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Competition between electron-phonon coupling and spin fluctuations in superconducting hole-doped CuBiSO

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CuBiSO is a band insulator that becomes metallic upon hole doping. Superconductivity was recently reported in doped Cu_{1-x}BiSO and attributed to spin fluctuations as the pairing mechanism. Based on first-principles calculations of the electron-phonon coupling, we argue that the latter is very strong in this material, and probably drives superconductivity. The critical temperature is, however, strongly depressed by the proximity to magnetism. Thus Cu_{1-x}BiSO is a quite unique compound where both a conventional phonon-driven and an unconventional triplet superconductivity are possible, and compete with each other. We argue that, in this material, it may be possible to switch from conventional to unconventional superconductivity by varying such parameters as doping or pressure.

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The study of spin fluctuations (SFs) as superconducting mediators dates back to the 1960s;[1,2] however, in contrast to the electron-phonon (EP) interaction, for which a detailed first-principles theory has been developed in the last 20 years, a quantitative theory is still lacking. In several materials where at some point ferromagnetic spin fluctuations (paramagnons) were considered as potential pairing agents, such as $ZrZn_2$,[3] $MgCNi_3$,[4] or Pd metal,[1] phonon and SF contributions either cancel, rendering the material nonsuperconducting ($ZrZn_2$, Pd), or the latter substantially reduces the superconducting transition temperature.

Recently, superconductivity with $T_c = 5.8$ K was discovered in hole-doped $Cu_{0.9}$BiSO.[5] CuBiSO crystallizes in the ZrCuAsSi-type structure, isostructural to the 1111 family of Fe-based superconductors, with Cu-S layers playing the role of Fe-As layers. While Cu-S hybridized dp bands *per se* are rather similar to the Fe-As bands in Fe pnictides, the different electronic filling brings about very different properties in the two systems. Stoichiometric CuBiSO is in fact a band insulator with Cu being in the d^{10} electronic configuration.[5–7] Upon hole doping it displays both a strong tendency to itinerant (ferro)magnetism, and a spectacularly strong EP coupling, hinting at unconventional, triplet p-wave,[8] and conventional, singlet s-wave superconductivity, respectively.

In this Rapid Communication, we study the interplay between these competing instabilities, using first-principles calculations of Cu_{1-x}BiSO as a function of doping and Stoner parameter, which we use as a proxy for the tendency to magnetism. We find that the EP coupling here is unusually strong for a doped semiconductor, therefore the conjecture of Ref. 8 is not necessarily true: It is likely that a conventional superconductivity, even though substantially weakened by SF, is more stable than an unconventional (e.g., p-wave) one. However, a small variation of parameters can reverse the situation and stabilize triplet superconductivity or long-range magnetism. We identify two large regions in the parameter space where, respectively, ferromagnetism (FM) or conventional s-wave superconductivity are the ground states, with an intermediate region where no FM long-range order is expected, yet SF are strong enough to destroy the s-wave superconductivity and possibly stabilize a triplet state.

We perform calculations in the linear-response approximation for the EP interaction, and in the local spin-density-functional version of the random-phase approximation (RPA) for SF, as described below; doping is treated in the rigid-band approximation (RBA).[9]

The generalized-gradient approximation (GGA) band structure and partial electronic density of states (DOS) are shown in Fig. 1; in agreement with previous calculations,[5,8,10] we find that the stoichiometric compound is a semiconductor[5,6] with an indirect gap of $\Delta \approx 0.5$ eV (in GGA); the top of the valence band occurs along the Γ-M line, and we choose it as the zero of the energy in the following. The electronic structure in an energy range $\sim$7 eV below the gap in CuBiSO is derived from Cu d and S p states (see top panel of Fig. 1). The Cu d states are centered around ~ -2 eV. They hybridize strongly with the S p states, forming antibonding bands within $\sim$1 eV below the semiconducting gap. The EP matrix element is large for these bands, as the electronic states are very sensitive to ionic displacements. On the contrary, the deeper, nonbonding, Cu d bands, centered around ~ -3 eV, are less sensitive to the Cu-S hopping parameters and exhibit a much weaker EP interaction. The tendency to magnetism is strong throughout the entire Cu d band, since the Stoner parameter of Cu is large ($I_{\mathrm{Cu}} \approx 0.9$ eV).

