

Properties of KCo_2As_2 and alloys with Fe and Ru: Density functional calculations

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Electronic-structure calculations are presented for KCo_2As_2 and alloys with KFe_2As_2 and KRu_2As_2 . These materials show electronic structures characteristic of coherent alloys with a similar Fermi surface structure to that of the Fe-based superconductors when the d -electron count is near 6 per transition metal. However, they are less magnetic than the corresponding Fe compounds. These results are discussed in relation to superconductivity.

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I. INTRODUCTION

A remarkable feature of the high-temperature superconductivity in iron compounds is the chemical richness of this phenomenon. Besides the oxypnictides,¹ superconductivity has been discovered in related ThCr_2Si_2 -structure materials (prototype BaFe_2As_2),² LiFeAs and related compounds,³ perovskite-pnictide intergrowth ($\text{Sr}_4\text{Sc}_2\text{Fe}_2\text{P}_2\text{O}_6$) compounds,⁴ and remarkably FeSe ,^{5,6} which contains no pnictogens.

In fact, the discovery of superconductivity in FeSe was an important development since it showed that pnictogen-coordinated Fe was not an essential part of Fe-based superconductivity. Nonetheless, in spite of this diverse chemistry the Fe-based superconductors do share a number of common features. In particular, they are all based on divalent iron-square planes with tetrahedral coordination by pnictogens or chalcogens. This leads to a characteristic electronic structure in which Fe occurs as Fe^{2+} and the band structure near the Fermi energy is derived from Fe d states with only modest hybridization of ligand p states.⁷

The band structures show relatively small disconnected Fermi surfaces, in particular hole sections near the two-dimensional (2D) zone center and electron sections at the zone corner. On the other hand, despite the low-carrier density, the density of states (DOS) $N(E_F)$ of these compounds is high ($\sim 2 \text{ eV}^{-1}$ per Fe), placing them near itinerant magnetism. An important feature is that hole and electron sheets of Fermi surface in these compounds are nested,^{8,9} which leads to a spin-density wave (SDW) instability in most of the undoped materials and which in any case places the materials near an SDW.¹⁰⁻¹² The association between the SDW, the related nesting, and superconductivity is much discussed and is one of the central issues in the physics of these materials.

A second much-discussed issue is the relationship of the Fe-based high- T_c compounds with the cuprates. Besides the obvious distinctions, such as multiorbital vs single-orbital band structures, a key point is that the Fe-based materials appear to be much more like conventional metallic compounds in their behavior. For example, a prominent Fermi edge is seen in spectroscopies with little evidence for Hubbard bands or other characteristic features of a Mott-Hubbard system.^{13,14} Perhaps related to this, and in strong contrast with cuprates, where the correlated atomic physics of Cu^{2+} is thought to be crucial, superconductivity can be induced in

the Fe compounds by alloying with other transition elements, in particular Co, Ni, Ru, and other $4d$ and $5d$ elements.¹⁵⁻¹⁸

This raises the question of how essential Fe is for Fe-based superconductivity. Specifically, is the phenomenon the result of a specific band structure with itinerant magnetism or is correlated atomic physics specifically associated with Fe^{2+} essential? As a step toward addressing this question, we focus on the ThCr_2Si_2 structure, which accommodates an exceptionally large variety of compositions,¹⁹⁻²¹ and on the possible replacement of Fe^{2+} by Co^{3+} . We note that in oxides where correlated behavior may play an important role, Co^{3+} compounds show very different behaviors from Fe^{2+} compounds (e.g., LaCoO_3 or NaCoO_2 vs FeO). In particular, we use electronic-structure calculations for KCo_2As_2 and pseudobinary alloys with KFe_2As_2 and KRu_2As_2 to show that the specific band-structure features of the Fe superconductors can be realized in phases with little or no Fe. From an electronic point of view, we find that $\text{KFe}_y\text{Co}_{2-y}\text{As}_2$ for Fe concentrations $y/2$ well below the nearest-neighbor square-lattice percolation threshold of 0.5927 (Ref. 22) is very closely analogous to superconducting $\text{BaFe}_{2-x}\text{Co}_x\text{As}_2$ and furthermore that $\text{KRu}_y\text{Co}_{2-y}\text{As}_2$ is similar but further from magnetism. We note that KCo_2As_2 is a known compound²³ as are KFe_2As_2 and KRu_2As_2 .^{23,24}

