Pis'ma v ZhETF, vol. 117, iss. 8, pp. 596 – 597

Coulomb correlations and electronic structure of $CuCo_2S_4$: a DFT + DMFT study

S. L. Skornyakov[+*1)], *I. O. Trifonov*[+*], *V. I. Anisimov*[+*]

[+]*M. N. Miheev Institute of Metal Physics, Russian Academy of Sciences, 620108 Yekaterinburg, Russia*

[*]*Institute of Physics and Technology, Ural Federal University, 620002 Yekaterinburg, Russia*

Submitted 9 March 2023
Resubmitted 9 March 2023
Accepted 20 March 2023

DOI: 10.31857/S1234567823080050, EDN: wcselb

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 $Na_xCoO_2 \cdot yH_2O$ ($T_c \sim 5\,\mathrm{K}$) [1, 2]. Later, SC was found in $LaCo_2B_2$ ($T_c \sim 4\,\mathrm{K}$) [3], $Lu_3Co_4Ge_{13}$ ($T_c \leq 1.4\,\mathrm{K}$) [4], and very recently in CuCoSi ($T_c \sim 4\,\mathrm{K}$) [5]. Also, it is worth noting that there is another exotic Co-containing system $PuCoGa_5$ exhibiting a rather high $T_c \sim 18\,\mathrm{K}$ [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 $T_c \sim 2\,\mathrm{K}$ 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 $T_c = 4.2\,\mathrm{K}$ [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 theory (DFT) methods neglecting the effect of electron-electron correlations in the partially filled Co $3d$ 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].

In this Letter, we explore the effect of Coulomb correlations on the electronic structure and magnetic properties of $CuCo_2S_4$ employing a combination of many-body dynamical mean-field theory (DMFT) with DFT (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.

We find that the spectral functions of $CuCo_2S_4$ computed by DFT + DMFT show little difference with those obtained by DFT. We observe that correlation effects only slightly shift and renormalize the spectral functions in the vicinity of the Fermi energy (E_F) leaving their shape almost unchanged. The calculated enhancement of the quasiparticle mass is $m^*/m = 1.18$ for the t_{2g} orbitals and $m^*/m = 1.22$ for the e_g states. The computed m^*/m are approximately twice smaller the characteristic values obtained in DFT + DMFT calculations for different Fe-based unconventional superconductors [22, 23].

Our DFT + DMFT calculations show significant correlation induced transformations of one of the FS sheets as compared to DFT (Fig. 1). 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 exhibit a weak sensitivity to correlation effects. On the contrary, within DFT + DMFT the outer sheet

[1)]e-mail: sergey.l.skornyakov@yandex.ru

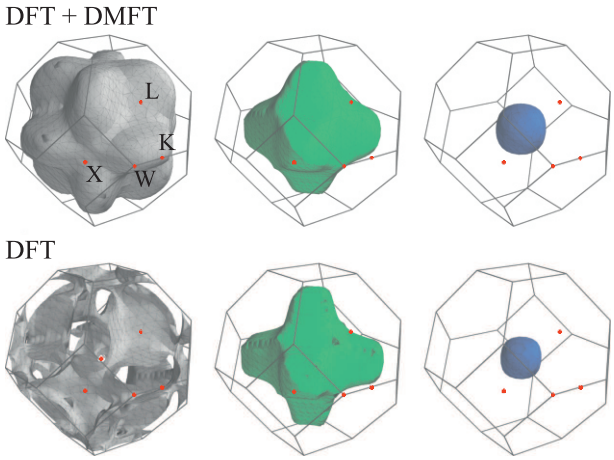

Fig. 1. (Color online) Fermi surface of $CuCo_2S_4$ as computed by DFT + DMFT (top row) at $T = 290$ K and DFT (bottom row). For clarity, different sheets are shown separately

represents a closed shape that fully fits the Brilouin zone (BZ). We demonstrate that these modifications of the FS occur due to the presence of shallow FS pockets in the electronic structure of $CuCo_2S_4$ along the W-L-K path in the BZ.

We obtain that DFT + DMFT gives 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 [24, 25] which show well-defined local moments and therefore implies a weaker localization of $3d$ 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) and estimate the local moment $M_{\rm loc} = (k_B T \int_0^{1/k_B T} d\tau \chi(\tau))^{1/2}$. Our calculations give $M_{\rm loc} \sim 0.18\ \mu_B$ which is at least two times smaller than that obtained by DFT + DMFT for the Fe-based pnictides and chalcogenides [24, 25]. The small magnitude of both $\sqrt{\langle m_z^2 \rangle}$ and $M_{\rm loc}$ is indicative of weak spin fluctuations and questions the spin-fluctuation-mediated origin of superconductivity of $CuCo_2S_4$.