In pure CuBiSO, Cu is in a nominal d^{10} state and thus not magnetic. Doping with holes, for $x \lesssim 0.5$, shifts the Fermi level down into the antibonding Cud_{xz}-Sp_x and Cud_{yz}-Sp_y bands. These bands have a large DOS because they are repelled from the Bi p bands above (Fig. 1).

If we could shift the Fermi level further down, so as to cut the band structure at ~ -1.4 eV (dash-dotted line in the top panel of Fig. 1), we would find a striking similarity with the low-energy electronic structure of Fe pnictides, with the xz, yz hole and electron pockets, centered at Γ and M, respectively. The DOS and the p-d hybridization here are small, thus the

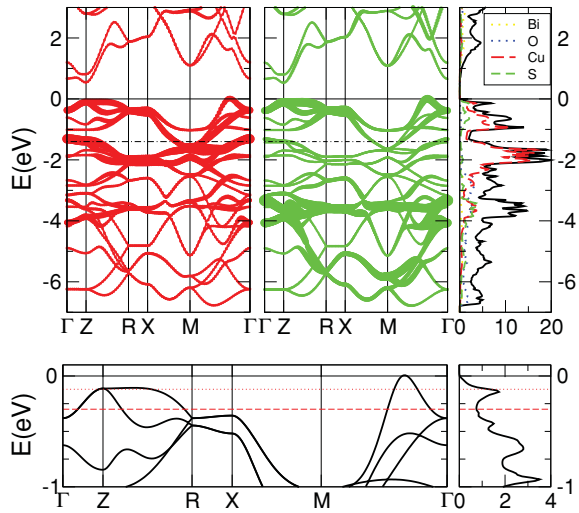

FIG. 1. (Color online) (Top) Band structure of CuBiSO, shaded according to the partial Cu d_{xz+yz} (left) and S p_{x+y} (right) characters: the continuous and dash-dotted lines mark, respectively, the position of the Fermi level in the undoped compound and that corresponding to the filling d^6 of Fe pnictides (see text); the corresponding DOS in states/(f.u. spin eV) is also shown. (Bottom) Low-energy band structure: Dotted and dashed lines mark the position of the Fermi level corresponding to the hole dopings $x = 0.1$ and $x = 0.5$, in RBA.

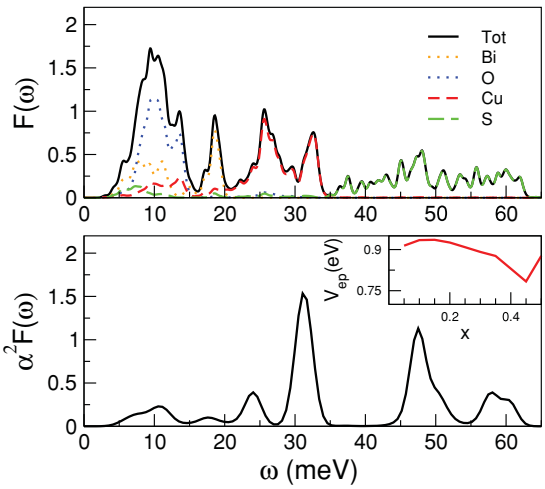

FIG. 2. (Color online) From top to bottom: Partial phonon density of states (PDOS), Eliashberg spectral function for $x = 0.1$, in RBA, and (inset) ratio between the coupling constant and $N_0(x)$ as a function of doping.

tendency to antiferromagnetism (rather than ferromagnetism), and low EP interaction. This is indeed what is found in first-principles calculations in Fe pnictides.[11]