II. APPROACH

The calculations shown here were performed within the local-density approximation (LDA) with the general-potential linearized-augmented planewave (LAPW) method, including local orbitals.²⁵ Well-converged zone samplings and basis sets, including local orbitals for semicore states and to relax linearization errors,²⁶ were used with LAPW sphere radii of 2.2 Bohr for K and 2.1 Bohr for the other elements. In all cases, we used the experimental-lattice parameters for the end-point compounds and linearly averaged values derived from them for the mixed compositions. The internal coordinates z_{As} were relaxed by energy minimization for ordered cells, while in the virtual-crystal calculations the values of z_{As} were interpolated between the compositions with ordered cells ($y=0, 1, \text{ and } 2$). The details are similar to those in our previous calculations for ThCr_2Si_2 pnictides.^{27,28}

III. KCo_2As_2

The calculated electronic density of states and Co d projection for KCo_2As_2 are shown in Fig. 1 and the band struc-

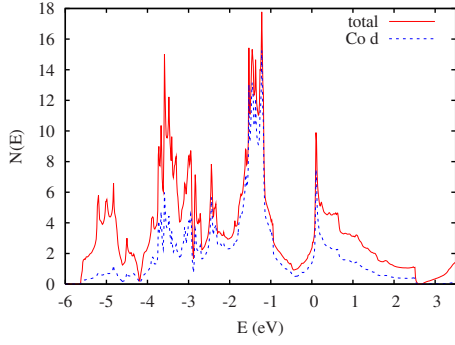


FIG. 1. (Color online) Calculated density of states for KCo_2As_2 and Co d contribution as obtained by projection onto the Co LAPW spheres with radius of 2.1 Bohr.

ture in Fig. 2. These are as obtained in a non-spin-polarized calculation with the LDA relaxed As position $z_{\text{As}}=0.3452$ and the experimental-lattice parameters.²³ The basic shape of the DOS is very similar to that of the Fe superconductors, except that the position of the Fermi energy is higher reflecting the higher electron count. In particular the DOS shows the characteristic d -derived density of states with a pseudogap at a d -electron count of 6 per Co and modest Co d -As p hybridization. However, the states where the Fermi energy, E_F , is positioned, i.e., at the lower edge of the upper DOS peak, are more hybridized with As than the states on the edge of the lower peak where E_F is positioned in the Fe-based materials. The value at the E_F is $N(E_F)=2.4 \text{ eV}^{-1}/\text{f.u.}$ both spins, of which 59% derives from the Co d projection. The reduced d contribution to $N(E_F)$ relative to the Fe-based superconductors places this material further from magnetism than those compounds, at least at the LSDA level. In particular, we found neither a stable ferromagnetic solution nor a stable checkerboard antiferromagnetic solution. However, it should be noted that there is a strong peak in the DOS $\sim 0.1 \text{ eV}$ above E_F so that nonsto-

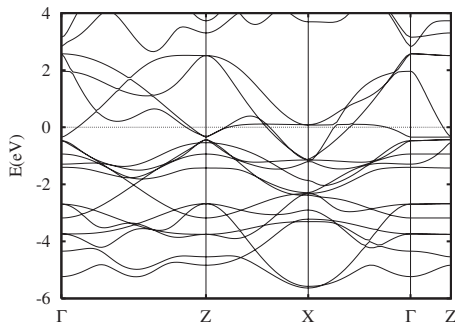
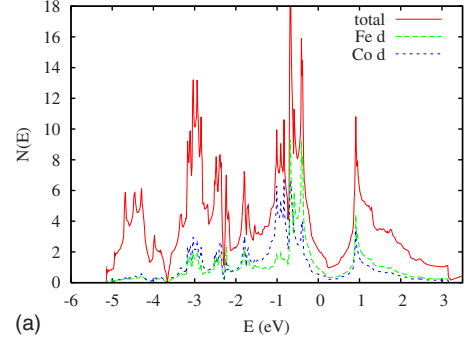
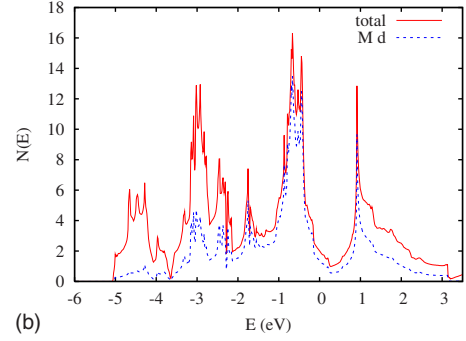


FIG. 2. Calculated band structure of KCo_2As_2 showing lines in the body-centered-tetragonal (bct) basal plane and perpendicular to it. The body-centered tetragonal reciprocal-lattice vectors are $(2\pi/a, 0, -2\pi/c)$, $(0, 2\pi/a, -2\pi/c)$, and $(0, 0, 4\pi/c)$. In terms of these, the long Γ -Z direction is from $(0, 0, 0)$ to $(1, 0, \frac{1}{2})$ in the body-centered tetragonal zone while the short Γ -Z direction is from $(0, 0, 0)$ to $(0, 0, \frac{1}{2})$. X denotes the zone boundary $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ 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.