This work was supported by the Russian Science Foundation (Project # 19-12-00012).

This is an excerpt of the article "Coulomb correlations and electronic structure of $CuCo_2S_4$: a DFT + DMFT study". Full text of the paper is published in JETP Letters journal. DOI: 10.1134/S0021364023600647

1. K. Takada, H. Sakurai, E. Takayama-Muromachi, F. Izumi, R. A. Dilanian, and T. Sasaki, Nature **422**, 53 (2003).
2. H. Sakurai, Y. Ihara, and K. Takada, Physica C **514**, 378 (2015).
3. H. Mizoguchi, T. Kuroda, T. Kamiya, and H. Hosono, Phys. Rev. Lett. **106**, 237001 (2011).
4. B. K. Rai, I. W. H. Oswald, J. K. Wang, G. T. McCandless, J. Y. Chan, and E. Morosan, Chem. Mater. **27**, 2488 (2015).
5. Z. He, R. Huang, K. Zhou, Y. Liu, S. Guo, Y. Song, Z. Guo, S. Hu, L. He, Q. Huang, L. Li, J. Zhang, S. Wang, J. Guo, X. Xing, and J. Chen, Inorg. Chem. **60**, 6157 (2021).
6. J. L. Sarrao, L. A. Morales, J. D. Thompson, B. L. Scott, G. R. Stewart, F. Wastin, J. Rebizant, P. Boulet, E. Colineau, and G. H. Lander, Nature **420**, 297 (2002).
7. N. J. Curro, T. Caldwell, E. D. Bauer, L. A. Morales, M. J. Graf, Y. Bang, A. V. Balatsky, J. D. Thompson, and J. L. Sarrao, Nature **434**, 622 (2005).
8. K. Miyatani, T. Tanaka, S. Sakita, M. Ishikawa, and N. Shirakawa, Jpn. J. Appl. Phys. **32**, Suppl. 32-3, 448 (1993).
9. Y. Furukawa, S. Wada, K. Miyatani, T. Tanaka, M. Fukugauchi, and M. Ishikawa, Phys. Rev. B **51**, 6159 (1995).
10. Y.-Y. Jin, S.-H. Sun, Y.-W. Cui, Q.-Q. Zhu, L.-W. Ji, Z. Ren, and G.-H. Cao, Phys. Rev. Mater. **5**, 074804 (2021).
11. H. Sugita, S. Wada, K. Miyatani, T. Tanaka, and M. Ishikawa, Physica B **284**, 473 (2000).
12. S. Wada, H. Sugita, K. Miyatani, T. Tanaka, and T. Nishikawa, J. Phys.: Condens. Matter **14**, 219 (2002).
13. G. Baskaran, Phys. Rev. Lett. **91**, 097003 (2003).
14. T. Fujimoto, G.-Q. Zheng, Y. Kitaoka, R. L. Meng, J. Cmaidalka, and C. W. Chu, Phys. Rev. Lett. **92**, 047004 (2004).
15. Q.-H. Wang, D.-H. Lee, and P. A. Lee, Phys. Rev. B **69**, 092504 (2004).
16. J. Hirsch, M. Maple, and F. Marsiglio, Physica C **514**, 1 (2015).
17. Z. Yue, Z. Hou, F. Yun, P. Liu, G. Yang, A. Bake, W. Zhao, D. Cortie, C. Shu, S. Hu, J. Cheng, and X. Wang, J. Mater. Chem. C **9**, 8874 (2021).
18. L. Wu, L. Sun, X. Li, Q. Zhang, Y. Zhang, J. Gu, K. Wang, and Y. Zhang, Small **16**, 2001468 (2020).
19. K. Miyatani, T. Tanaka, and M. Ishikawa, J. Appl. Phys. **83**, 6792 (1998).
20. A. Georges, G. Kotliar, W. Krauth, and M. J. Rozenberg, Rev. Mod. Phys. **68**, 13 (1996).
21. V. I. Anisimov, A. I. Poteryaev, M. A. Korotin, A. O. Anokhin, and G. Kotliar, J. Phys. Condens. Matter **9**, 7359 (1997).
22. Z. P. Yin, K. Haule, and G. Kotliar, Nat. Mater. **10**, 932 (2011).
23. I. A. Nekrasov, N. S. Pavlov, and M. V. Sadovskii, JETP Letters **102**, 30 (2015).
24. S. L. Skornyakov and I. Leonov, Phys. Rev. B **100**, 235123 (2019).
25. S. L. Skornyakov, V. I. Anisimov, and I. Leonov, Phys. Rev. B **103**, 155115 (2021).