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CONDENSED MATTER

Coulomb Correlations and Electronic Structure of $CuCo_2S_4$: a DFT + DMFT Study

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By employing a combined method of density functional theory and dynamical mean-field theory (DFT + DMFT) we study the spectral properties and local moment formation in the normal state of a Co-based superconductor $CuCo_2S_4$. The obtained quasiparticle mass enhancement $m^*/m \sim 1.2$ is smaller than that in iron-based parent compounds indicating weak correlations in the Co 3*d* states. We show that the mass enhancement is accompanied by an insignificant renormalization and shift of the bands in the vicinity of the Fermi level. This subtle modification is sufficient to induce a substantial transformation of one of the Fermi surface sheets and occurs due to the presence of shallow Fermi surface pockets in the electronic structure of $CuCo_2S_4$. The calculated local and fluctuating moments are smaller than those in iron-based superconductors questioning the importance of spin fluctuations for understanding the pairing mechanism of $CuCo_2S_4$.

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INTRODUCTION

Superconductivity (SC) of Co-based compounds occurs extremely rare compared to other transition metal counterparts. For a long time, the only known example of a Co-based SC was the oxide hydrate $Na_xCoO_2{\cdot}yH_2O$ ($T_c \sim 5$ K) [1, 2]. Later, SC was found in $LaCo_2B_2$ ($T_c \sim 4$ K) [3], $Lu_3Co_4Ge_{13}$ ($T_c \leq 1.4$ K) [4], and very recently in CuCoSi ($T_c \sim 4$ K) [5]. Also, it is worth noting that there is another exotic Co-containing system $PuCoGa_5$ exhibiting a rather high $T_c \sim 18$ K [6, 7] however its SC stems from Pu electrons.

The thiospinel compound $CuCo_2S_4$ shows many similarities with $Na_xCoO_2{\cdot}yH_2O$ including Co coordination, Co formal valence, and geometric frustration. First report on SC of $Cu_{1+x}Co_{2-x}S_4$ multiphase powder samples with an estimate $T_c \sim 2$ K is dated back to 1993 [8]. Later, the SC-like behavior was confirmed by nuclear magnetic resonance (NMR) measurements of a multiphasic $Cu_{1.5}Co_{1.5}S_4$ revealing the growth of antiferromagnetic spin correlations at low temperatures [9]. Recent magnetic and transport measurements of the new generation of nearly stoichiometric $CuCo_2S_4$ samples detected Pauli paramagnetism and a SC transition at $T_c = 4.2$ K [10].

Investigations of the symmetry of the SC gap of $CuCo_2S_4$ arrived at different conclusions. Early NMR measurements suggested a gapless SC state developing in line with an enhancement of antiferromagnetic fluctuations [9]. By contrast, later NMR experiments indicated a full isotropic SC gap yet confirmed the presence of weak antiferromagnetic spin correlations [11, 12]. In this context, it is interesting that the order parameter of the related Co-based system $Na_xCoO_2{\cdot}yH_2O$ is presumably anisotropic [13–15]. Thus, it is not clear whether $CuCo_2S_4$ should be classified an unconventional SC [16].

Until now, there are only few research papers reporting microscopic analysis of the electronic properties of $CuCo_2S_4$ using standard density functional-based methods neglecting the effect of electron–electron correlations in the partially filled Co 3*d* shell [17, 18]. At the same time importance of electron correlations in $CuCo_2S_4$ is traced from resistivity measurements as indicated by the authors of [19]. Therefore, a careful theoretical study of the interplay between the Coulomb interaction and the electronic structure and magnetism in the normal state of $CuCo_2S_4$ would be very helpful for understanding the anomalous properties of this material and can be used in further works to clarify the nature of its SC.

In this Letter, we explore the effect of Coulomb correlations on the electronic structure and magnetic properties of $CuCo_2S_4$ employing the DFT + DMFT method [20, 21]. We analyze the impact of electron–electron interaction on the spectral functions, Fermi surface (FS) shape, quasiparticle effective mass renormalization m^*/m, and formation of the local

moments. Our results demonstrate that $CuCo_2S_4$ is a weakly correlated compound with a high degree of electronic itinerancy. Nevertheless, it is found that correlation effects are strong enough to cause a significant modification of one the FS sheets.