(a)



(b)

FIG. 3. (Color online) Calculated density of states for KFeCoAs_2 as obtained in an ordered cell (top) and in the virtual-crystal approximation (bottom).

ichiometry that results in electron doping would be expected to result in ferromagnetism. Also, in the absence of spectroscopic or other experimental data for KCo_2As_2 , the possibility that the correlation effects beyond the LSDA could lead to magnetism cannot be excluded. In any case, this is in contrast to our results for KFe_2As_2 , which show a weak-magnetic ground state, ferromagnetic in character, with moments of $1.1 \mu_B/\text{Fe}$ but energy only 13 meV/f.u. lower than the non-spin-polarized case in the LSDA.

IV. FE-CO ALLOYS

Considering the similarity of the electronic structure to that of BaFe_2As_2 with a Fermi energy shift, we next consider an alloy of composition KFeCoAs_2 (i.e., $y=1$). This composition has the same valence-electron count as BaFe_2As_2 . Figure 3 shows the calculated DOS for KFeCoAs_2 as obtained with a checkerboard ordering of Fe and Co and as obtained in the virtual-crystal approximation. A comparison of the ordered cell and virtual-crystal Fermi surfaces is given in Fig. 4. In the ordered cell, the Fe d and Co d projections of the DOS are very similar in shape and furthermore the results of the virtual-crystal calculation are very similar to those of the ordered cell. Similarly, the virtual-crystal Fermi surface is very much the same as that of the ordered cell. The implication is that Fe and Co form an alloy with a coherent electronic structure in this system, similar to the $\text{Ba}(\text{Fe}, \text{Co})_2\text{As}_2$ system, and that we can use the virtual-crystal approximation to study the electronic structure for other values of the composition y . A key point is that the Fermi surface and electronic structure are rather similar to those of BaFe_2As_2 , and

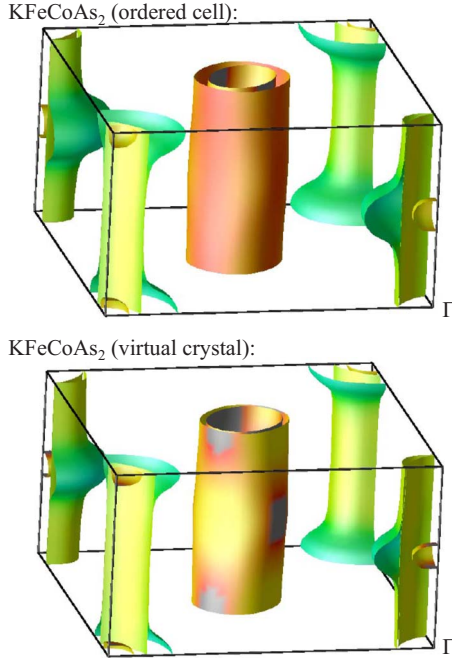


FIG. 4. (Color online) Comparison of the Fermi surface of KFeCoAs_2 from an ordered cell and in the virtual-crystal approximation.

in particular that it shows disconnected, nested hole and electron Fermi surfaces. The implication is that $\text{KFe}_y\text{Co}_{2-y}\text{As}_2$ with $y \sim 1$ is similar to BaFe_2As_2 . Therefore it will be interesting to determine if this material is superconducting either under ambient conditions or with pressure or doping.

Figure 5 shows the evolution of the Fermi surface of $\text{KFe}_y\text{Co}_{2-y}\text{As}_2$ as a function of y , as obtained in the virtual-crystal approximation. As may be seen, the behavior of the Fermi surface is different for electron and hole doping away from $y=1$. In particular, the characteristic of having disconnected hole and electron-Fermi surfaces persists all the way to $y=2$ on the hole-doped side but only up to $\sim y=3/4$ on the electron-doped side. This reflects the fact that the bands making up the electron-Fermi surfaces at the zone corner are lighter than those forming the hole sections. The near vanishing of the electron-Fermi surface for KFe_2As_2 is consistent with photoemission results.²⁹

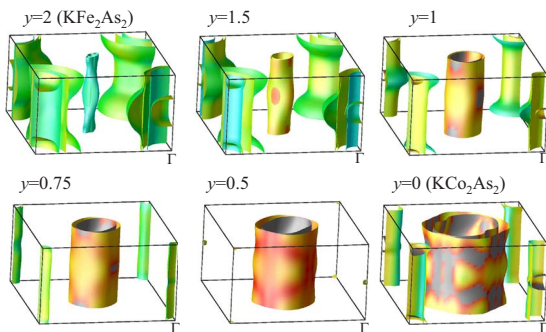


FIG. 5. (Color online) Calculated Fermi surface of $\text{KFe}_y\text{Co}_{2-y}\text{As}_2$ for various values of y . Note that the Fermi-surface sections around the zone center for KCo_2As_2 are different in nature from those at the other compositions; in particular they are electron sections and not the d_{xz}, d_{yz} hole sections.

