

Do Transition-Metal Substitutions Dope Carriers in Iron-Based Superconductors?

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We investigate the currently debated issue concerning whether transition-metal substitutions dope carriers in iron-based superconductors. **From first-principles calculations of the configuration-averaged spectral function of BaFe_2As_2 with disordered Co or Zn substitutions of Fe, important doping effects are found beyond merely changing the carrier density. While the chemical potential shifts suggest doping of a large amount of carriers, a reduction of the coherent carrier density is found due to the loss of spectral weight.** Therefore, none of the change in the Fermi surface, density of states, or charge distribution can be solely used for counting doped coherent carriers, let alone presenting the full effects of the disordered substitutions. **Our study highlights the necessity of including disorder effects in the studies of doped materials in general.**

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Doping is one of the most powerful tools for tuning the electronic properties of functional materials. Well known examples include *n*- and *p*-type semiconductors, dilute magnetic semiconductors, and numerous heavy fermions and strongly correlated oxides (e.g., manganites, cobaltates, and cuprates). In most of these cases, inclusion of doped impurities is considered an effective way to introduce carriers, but recently the amount of carrier doping has become the center of a serious debate in the field of iron-based superconductors (FeSCs). A density functional theory (DFT) study [1] reported that the additional charge density in transition-metal (TM) substituted FeSCs is fully localized at the TM dopant site, which leads [1] to the surprising conclusion that the TM substitutions do not dope carriers. While the lack of additional density at the Fe sites has recently been confirmed experimentally [2,3], this widely discussed conclusion of the system being undoped, however, seems to be in contradiction with several experimental [4–6] and theoretical [5–8] studies that indicate a change of Fermi surfaces (FSs) consistent with carrier doping. A serious debate was thus initiated in the field: Do the TM substitutions dope carriers into the FeSCs or not?

In this Letter, we investigate this issue via first-principles DFT calculation of *disordered* substitutions. Contrary to the previous theoretical studies, which employed rather small periodic supercells, we compute the configuration-averaged spectral function of disordered TM substitutions in BaFe_2As_2 , using the weak Co and strong Zn impurities as representative examples. In the case of Co substitution, despite the localized charge distribution, no apparent localized states are found, and a large chemical potential shift results from the injection of additional carriers to the system. In the case of Zn substitution, while both strongly and weakly localized states are found, the chemical

potential is still shifted noticeably, reflecting real carrier doping to the system. However, an important loss of coherent spectral weight results from scattering against the disordered impurities. Consequently, the actual number of coherent carriers in the system reduces noticeably from the Luttinger count of the FSs. Our findings illustrate that none of the FSs, density of states, or the charge density can be used for a physically meaningful counting of coherent carriers in a disordered system in general. More importantly, physical effects of the disordered impurities are much richer than simply adding carriers. Specifically, the emergence of incoherent carriers and loss of coherent carriers hold interesting potentials to strengthen superconductivity over magnetism and should be taken into account in future studies.

The configuration-averaged Wannier-based spectral function $\langle A_n(k, \omega) \rangle$ of Wannier orbital *n*, frequency ω , and crystal momentum *k* (in the 2-Fe Brillouin zone [9]) is obtained by averaging over 10 large random-shaped supercells containing 400 atoms on average, including 12.5% random TM substitutions [e.g., Fig. 1(a)]. [For the spectral functions at fixed *k* points in Figs. 2(c)–2(f), 3(b), and 3(c), 100 supercells of 800 atoms on average are used.] The spectral functions are calculated directly from the supercell eigenvalues and eigenvectors, by applying the recently developed unfolding method [10]. The first-principles simulations of the large supercells, necessary for a proper treatment of disorder, are made affordable by the recently developed Wannier function [11] based effective Hamiltonian method for disordered systems [12]. The influence of the TM substitutions on the Hamiltonian is extracted from three DFT [13–15] calculations: the undoped BaFe_2As_2 and the impurity supercells $\text{Ba}_2\text{Fe}_3\text{CoAs}_4$ and $\text{Ba}_8\text{Fe}_{15}\text{ZnAs}_{16}$. The low energy Hilbert space is taken within $[-10, 3]$ eV consisting of