COMPUTATIONAL DETAILS

In our work we use the DFT + DMFT computational scheme fully self-consistent in charge density [22, 23]. This approach merges the many-body dynamical mean-field theory of correlated electrons (DMFT) [24, 25] and density functional theory (DFT) and has proven to be a powerful theoretical tool for investigation of the spectral, structural and magnetic properties of real materials including the normal state of unconventional Fe-based superconductors [26]. We adopt the experimental crystal structure of $CuCo_2S_4$ [27] (space group $Fd\bar{3}m$) and employ the pseudopotential based generalized gradient approximation within DFT [28, 29] to calculate the non-interacting band structure. The basis set of atomic-centered symmetry-constrained Wannier functions is used to construct the effective Hamiltonian in DMFT. The Wannier functions are computed by the projection procedure [30, 31] for the energy window including Co $3d$, S $3p$, and Cu $3d$ states. The DMFT realistic many-body problem is solved by the continuous-time quantum Monte Carlo (CT-QMC) method [32, 33] using the on-site Hubbard parameter $U = 4$ eV and Hund's rule coupling $J = 0.7$ eV for the partially filled Co $3d$ states of $CuCo_2S_4$. In DFT + DMFT we employ the fully localized limit for the double-counting correction and use the Padé approximant method [34] for analytical continuation of the self-energy.

RESULTS AND DISCUSSION

We start with an analysis of the effect of Coulomb correlations on the spectral properties. To this end, we first compare the spectral functions of $CuCo_2S_4$ calculated by DFT with those obtained within DFT + DMFT (Fig. 1). Our DFT results (Fig. 1, shaded areas) show that the total spectral function corresponds to a metal and features a broad peak at the Fermi energy (E_F). This peak originates from the almost fully occupied Co t_{2g} orbitals (filling $n_{t_{2g}} = 0.96$ per spin-orbital) strongly hybridized with the S $3p$ states. By contrast, the Co e_g states are close to half-filling ($n_{e_g} = 0.55$), however their spectral function exhibits a dip in the vicinity of E_F. We also note that the Cu $3d$ orbitals show a minor contribution to the spectral weight close to E_F forming a broad band from -5 to -1.5 eV. These results imply that the effect of local Coulomb correlations on the spectral properties of $CuCo_2S_4$ is presumably not significant due to the small spectral weight of partially filled states at the Fermi level yet the total Co $3d$ band width $W \sim 4$ eV is close to the value of the on-site Coulomb parameter U.

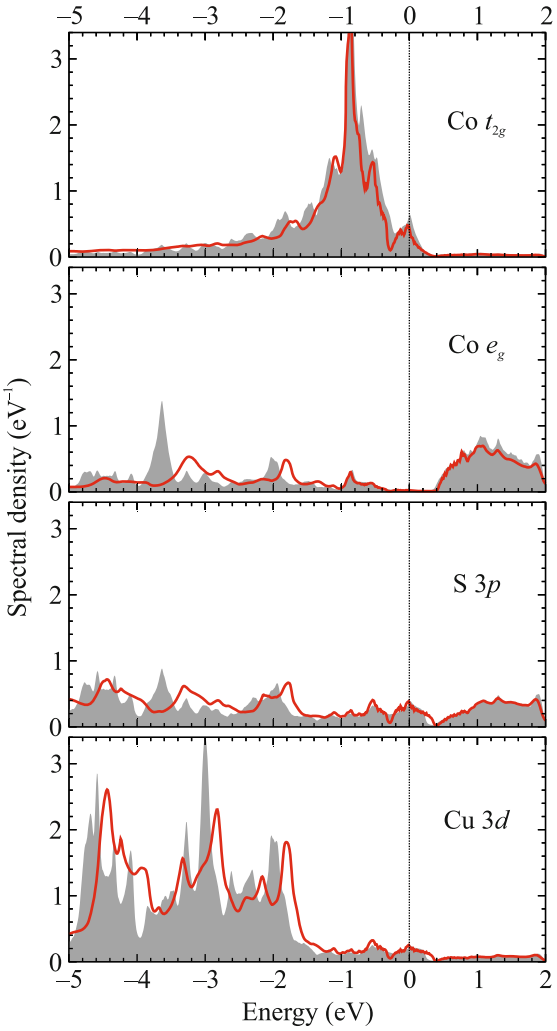

Fig. 1. (Color online) Atomic- and orbitally-resolved spectral functions of $CuCo_2S_4$ computed by (shaded areas) DFT and (solid lines) DFT + DMFT at $T = 290$ K. The energy is measured from the Fermi level.