We now go back to discuss the behavior of $Cu_{1-x}BiSO$ for $x \leqslant 0.5$, using the bottom panel of Fig. 1. For $x \geqslant 0.1$, we find that the ground state of the system is FM, both in the local spin-density approximation (LSDA) and in the GGA.[8] Upon hole doping, the Cu state is reduced from d^{10} to d^9 and the Fermi level moves into a flat region of the band structure, which gives rise to the high peak in the DOS ($N_0 = 2.1$ states/eV spin).[12] Since the Stoner parameter of atomic Cu is $I_{Cu} \approx 0.9$ eV, this DOS is well above the Stoner criterion for FM, $N_0 > 1/I$. In $Cu_{1-x}BiSO$ the actual value of I is $I \leqslant I_{Cu}$, due to hybridization. It can be estimated from the splitting $\Delta E = mI$ between majority and minority bands in the FM state, where m is the value of the self-consistent magnetic moment. We find $m \lesssim 0.1$ for all dopings considered, and $I = 0.53$ eV in LSDA and $I = 0.67$ eV in GGA, independent of doping.

So far, however, experiments have seen no trace of static magnetism; as usual, LSDA calculations here overestimate the tendency to itinerant magnetism in the vicinity of a magnetic quantum critical point (QCP), where the system exhibits strong SFs.[13] We will return to this issue in more detail, after discussing the results for the EP interaction.

Figure 2 summarizes the EP properties of the hole-doped $Cu_{1-x}BiSO$. The partial phonon density of states (PDOS) of the undoped compound extends up to 65 meV; vibrations of the Bi-O layers are concentrated at energies $\leqslant$20 meV, while modes involving the Cu-S layers are found at higher energies. The S atoms give rise to a very broad feature in the PDOS, from 40 to 65 meV. Using this phonon spectrum, we calculate the Eliashberg spectral function $\alpha^2F(\omega)$ of the hole-doped $Cu_{1-x}BiSO$:

$$\alpha^2 F(\omega) = \frac{1}{N_0} \sum_{\mathbf{k},\mathbf{q},\nu,n,m} \delta\left(\epsilon^n_{\mathbf{k}}\right)\delta\left(\epsilon^m_{\mathbf{k}+\mathbf{q}}\right)\left|g^{\nu,n,m}_{\mathbf{k},\mathbf{k}+\mathbf{q}}\right|^2 \delta(\omega - \omega_{\nu\mathbf{q}}),$$

evaluating the average of the EP matrix elements $g^{\nu,n,m}_{\mathbf{k},\mathbf{k}+\mathbf{q}}$ on the Fermi surface $\delta(\epsilon^n_{\mathbf{k}})$, obtained by a rigid-band shift corresponding to the doping level. From the Eliashberg function we calculate the EP coupling constant: $\lambda_{ep} = 2\int_0^\infty d\Omega \alpha^2 F(\Omega)/\Omega$.

For all dopings $x \leqslant 0.5$, we find that only two groups of phonon modes, corresponding to the out-of-plane vibrations of the Cu-S layers, have sizable EP matrix elements $g^{\nu,n,m}_{\mathbf{k},\mathbf{k}+\mathbf{q}}$: These give rise to two narrow peaks in $\alpha^2F(\omega)$, centered at 32 and 48 meV. The lower panel of Fig. 2 shows $\alpha^2F(\omega)$ for $x = 0.1$.

Since the *shape* of the Eliashberg function hardly depends on x for the dopings considered, the total EP coupling depends on doping mainly through DOS at the Fermi level N_0. We thus rewrite λ_{ep} as $\lambda_{ep} = N_0 V_{ep}$. As the inset of Fig. 2 shows, $V_{ep} \simeq 0.9$ eV spin f.u. at all dopings for $x \leqslant 0.5$. For comparison, $V_{ep} = 0.1$ eV in LaOFeAs and $V_{ep} = 0.3$ eV in Pd (i.e., in metals where the lattice plays a minor role compared to SF) while it is much larger in good EP superconductors: $V_{ep} = 2.5$ eV in MgB_2 or $V_{ep} = 6.6$ eV in Pb.

