Properties of KCo$_2$As$_2$ and Alloys with Fe and Ru: Density Functional Calculations

D.J. Singh

Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6114

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Electronic structure calculations are presented for KCo$_2$As$_2$ and alloys with KFe$_2$As$_2$ and KRU$_2$As$_2$. 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 six 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, superconductivity has been discovered in related ThCr$_2$Si$_2$ structure materials (prototype BaFe$_2$As$_2$) LiFeAs and related compounds, perovskite - pnictide intergrowth (Sr$_5$Sc$_2$Fe$_2$P$_4$O$_9$) compounds, and remarkably FeSe, 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.

The band structures show relatively small disconnected Fermi surfaces, in particular hole sections near the 2D zone center and electron sections at the zone corner. On the other hand, despite the low carrier density, the density of states, $N(E_F)$ of these compounds is high ($\sim 2$ 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, 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. 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 multi-orbital 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. 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.

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 towards addressing this question, we focus on the ThCr$_2$Si$_2$ structure, which accommodates an exceptionally large variety of compositions, 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$_2$As$_2$, and pseudobinary alloys with KFe$_2$As$_2$ and KRU$_2$As$_2$ 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 KFe$_5$Co$_9$-yAs$_{2y}$ for Fe concentrations y/2 well below the nearest neighbor square lattice percolation threshold of 0.5927, is very closely analogous to superconducting BaFe$_{2.5}$Co$_{0.5}$As$_{2y}$, and furthermore that KRU$_5$Co$_9$-yAs$_{2y}$ is similar but further from magnetism. We note that KCo$_2$As$_2$ is a known compound, as are KFe$_2$As$_2$ and KRU$_2$As$_2$.

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. Well converged zone samplings and basis sets, including local orbitals for semicore states and to relax linearization errors 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 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\(_2\)Si\(_2\) pnictides\(^{27,28}\).

### III. KCO\(_2\)As\(_2\)

The calculated electronic density of states (DOS) and Co \(d\) projection for KCO\(_2\)As\(_2\) is shown in Fig. 1 and the band structure in Fig. 2. These are as obtained in a non-spin polarized calculation with the LDA relaxed As position \( z_{As} = 0.3452 \) and the experimental lattice parameters.\(^{22}\) 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 six 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 \( N(E_F) = 2.4 \text{ eV}^{-1} \) per formula unit 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 non-stoichiometry that results in electron doping would be expected to result in ferromagnetism. Also, in the absence of spectroscopic or other experimental data for KCO\(_2\)As\(_2\), the possibility that correlation effects beyond the LSDA could lead to magnetism cannot be excluded. In any case, this is in contrast to our results for KFe\(_2\)As\(_2\), which show a weak magnetic ground state, ferromagnetic in character, with moments of 1.1 \( \mu_B/\text{Fe} \) but energy only \( 13 \text{ meV/formula unit} \) 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\(_2\)As\(_2\) 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\(_2\)As\(_2\). Fig. 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 Ba(Fe,Co)\(_2\)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\(_2\)As\(_2\), and in particular that it shows disconnected, nested hole and electron Fermi surfaces. The implication is that KFe\(_{1-y}\)Co\(_y\)As\(_2\) with \( y \sim 1 \) is similar to BaFe\(_2\)As\(_2\). Therefore it will be interesting to
determine if this material is superconducting either under ambient conditions or with pressure or doping.

Fig. 5 shows the evolution of the Fermi surface of KFe$_y$Co$_{2-y}$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 size, 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$_2$As$_2$ is consistent with photoemission results.

One difference from the pure Fe compounds (e.g. BaFe$_2$As$_2$) is that we find less tendency towards 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. $a=3.794$ Å, in KCo$_2$As$_2$, vs. 3.9625 Å, in BaFe$_2$As$_2$. This leads to a reduction in the value of $N(E_F)$, e.g. $N(E_F)=2.2$ eV$^{-1}$ per formula unit (two transition metal...
FIG. 6: (Color online) Calculated DOS for ordered KRuCoAs$_2$.

FIG. 7: (Color online) Fermi surface for ordered KRuCoAs$_2$.

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 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 towards magnetism resulting from the more extended orbitals in 4$d$ compounds as compared to 3$d$ compounds (i.e. weaker Hund’s coupling).

VI. SUMMARY AND CONCLUSION

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