Indeed, we find that the spectral functions of $CuCo_2S_4$ computed by DFT + DMFT (Fig. 1, solid lines) show little difference with those obtained by DFT. In particular, we observe that correlation effects only slightly shift the peaks of the spectral functions below the Fermi level leaving their shape in the vicinity of E_F almost unchanged. To give a quantified characterization of the effect of Coulomb correlations we calculate the orbitally resolved enhancement of the quasiparticle mass, $m^*/m = 1 - \partial \mathrm{Re}\Sigma_{ii}(\omega)/\partial\omega|_{\omega\to 0}$ where $\Sigma_{ii}(\omega)$ is the diagonal element of the self-energy. We obtain $m^*/m = 1.18$ for the t_{2g} orbitals and

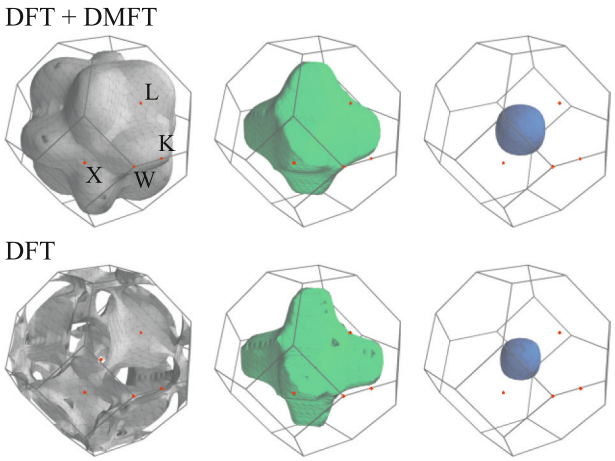

Fig. 2. (Color online) Fermi surface of $CuCo_2S_4$ as computed by (top row) DFT + DMFT at $T = 290$ K and (bottom row) DFT. For clarity, different sheets are shown separately.

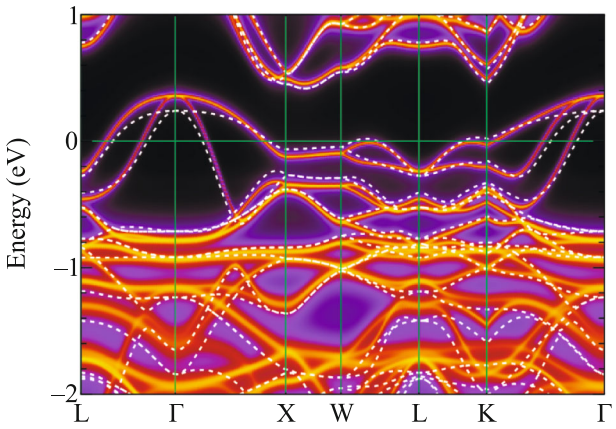

Fig. 3. (Color online) (Contours) Momentum-resolved spectral function of $CuCo_2S_4$ along the high-symmetry path in the fcc Brillouin zone obtained by DFT + DMFT at $T = 290$ K compared to (dashed lines) the DFT energy bands. The energy is measured from the Fermi level.

$m^*/m = 1.22$ for the e_g states. These values accord to the observed small renormalization of the DFT spectral functions by correlation effects accompanied by an insignificant reduction of the quasiparticle spectral weight in the vicinity of E_F. We also note that these renormalization factors are approximately twice smaller than characteristic values of m^*/m obtained in DFT + DMFT calculations for different Fe-based unconventional superconductors [35, 36] and resemble those in the classical itinerant magnet $ZrZn_2$ [37].

To investigate the effect of Coulomb correlations on the spectral properties of $CuCo_2S_4$ in more detail we compute the Fermi surface and the momentum-resolved spectral function $A(\mathbf{k}, \omega)$. We found that within DFT the FS exhibits three sheets (Fig. 2, lower panel). The first (inner) and the second hole-like sheets represent closed geometrical shapes centered at and enveloping the Γ point of the fcc Brillouin zone (BZ). The first FS to a good approximation can be considered a sphere while the second FS features "outgrowths" directed to the X points of the BZ. The third (outer) FS exhibits a complex shape that intersects the BZ border.