For $x = 0.1$, $N_0 = 1.93$ st/eV spin f.u., $\lambda_{ep} = 1.74$, and the logarithmically averaged phonon frequency $\omega_{log} = 263$ K. This EP interaction would then give rise to a T_c of 33 K, assuming a typical value for the Coulomb pseudopotential, $\mu^* = 0.1$.

This is much larger than the experimental value $T_c = 5.8$ K,[5] which would correspond to $\lambda_{ep} = 0.6$.[14] A factor of 3 discrepancy is well above the typical uncertainty of T_c in similar calculations, stemming from the computational uncertainty on λ_{ep}, typically 10%, or from the uncertainty of μ^*.

The most straightforward explanation, in the present case, is a suppression of phonon-mediated pairing by paramagnons, due to proximity to a FM QCP. We now estimate this effect,

using the RPA. Let λ_{sf}^{s} be the coupling to SF in the singlet channel; the effect of paramagnons is to suppress superconductivity in the singlet channel by depressing the effective coupling constant ($\lambda_\Delta = \lambda_{ep} - \lambda_{sf}^{s}$) and increasing the effective mass of the carriers by the factor $1 + \lambda_Z = 1 + \lambda_{ep} + \lambda_{sf}^{s}$. This effect has been studied in Ref. 15 where the following expression for T_c was derived (and verified by comparison with numerical solutions of the Eliashberg equations):

$$T_c = \frac{\omega_{\log}}{1.45} \exp\left\{ \frac{-(1+\lambda_Z)}{\lambda_\Delta - \mu^*\left(1 + 0.5\frac{\lambda_\Delta}{1+\lambda_Z}\right)} \right\}. \qquad (1)$$

Here we assume for simplicity that the characteristic frequencies of phonons and paramagnons are the same. Equation (1) can also be generalized to triplet superconductivity, with the substitution $\lambda_\Delta \to \lambda_{sf}^{t}$; $\lambda_Z \to \lambda_Z^{t} = \lambda_{ep} + \lambda_{sf}^{t}$, where $\lambda_{sf}^{t} = \frac{1}{3}\lambda_{sf}^{s}$ is the coupling to SF in the triplet channel.[16] Equation (1) gives an appreciable T_c only if the denominator in the exponential is positive. For small μ^*, this is the case when $\lambda_\Delta > 0$. We therefore use λ_Δ to define the phase diagram of hole-doped $Cu_{1-x}BiSO$: Using the RBA, we take $\lambda_{ep}(x) = V_{ep}N_0(x)$, where $N_0(x)$ is the DOS at the Fermi level at doping x. For the coupling to SF we use the following expression:

$$\lambda_{sf}^{s}(x) = \frac{3}{2}\frac{N_0^2(x)I^2}{1 - IN_0(x)}, \qquad (2)$$

where I is, in the LDA parlance, the Stoner parameter.[17] Equation (2) is similar to the well-known expression for the SF induced interaction in the singlet channel,[16] averaged over the Fermi surface. Note that in the triplet channel the SF interaction is three times smaller, and also the averaging for both λ_{sf} and λ_{ep} is performed with a weighting factor $\hat{v}_F(\mathbf{k}) \cdot \hat{v}_F(\mathbf{k}')$.[18]

A well-known LDA problem is that, due to its mean-field character, it overestimates the tendency to static magnetism.[19] This can be corrected by introducing a phenomenological Stoner I, reduced from its LDA value. In this spirit, in the following, we treat I as a free parameter, and plot the phase diagram of CuBiSO in the (x, I) space. The results are shown in Fig. 3.

If $\lambda_\Delta \gg \mu^*$, a conventional EP superconductivity, albeit weakened by SF, is a stable zero-temperature ground state. As the Stoner parameter is increased, λ_Δ goes down, and a competing instability against a triplet state emerges when the critical temperature in the singlet channel T_c^{s}, defined by Eq. (1), becomes equal to that in the triplet channel (T_c^{t}). Finally, as the tendency to magnetism is increased even further, the Stoner criterion $N_0 I > 1$ is satisfied, and the system becomes ferromagnetic (Fig. 3).