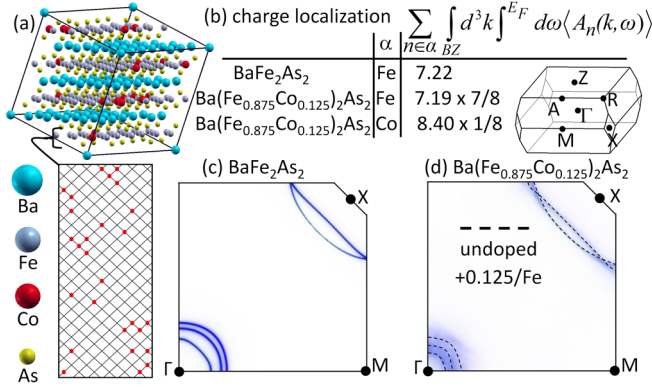


FIG. 1 (color online). Two seemingly contradicting results: charge localization and carrier doping. (a) An example of large sized supercells used for the configurational average. (b) The average occupation of the atomic Wannier orbitals showing the doped charge to be localized at the Co site. The FSs of (c) BaFe₂As₂ and (d) Ba(Fe_{0.875}Co_{0.125})₂As₂ showing the hole pockets at Γ to shrink and the electron pockets at X to grow, consistent with adding 0.125 electrons per Fe to the undoped system.

Wannier orbitals of Fe d , Co d or Zn d , and As p character. The accuracy of the calculated effective Hamiltonian is benchmarked [15] against full DFT calculations.

Let us first reexamine the previously reported charge localization [1] and chemical potential shift [7,8] within our disordered Co substitution case. Figure 1(b) shows the average occupation of each atom calculated from frequency and momentum integration and orbital summation of $\langle A_n(k, \omega) \rangle$. Comparing the occupations in the doped system with that in the undoped system shows that, in agreement with Refs. [1,7,8], the additional charge is indeed distributed at the Co impurity, seemingly implying that Co does not dope carriers. On the other hand, compared with the FSs of the undoped [Fig. 1(c)] system, the doped system [Fig. 1(d)] contains smaller (larger) hole (electron) pockets around the Γ (X) point, in agreement with the previous experimental and theoretical findings [4–8]. Furthermore, the FSs of the doped system are found to be consistent with the undoped system upon adding the nominal doping of +0.125 electrons per Fe [the dotted line in Fig. 1(d)]. The same can also be observed from the band structure in Fig. 2(b). So, our results of disordered Co substitutions confirm both the localized distribution of additional charge [1,7,8] and the chemical potential shift [7,8], which still leaves us with the question: Do TM substitutions dope carriers or not?

To reconcile these seemingly contradicting results, a notion of impurity potential [7,8] (or self-energy [16]) induced “effective doping” was previously proposed [7,8]. However, our results give a different physical explanation and show that such a notion is not only unnecessary but also negligible in effect for the case of Co

