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# Superconductivity and magnetism in CuBiSO from first principles

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$Cu_{1-y}BiSO$ was recently reported to superconduct at $T \approx 5.8$ K at $y \approx 0.15$. Band-structure calculations indicate that the stoichiometric CuBiSO is a band insulator. In this Rapid Communication, I show that the hole-doped (whether in the virtual crystal approximation or with actual Cu vacancies) CuBiSO is on the verge of a ferromagnetic instability (cf. Pd metal) and therefore a conventional superconductivity with $T_c \sim 6$ K is quite unlikely. Presumably, the hole-doped CuBiSO is another example of superconductivity mediated by spin fluctuations.

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Recently, Ubaldini *et al.*[1] reported that in the quaternary compound $Cu_{1-y}BiSO$ superconductivity at $T_c=6$ K can be induced by a small Cu deficiency ($y \sim 15\%$) although not by an electron doping (when substituting O with F). Although another similar study has not confirmed the superconductivity,[2] this result has triggered some interest in the community.[2,3] I will show below that this interest is well justified, for this material is very unlikely to be a conventional *s*-wave superconductor, and, if superconducting, is probably another example of a spin-fluctuation-mediated superconductivity.

CuBiSO crystallizes in the well-known tetragonal ZrCuSiAs structure,[2,4] recently made famous by some Fe-based high-temperature superconductors (although there is no commonality whatsoever between the latter and the material in question). The lattice parameters reported in Ref. 1 are 3.8726 and 8.5878 Å, in Refs. 4 3.8691 and 8.5602 Å, and in Ref. 2 3.868 and 8.557 Å. The internal coordinates of Bi and S, respectively, are reported as 0.14829 and 0.6710 (Ref. 4) and 0.151 and 0.648 (Ref. 2).

In my calculations I used the structure reported in Ref. 4. The variation in crystallographic parameters within these limits does not affect any conclusions of this work. In agreement with the previous first-principles calculations[3,4] I found[5] that in the scalar-relativistic approximation the stoichiometric compound is a band insulator, with a direct gap underestimated compared to the measured optical gap,[4] as common in the density-functional calculations. Adding spin-orbit interaction on Bi reduces the gap even further, from 0.75 to 0.55 eV, by affecting the unoccupied states. The states right below the gap are formed predominantly by the Cu *xz* and *yz* orbitals while the empty states above the gap have quasifree-electron character [the interstitial region, being ≈60% in volume, contributes up to 50% of the density of states (DOS) of these bands]. In agreement with, especially, the full-potential all-electron calculations of Ref. 3, I found a flat band right at the top of the valence band at the Z point (Fig. 1), essentially not dispersing up to halfway between Z and X.[6] This band results in a small but very sharp DOS peak right below the band gap (Fig. 2), with the total weight of slightly less than 0.3 electron per copper, and a maximum DOS of 4.1 states/eV. f.u. at 130 meV below the gap (corresponding to 0.10–0.12 hole/Cu). One can see that this peak indeed originates from the flat band along *Z-A*, by looking at the Fermi surface for $E_F$ set at 120 meV below the band gap, where the peak just starts (approximately 0.07 hole/Cu doping). This feature appears as cross-shaped Fermi surface pockets emerging from Z (Fig. 3).

Given that Cu *d* orbitals have sizeable Hund rule coupling this result suggests that Cu ions under 10–20 % hole doping should be magnetic. Indeed, ferromagnetic (antiferromagnetic calculation, however, were invariably converging to zero magnetization[7]) calculations for $y=0.2$ in the virtual crystal approximation (0.2 hole per Cu) converge to a stable solution with the magnetic moment $M \approx 0.12$–$0.13 \mu_B$ per

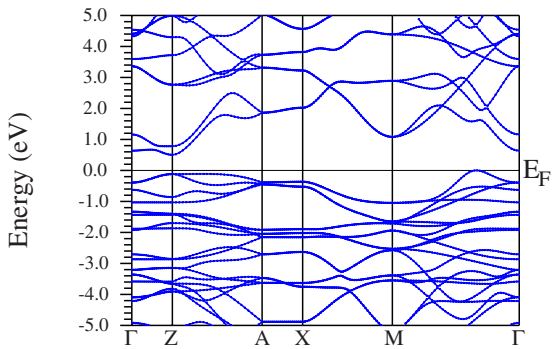


FIG. 1. (Color online) Band structure of CuBiSO near the Fermi level. Note a flat band in the *Z-A* direction.

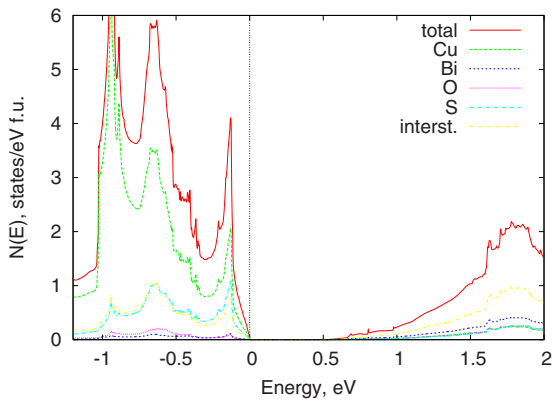


FIG. 2. (Color online) Density of states of CuBiSO near the Fermi level. Note a peak right below the gap, and the leading contribution of the Cu states below, and the interstitial states above the band gap.