One can see that, had we used the LDA or GGA value for I, for dopings close to $x = 0.1$, we would have found CuBiSO inside the FM region. However, at $x = 0.1$ experiments show no trace of static FM order, a sign of inadequacy of the mean-field character of magnetism in LSDA. Reducing the LDA value of I to $I_{\text{eff}} = 0.51$ eV suppresses the magnetic instability at $x = 0.1$; a reduction to $I_{\text{eff}} = 0.39$ eV brings the estimated triplet T_c into agreement with the experimental one, and a reduction to 0.25 eV does the same with the conventional singlet T_c. For typical itinerant magnets renormalizing I_{LDA} by ∼30–40% provides reasonable agreement with the experimental magnetic susceptibilities,[19] in the same ballpark as the reduction introduced above.

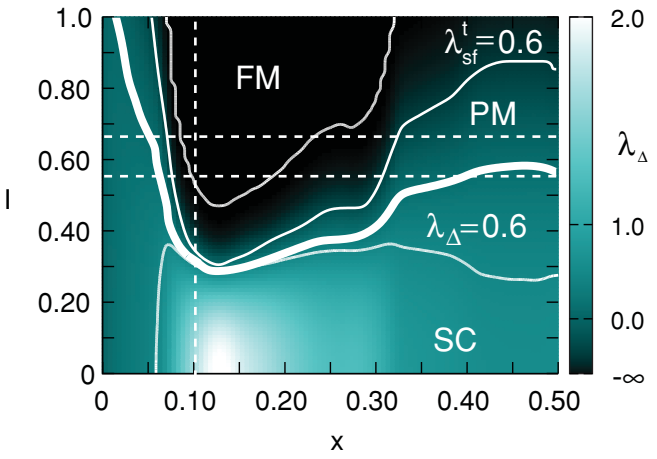

FIG. 3. (Color online) Phase diagram of $Cu_{1-x}BiSO$, defined by λ_Δ as a function of doping (x) and Stoner parameter I, whose value is represented by the color scale. The two horizontal dashed lines correspond to $I_{\text{LDA}} = 0.53$ eV and $I_{\text{GGA}} = 0.67$ eV. The vertical dashed line indicates the doping for which superconductivity was observed in Ref. 5. In the region (FM) the system shows a FM instability, defined by the condition ($N_0 I \geqslant 1$); elsewhere the system is paramagnetic (PM). Below the bold line (which marks the condition $T_c^{s} = T_c^{t}$) the ground state is a conventional singlet superconductor. Above the bold line a triplet superconducting state is more stable. The isolines $\lambda_\Delta = 0.6$ and $\lambda_{sf}^{t} = 0.6$ indicate the values of I,x, which reproduce the experimental $T_c = 5.8$ K of Ref. 5 in the singlet and triplet channels, respectively.

In other words, $Cu_{0.9}BiSO$ is a unique example where a SF driven triplet superconductivity is nearly degenerate with the phonon-driven singlet superconductivity, and the critical temperature is sizable for both symmetries. Given that the actual $Cu_{0.9}BiSO$ samples are rather dirty, one may conjecture that samples studied in Ref. 5 are on the conventional side of the phase diagram, but the fact that superconductivity appears to be so difficult to reproduce may be due to the fact that slightly different samples may appear outside of the stability range of singlet pairing in the phase diagram in Fig. 3. In principle, one can use pressure or doping, which control I, V_{ep}, and N_0, to scan the proposed phase diagram.

This tunability comes about because of the combination of two factors: an exceptionally strong EP interaction in the singlet channel that is essentially canceled out in the triplet channel, and a strong SF coupling that competes with EP interaction in the singlet channel. The occurrence of these two large coupling constants can be seen as the result of three concurring elements: a strong d-p hybridization, which causes large EP matrix elements; the large value of the Stoner parameter of Cu, which causes a strong tendency to magnetism; and, finally, the presence of a large peak in the electronic DOS, which favors FM and enhances the coupling constants for superconductivity both in the singlet and triplet channels.

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