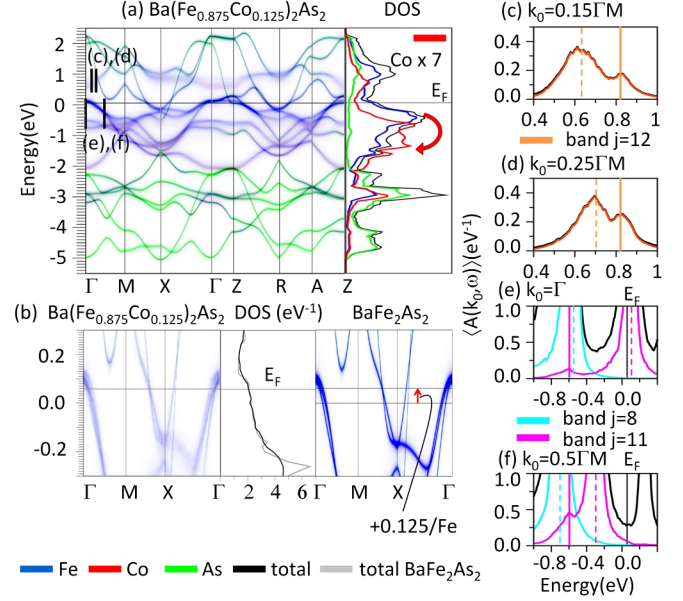


FIG. 2 (color online). Configuration-averaged spectral function of disordered Ba(Fe_{0.875}Co_{0.125})₂As₂ in the full low energy Hilbert space (a) where the partial DOS of Co is enhanced by a factor of 7. (b) Comparison of the spectral function and DOS of the disordered system (black) with the undoped one (gray) near the chemical potential. Bloch-based spectral function of band $j = 12$ at (c) $k_0 = 0.15 \Gamma M$ and (d) $k_0 = 0.25 \Gamma M$ and of bands $j = 8, 11$ at (e) $k_0 = \Gamma$ and (f) $k_0 = 0.5 \Gamma M$, where the dashed (solid) lines indicate the centers of the dispersive (nondispersive) components. The black curves in (c)–(f) correspond to the total spectral function.

substitution. Let us focus on the (k, ω) dependence of $\langle A_n(k, \omega) \rangle$ in Fig. 2. Notice first that, while the band dispersion resembles well the undoped system, important effects of disorder scattering can be observed. For example, the Fe d bands (even at the chemical potential) develop linewidths in both momentum and frequency, reflecting their finite mean free path and lifetime from scattering against Co impurities. Also notice that, besides these features, no apparent localized state (flat band) is found in Fig. 2 to host one electron per Co. Therefore, the localized distribution of additional charge must originate from *slight* enhancement of the wave function near the Co sites in a *large number* of extended occupied states, instead of a small number of strongly localized or resonant states. This deduction is further supported by the density of states (DOS) in Fig. 2(a), in which the *broad* Co spectral weight ($\times 7$ for better comparison) is shown to be transferred to slightly lower energy, in relation to the Fe spectral weight. That is, contrary to the previous interpretations [1,7,8], our result shows that practically no carriers are “trapped” around Co, but instead a large number of itinerant carriers conspire to enhance the charge distribution around Co in order to screen the additional proton. Therefore, the notion of effective doping is

unnecessary in this case and, in fact, negligible in effect. Since the changes of the wave functions and the band dispersion are rather small in this simplest case, from any physically meaningful consideration concerning doping, Co substitution really just adds about one more itinerant electron per Co to the system.

However, these itinerant carriers are not all the same in nature, as some of these carriers lose their coherence due to scattering against disordered impurities. The lack of a well-defined dispersion indicates diffusive propagation of these incoherent carriers, in contrast to the particlelike propagation of the coherent carriers. A clear example of nondispersive spectral weight can be found in band 12 around $k_0 = \Gamma$. As illustrated in Figs. 2(c) and 2(d), the band consists of two components: a peak (dashed line) that disperses from 0.6 to 0.7 eV along ΓM and a nondispersive satellite (solid line) that remains fixed a little above 0.8 eV. Other incoherent features are more difficult to recognize due to the presence of multiple bands in the same frequency range. To resolve the different bands, in Figs. 2(c)–2(f), 3(b), and 3(c), we analyze the spectral function $A_j(k, \omega) = -\frac{1}{\pi} \text{Im} \langle k|G(\omega)|k\rangle$ on the basis of the undoped Bloch states $|kj\rangle$ of crystal momentum k and band index j [15]. In Figs. 2(e) and 2(f), an incoherent component in the hole pocket is illustrated. While along ΓM the main peak in band 11 disperses from 0.1 to -0.3 eV, the satellite around -0.6 eV remains fixed. Note also that, while nearby in frequency, the nondispersive satellite of band 11 is not part of the dispersing band 8. Because of the proximity of the incoherent features to the main peaks, an unambiguous quantification of the obviously reduced coherent spectral weight is challenging in this case.

From the perspective of disordered impurities, Co substitution of Fe introduces only a weak impurity potential ~ -0.5 eV to the d orbitals, much smaller than the bandwidth of the d bands, and thus can be considered as a small perturbation to the system. This is ultimately the reason why the Fermi surfaces resemble very much the undoped system added with nominal doping of $+0.125$ electrons per Fe [e.g., Fig. 1(d)], even though the Luttinger theorem should not apply to disordered systems. Therefore, it is instructive to explore the Zn substitution of Fe, which represents the other limit with a very strong impurity potential (~ -7 eV) much larger than the bandwidth of the d bands.

