e/Bohr^3.

is primarily of *sp* type involving the As and Cu atoms. This is seen both in the density of states, which shows partial filling of the pnictogen *p* states and in the charge density (Fig. 6, for $BaCu_2As_2$). In contrast, in the Fe, Co, and Ni compounds, As is nearly anionic, and metal-metal bonding is important in addition to weaker pnictogen interactions. In the Cr and Mn compounds there is strong covalency between the metal *d* states and the As states, in addition to pnictogen-pnictogen covalency as evidenced by the three-dimensional character of those compounds. In this regard, one may note that the *c*-axis lattice parameter of $BaCu_2As_2$ is shorter by more than 1.5 Å, as compared to that of $BaNi_2As_2$. This is highly suggestive that the bonding of these two compounds is different, and in particular the shorter As-As distances in the Cu compounds reflect As-As bonding. This classification also provides an explanation for the fact that $BaFe_2Sb_2$, $BaCo_2Sb_2$, and $BaNi_2Sb_2$ are not formed.[33–35] In particular, antimony has a greater tendency toward formation of compounds with pnictogen-pnictogen bonding than arsenic and, as mentioned, in the Fe, Co, and Ni compounds the pnictogens are anionic with a central role played by metal-metal bonding.

To summarize, density-functional calculations for $BaCu_2As_2$ and $SrCu_2As_2$ show that these materials are *sp* metals with dispersive bands at the Fermi energy. The Cu *d* bands are at high binding energy in excess of 3 eV and are therefore inert in these compounds. These materials are not near magnetism. Therefore, the characteristic electronic structure associated with the Fe-based superconductors, in particular an electronic structure associated with anionic pnictogens and metal-metal *d* bonding exists in the $ThCr_2Si_2$ structure pnictides for Fe, Co, and Ni, but not Cu. The implication is that while Co and Ni can be used effectively to dope $BaFe_2As_2$ to produce a coherent alloy with superconductivity, the other 3*d* elements, Mn, Cr, and Cu will behave differently. It should be noted that this last conclusion does not apply to the α-PbO structure chalcogenides, since the bonding and chemistry of chalcogenides are different than those of arsenides.

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