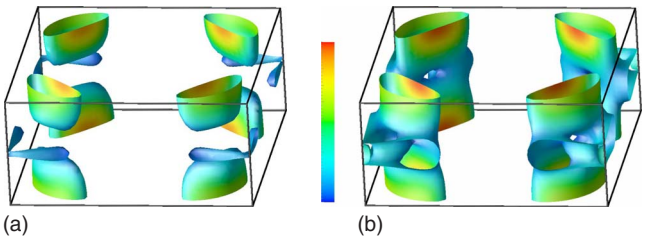


FIG. 3. (Color online) Left panel: the Fermi surface of $Cu_{1-y}BiSO$ at $E_F$ 120 meV below the gap, where a sharp peak in DOS starts. Note a cross-shaped pocket emerging along the *Z-A* direction, responsible for this peak. For comparison, in the right panel the Fermi surface at $E_F$=150 meV ($y \sim 0.15$) is shown, where the peak is already fully developed. Both Fermi surfaces are colored according the absolute value of the Fermi velocity using the same scale (the lowest value, blue in color, is zero).

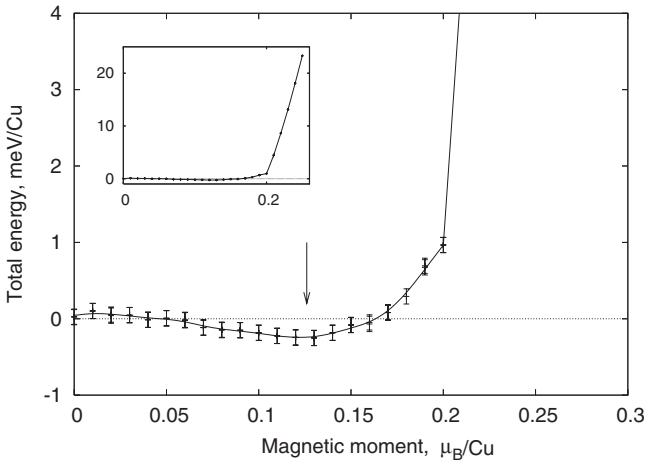


FIG. 4. Fixed spin moment calculations for $Cu_{1-y}BiSO$ for $y$ =0.2. The self-consistent solution is indicated by the arrow. Note that the energy is essentially independent of the magnetic moment up to the half-metallic magnetization of $y\mu_B$/Cu. The inset shows a linear growth of the total energy when magnetization exceeds the half-metal limit.

Cu, but with hardly any energy gain. Correspondingly, fixed spin moment calculations (Fig. 4) show that in the generalized gradient approximation (GGA) approximation the energy, within the computational accuracy, does not depend on magnetization up to $M=y\mu_B$. Note that this magnetization would correspond to a half-metallic state similar to that in the Co-doped $FeS_2$ (Ref. 8) (in fact the physics of the formation of a magnetic state is quite similar here). This means that the calculated spin susceptibility is essentially infinite, a situation extremely close to Pd metal, where GGA calculations also yield infinite susceptibility.[9] As in Pd, or, for that matter, in Fe pnictides, fluctuations beyond the mean-field level should suppress magnetization and reduce the susceptibility to a large, but finite value. But, again as in Pd, strong spin fluctuations are bound to destroy any conventional *s*-wave superconductivity, particularly given that with this relatively modest carrier-density electron-phonon coupling cannot be too strong.

This leads us to the conclusion that the superconductivity in the hole-doped $Cu_{1-y}BiSO$ must be unconventional, and probably magnetically mediated, although it is not clear yet what particular pairing symmetry can be generated in this material. One can question the validity of the virtual crystal approximation, given that holes are introduced not through substitution, but through Cu vacancies. To verify that, I have performed supercell calculations using four formula units with one vacancy, that is to say, $Cu_3Bi_4S_4O_4$, corresponding to $y$=0.25. The calculations converged to a ferromagnetic state with $M=0.2\mu_B$ per formula unit ($0.8\mu_B$ per supercell), again slightly below the half-metallic limit of $0.25\mu_B$, thus confirming the validity of the virtual crystal calculations. Interestingly, the magnetization was quite delocalized, with Cu ions carrying $0.1-0.13\mu_B$, and the rest of the magnetic moment distributed among the sulfur ions and in the interstitial region.

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[5] The full-potential LAPW method, as implemented in the WIEN2K package, has been used for all calculations. Up to 840 inequivalent *k* points have been utilized to achieve the self-consistency with the energy convergency better than 0.05 meV.

[6] In Ref. 3, unconventional notations for the high symmetry points are used; conventional *A* $(\pi,0,\pi)$ is called *R*, and conventional *R* $(\pi,\pi,\pi)$ is called *A*. I am using the standard notations.

[7] I have tried only a checkerboard antiferromagnetic arrangement since I do not see any *a priori* reason for any other antiferromagnetic ordering (the fact that the crystal structure coincides with that of pnictide superconductors is not an argument at all that this material would assume the same exotic magnetic structure). Of course, this does not mean that there are no spin fluctuations with a finite wave vector; it only tells us that if such fluctuations occur, they occur at a wave vector, different from $\pi,\pi$ (in the unfolded Brillouin-zone notation).

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