As expected, the strong impurity potential of Zn substitution is able to induce real localization, in great contrast to the Co substitution. Figure 3(a) shows our resulting band structure of the Zn substituted system with flat core levels of Zn d character, which are good examples of strongly localized states created by the large impurity potential. More interestingly, weakly localized As states can also be observed clearly within $[-6, -5]$ eV, right below the As p bands [17]. The small region of k space in which

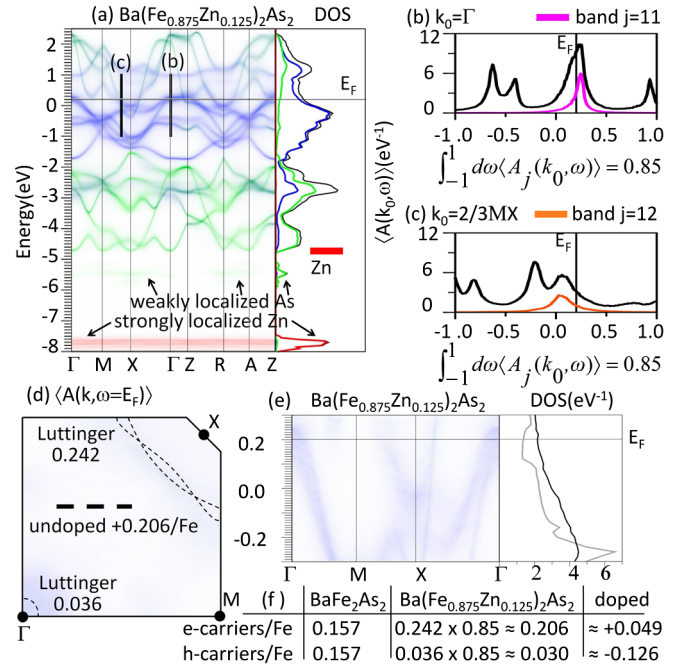


FIG. 3 (color online). Configuration-averaged spectral function of disordered $\text{Ba}(\text{Fe}_{0.875}\text{Zn}_{0.125})_2\text{As}_2$ in the low energy Hilbert space (a) Bloch-based spectral function (b) of band $j = 11$ at $k_0 = \Gamma$ and (c) of band $j = 12$ at $k_0 = 2/3 \text{MX}$. (d) FSs of the doped system compared with the undoped system with ~ 0.2 additional electrons per Fe. (e) Band structure and DOS of the doped (black) and undoped (gray) system near the chemical potential. (f) The estimated number of doped coherent carriers. The black curves in (b) and (c) correspond to the total spectral function.

these weakly localized states reside reflects their large size compared to the 2-Fe unit cell (similar to the oxygen vacancy states in ZnO [18]).

Because of the very strong impurity potential, the influence of the impurity can no longer be considered as a small perturbation, and consequently the counting of the carriers would become nontrivial. Indeed, the broadening of the Fe d spectrum in Fig. 3(b) is significantly stronger than the previous case, indicating a much shorter lifetime and mean free path. In fact, even As p bands scatter strongly in Fig. 3(a). Now, from a comparison of the valence of Fe^{2+} and Zn^{2+} , one could have expected that Zn substitutions do not dope carriers to the system. This is obviously not the case, since the chemical potential has been shifted so much that the hole carriers are almost entirely removed from the system. The new FSs in Fig. 3(d) appear to have been doped with 0.206 electrons per Fe, a number that cannot be easily rationalized from simple counting of the valence, in great contrast to the case of Co substitution. This illustrates clearly the general inapplicability of the Luttinger theorem to disordered systems.

Of course, the physically meaningful count should distinguish the coherent carriers from the incoherent features. For this purpose we analyze the components of the

Bloch-based spectral function. Two examples are illustrated in Figs. 3(b) and 3(c), representing the bands in the hole and electron pockets, respectively. An integration of the Bloch-based spectral function within $[-1, 1]$ eV gives an estimated coherence factor of ~ 0.85 . This results in an effective doping of $\sim +0.049$ (~ -0.126) per Fe in the electron (hole) pockets [see Fig. 3(f)]. A simple Luttinger count would lead to a large overestimation of 73% of the number of doped electron carriers.