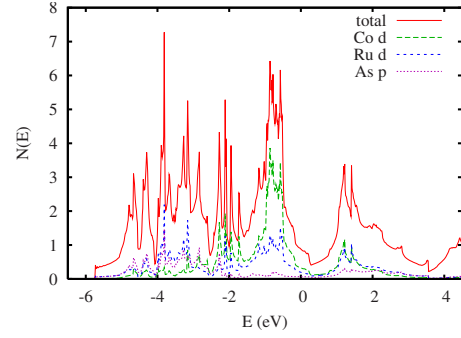


FIG. 6. (Color online) Calculated DOS for ordered KRuCoAs_2 .

One difference from the pure Fe compounds (e.g., BaFe_2As_2) is that we find less tendency toward magnetism and in fact at $y=1$ we do not find an SDW ground state. This may be a result of the fact that the in-plane lattice parameter is smaller in the Co compounds, e.g., $a=3.794 \text{ \AA}$ in KCo_2As_2 vs 3.9625 \AA in BaFe_2As_2 . This leads to a reduction in the value of $N(E_F)$, e.g., $N(E_F)=2.2 \text{ eV}^{-1}$ per f.u. (two transition metals) for ordered KFeCoAs_2 vs 3.0 eV^{-1} for nonspin-polarized BaFe_2As_2 calculated the same way.²⁷

In any case, the above results indicate that superconductivity due to disconnected nested hole and electron Fermi surfaces is possible for Fe concentrations greater than $y/2 \sim 0.4$, i.e., including a range of concentrations below the percolation limit for Fe on a square lattice. One caveat is that there is considerable evidence linking Fe-based superconductivity with magnetism and these Co compounds are less magnetic than the Fe-based materials. Discovery of superconductivity in this system would therefore imply that local physics on the Fe site is not an essential ingredient in Fe-based superconductivity.

V. CO-RU ALLOYS

Finally, we did calculations for an ordered cell KRuFeAs_2 in order to determine whether the characteristic electronic structure of the Fe-based superconductors is maintained for alloys involving Co and Ru. These calculations were motivated by the recent demonstration that superconductivity can

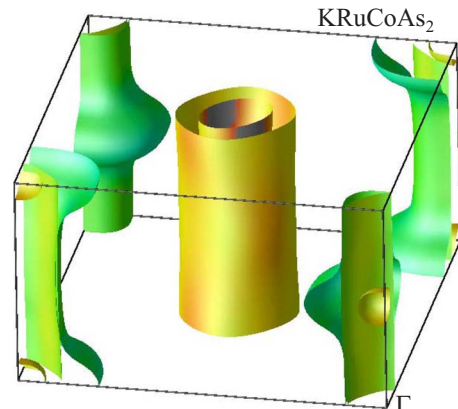


FIG. 7. (Color online) Fermi surface for ordered KRuCoAs_2 .

be induced in Fe-based materials by alloying with Ru.¹⁷ In fact, we find that this structure is maintained. The DOS and Fermi surface are shown in Figs. 6 and 7, respectively. However, one may note that the Ru d states are more strongly hybridized with As p than the Co states—a fact that would work against magnetism, in addition to the already reduced tendency toward magnetism resulting from the more extended orbitals in $4d$ compounds as compared to $3d$ compounds (i.e., weaker Hund's coupling).

VI. SUMMARY AND CONCLUSION

In summary, we show that the electronic structure of Co-rich $K(\text{Fe},\text{Co})_2\text{As}_2$ is similar to those of the Fe-based superconductors, in particular Fe-rich $\text{Ba}(\text{Fe},\text{Co})_2\text{As}_2$, when the electron count is similar, and that $K(\text{Ru},\text{Co})_2\text{As}_2$ also shows

similar features but is less magnetic. These results suggest that these systems should be explored for possible superconductivity or magnetism associated with the Fermi-surface nesting. Should an SDW be found, pressure experiments, again searching for superconductivity, would be desirable. While the air sensitivity of the K -based ThCr_2Si_2 arsenides will no doubt complicate such measurements, an observation of superconductivity in these systems would be of value as it would impose significant constraints on the model for superconductivity in the Fe-based materials, in particular by showing that Fe and local correlation effects associated with Fe are not essential.

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