Unlike the integral spectral functions our DFT + DMFT calculations show significant correlation induced transformations of one of the FS sheets (Fig. 2, upper panel). In particular, we observe an increase of the radius of the inner sheet and a stretch of the middle sheet along the Γ–L direction. These parts of the FS however exhibit a weak sensitivity to correlation effects and mostly preserve their shape in DFT + DMFT. On the contrary, the outer sheet now represents a closed shape that fully fits the BZ.

The above mentioned modifications of the FS can be understood from a comparison of the DFT + DMFT spectral function $A(\mathbf{k}, \omega)$ with the energy bands from DFT (Fig. 3). We note that due to the small quasiparticle damping (both $\mathrm{Im}\Sigma_{t_{2g}}(E_F)$ and $\mathrm{Im}\Sigma_{e_g}(E_F) \sim -0.005$ eV) the spectral function $A(\mathbf{k}, \omega)$ describes a coherent distribution of the spectral weight close to E_F that allows an unambiguous interpretation of the DFT + DMFT results. One can see that the effect of Coulomb correlations on the electronic structure primarily corresponds to a shift and renormalization of the bands in close similarity to the situation in parent compounds of Fe-based superconductors [38, 39]. In $CuCo_2S_4$ however due to the presence of shallow pockets along the W–L–K path these transformations induce a significant change of the FS shape. Specifically, we observe that the DFT bands crossing the Fermi level along the W–L–K path and one band in the vicinity of the K point on the Γ–K direction shift below E_F in DFT + DMFT. As a result, the outer FS sheet loses its intersection with the W–L–K plane of the BZ and transforms into a closed shape. The observed transformations of the FS presumably indicate the need of taking into account the electronic correlations for interpretation of the temperature behavior of the resistivity of Cu–Co–S superconducting samples as noted in [19] and require a thorough study.

As the final step of our study of the electronic properties of $CuCo_2S_4$ we analyze the local moment formation. Namely, our DFT + DMFT calculations give the fluctuating magnetic moment $\sqrt{\langle m_z^2 \rangle} \sim 1\ \mu_B$. This value is significantly (by a factor ~2.5) smaller than that reported for parent compounds of pnictide and chalcogenide Fe-based superconductors [40, 41] which show well-defined local moments and therefore implies a weaker localization of 3*d* electrons in

$CuCo_2S_4$. To illustrate the higher degree of electronic itinerancy we compute the local spin correlator $\chi(\tau) = \langle \hat{s}^z(\tau)\hat{s}^z(0)\rangle$ (where $\hat{s}^z(\tau)$ is the instantaneous Co spin at imaginary time τ computed by CT-QMC) and estimate the local moment $M_{\text{loc}} = \left(k_B T \int_0^{1/k_B T} d\tau \chi(\tau)\right)^{1/2}$. Our calculations give $M_{\text{loc}} \sim 0.18\ \mu_B$ which is at least two times smaller than that obtained by DFT + DMFT for the Fe-based pnictides and chalcogenides [40, 41]. The small magnitude of both $\sqrt{\langle m_z^2\rangle}$ and M_{loc} (compared to those in Fe-based superconductors) is indicative of weak spin fluctuations. This result questions the spin-fluctuation-mediated origin of the superconducting state in $CuCo_2S_4$. We note however that absence of strong spin fluctuations due to correlation effects does not necessarily exclude importance of the latter for understanding the pairing mechanism. For example, it is known that not only Coulomb correlations affect the phonon anomalies [42] but also significantly enhance the electron–phonon coupling [43] leaving the possibility to explain the superconductivity of $CuCo_2S_4$ within the standard Bardeen–Cooper–Schrieffer theory.

CONCLUSIONS

In conclusion, using the DFT + DMFT method we have investigated the effect of Coulomb correlations on the spectral properties and local moments of $CuCo_2S_4$. Our calculations have shown that $CuCo_2S_4$ is a weakly correlated material characterized by the quasiparticle effective mass enhanced by a factor of $m^*/m \sim 1.2$. We have demonstrated that the mass enhancement is accompanied by a weak renormalization and shift of the DFT spectral functions and energy bands. Surprisingly, we have found that these shifts induce a significant transformation of one of the FS sheet due to the presence of shallow FS pockets along the W–L–K path indicating the possible importance of correlation effects for transport properties of $CuCo_2S_4$. Finally, our results for the local and fluctuating magnetic moments allow us to speculate that the spin-fluctuation scenario of unconventional pairing is unlikely applicable to explain the pairing mechanism in $CuCo_2S_4$.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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