Interestingly, the Co and Zn substitutions are more efficient in removing the coherent hole carriers than adding the electron ones, an effect relevant to the doping dependence of Hall coefficient [19–21]. Of the ~ 0.15 spectral weight loss with Zn substitutions, ~ 0.09 comes from the trivial strongly localized Zn *d* orbitals, while the remaining ~ 0.06 corresponds to the decoherence of Fe bands. (Similar spectral weight losses can be expected in the case of Fe vacancies.) Finally, Fig. 3(e) shows an enhanced DOS upon substitution, even though the coherent fraction of DOS actually decreases. This is quite alarming, considering that DOS is routinely used in the standard studies of doped materials but actually provides no distinguishability of coherent features from the incoherent ones.

The above disorder effects have important physical implications that immediately impact on experimental and theoretical studies of FeSCs. At the simplest level, one expects a doping dependence of the broadening of the bands, as found in the raw angle-resolved photoemission spectroscopy data [4,5], and a contribution to the incoherent features in other spectroscopies [22–24]. But deeper issues are present. As demonstrated above, other than the appearance of incoherent features, the chemical potential and the associated phase space of coherent carriers are no longer related to the coherent carrier density. Indeed, we have found the Fermi velocities of the electron and hole carriers to resemble those of a highly doped system but, instead, with a much smaller coherent carrier density. This cannot be possibly described with merely adding carriers to the undoped system and is in contradiction with the textbook theories, based on which most experiments are analyzed. For instance, in optical conductivity and dielectric function, one might now find a spectral line shape similar to that of an undoped system with additional electrons (since its band dispersion resembles the real disordered system) but with an overall reduction in the intensity (due to the weight loss of coherent carriers) as dictated by various sum rules. The same consideration should apply to transport and other spectroscopies as well, since they are all sensitive to both the phase space controlled by the band structure and the spectral weight related to the coherent carrier density.

More importantly, besides the impurities' standard role of suppressing T_c via scattering [25–27], the emergence of incoherent carriers and the loss of coherent spectral weight

can also affect the competition between magnetic and superconducting instabilities in the underdoped regime. Both effects serve to suppress long-range antiferromagnetic order, allowing a stronger superconductivity to develop. This is because the nesting condition is reduced by the loss of coherent spectral weight, while the ill-defined momentum of the incoherent carriers give negligible contribution. This explains, at least in part, why electron doping and hole doping both suppress the antiferromagnetic order, despite the degree of nesting condition. On the other hand, the zero momentum superconductivity still benefits from all the incoherent carriers. In fact, the slow propagation of the incoherent carriers makes them more susceptible to the strong coupling regime of superconductivity [28] that hosts stronger local pairing but weaker phase coherence. (This might offer a resolution to the current issue of power law behavior of the penetration depth [29].) Coupled to the lighter coherent carriers, this can actually help enhance the superconductivity by providing a stronger local pairing. Such opposite effects on the magnetism and superconductivity have in fact been observed recently in Zn substitution of *F*-underdoped LaOFeAs [21]. Finally, the loss of coherent spectral weight would allow practically the current itinerant pairing theories [30–33] to incorporate stronger interaction parameters without triggering a long-range magnetic order and, thereby, to further enhance the superconducting instability.

In conclusion, by computing the configurational-averaged spectral function of disordered Co or Zn substituted BaFe₂As₂, we identify important physical effects of TM substitution that cannot be captured by merely adding carriers to the undoped systems. While both strongly and weakly localized states are found via Zn substitution, no apparent localization is found via Co substitution, despite the localized distribution of additional charge. On the one hand, the FSs and Fermi velocities are modified as a consequence of chemical potential shift, reflecting injection of doped carriers. On the other hand, some incoherent carriers emerge, in association with a loss of the coherent spectral weight that reduces considerably the actual number of coherent carriers. Our results illustrate clearly that, generally in disordered systems, none of the FSs, DOS, or the charge distribution can be solely used for the counting of coherent carriers. Physically, our reported features would produce unusual behaviors in various spectroscopies and other physical properties beyond the standard textbook descriptions and, thus, need to be taken into account in future experimental and theoretical studies. In addition, they offer new possibilities to tip the balance from magnetism toward superconductivity, an important aspect that deserves to be considered in future studies of superconductivity in general.

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