To dope or not to dope: Electronic structure of Ba-site and Fe-site substituted single-crystalline BaFe₂As₂

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The substitutional dependence of (Ba,K)(Fe,TM)₂As₂ (TM = Mn, Co, Ni, and Cu) is investigated with single-crystal x-ray diffraction and with near-edge x-ray absorption fine structure at the Fe-La₃ edges. The present study shows that only for Ba/K replacement charge carriers are directly doped to Fe 3d states. In the case of Fe/Co substitution the additional electrons contribute to the ensemble of all 3d electrons and seem to screen the impurity whereas for Fe/Mn, Fe/Ni, and Fe/Cu replacement the data indicate that TM 4s/4p-derived impurity states become important for the electronic structure of Fe-site substituted BaFe₂As₂.

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High-temperature superconductivity in iron-based pnictides [1] is at present one of the most intensely studied topics in condensed matter physics. Even though the understanding of the phase diagram and of the physical properties of these systems has considerably advanced in the last years, unanswered issues still remain. Among these, the substitution-dependent electronic structure is most intriguing, especially the question if and how charge carriers (holes or electrons) are introduced to the system upon (i) substitution of Ba with alkali metals (like K) or (ii) replacement of Fe by other transition metals (like TM = Mn, Co, Ni, or Cu) on the more “active” Fe site.

In particular, the assumed electron doping induced by the replacement of Fe by Co, Ni, or Cu has recently been discussed controversially: While some investigations indeed seem to support electron doping [2,3] others clearly contradict such a doping effect [4,5]. This ongoing debate was further inspired by recent theoretical studies which have shown that TM substitution does not seem to dope the system with electrons at all [8]. Further theoretical calculations suggest short-range screening as an important ingredient [8,11]: in this picture, the ensemble of d electrons in the pnictides screens the extra positive charge of the TM impurity on such a short length scale that the total electron density peaks around the impurity and the TM atom appears isovalent to Fe [8,11].

To shed more light on this important debate on substitution-dependent changes in the electronic structure of the iron pnictides, we have investigated the family Ba₁₋ₓKₓ(Fe,TM)₂As₂ (TM = Mn, Co, Ni, and Cu) with single-crystal x-ray diffraction (XRD) [12] and near-edge x-ray absorption fine structure (NEXAFS) [13] where partial substitution was introduced on the Ba site, on the Fe site, or on both sites simultaneously (“co-doped”).

Single crystals were grown from self-flux in glassy carbon or Al₂O₃ crucibles as described elsewhere [14,15]. The composition of the samples was determined using energy dispersive x-ray spectroscopy (EDX) and bond lengths were determined using XRD on samples from the same batch. Selected distances such as the average 〈Fe-Fe〉 and 〈Fe-As〉 bond lengths as well as the As height above the Fe 〈h₃₃,₃₃,₃₃〉 are plotted in Fig. 1.

From Fig. 1(a) it is evident that 〈h₃₃,₃₃,₃₃〉, when compared with undoped BaFe₂As₂, is clearly increased upon Ba/K and Fe/Mn substitution. Surprisingly and contrary to what is expected for an element with an atomic number higher than Fe, 〈h₃₃,₃₃,₃₃〉 is slightly enhanced for Fe/Cu replacement as well. For Fe/Co and Fe/Ni substitution, however, 〈h₃₃,₃₃,₃₃〉 is significantly reduced.

Figure 1. Selected structural data of Ba-site substituted, Fe-site substituted, and co-doped BaFe₂As₂. The substitution-dependent changes of the As height above the Fe site, 〈h₃₃,₃₃,₃₃〉, is displayed in (a), of the 〈Fe-Fe〉 distance in (b), and of the 〈Fe-As〉 bond length in (c).
This seems to indicate that Ba/K, Fe/Mn as well as Fe/Cu substitution lead to hole doping of the system while Fe/Co and, even more so, Fe/Ni replacement induce electron doping. Fig. 1(b) illustrates that the $\langle$Fe-Fe$\rangle$ distance is decreased upon Ba/K substitution while it is increased for Fe/Mn, Fe/Ni, and Fe/Cu replacement. Only in the case of Fe/Co substitution does $\langle$Fe-Fe$\rangle$ remain almost unaffected. Fig. 1(c) shows that the $\langle$Fe-As$\rangle$ bond length decreases for Fe/Co and Fe/Ni substitution whereas it increases upon Fe/Mn and Fe/Cu replacement. In the case of Ba/K substitution, $\langle$Fe-As$\rangle$ remains almost unchanged. We will come back to this behavior below when we combine the XRD and NEXAFS results to yield a consistent picture.

In Fig. 2(a) the Fe $L_{2,3}$ NEXAFS spectra of BaFe$_2$As$_2$ and Ba(Fe$_{0.25}$Ni$_{0.75}$)$_2$As$_2$ are compared as representatives. The apparent discrepancies in intensity scale with the Fe content and are predominantly due to self-absorption and saturation effects (SAE). After SAE correction (not shown), the spectral shape of the whole $L_{2,3}$ edge is consistent with our previously investigated Fe $L_{2,3}$ NEXAFS on Sr(Fe$_{1-x}$Co$_x$)$_2$As$_2$ and corroborates an Fe$^{2+}$ high-spin (HS) configuration in tetrahedral coordination.

In the current Letter we focus on the energy position of the peak maximum. Since the Fe $L_{2,3}$ NEXAFS shows only small anisotropies, we will concentrate on the normal-incidence data. Fig. 2(b) shows the Fe $L_3$ peak region. It is obvious that the peak maximum significantly shifts to higher energies with increasing K content $u$. This directly manifests two conclusions: first, that holes are doped to the system upon Ba/K substitution and, second, that the doped holes are directly found on Fe 3d orbitals. In contrast, no indication for an energetic shift of the peak maximum is observed upon Fe-site (Fe/Co, Fe/Ni, Fe/Cu, or Fe/Mn) replacement at any of the substitution levels studied. This rules out that charge carriers (whether holes or electrons) are introduced to the Fe 3d states upon Fe-site substitution and is a massive “violation” of the rigid-band model. It is interesting to note that for co-doped (Ba,K)(Fe,Mn)$_2$As$_2$, the peak maximum is found exactly at the energy position expected for the respective K content while the Fe/Mn replacement does not lead to any additional shift. Therefore, only substitution on the Ba site leads to an effective doping of charge carriers directly on Fe 3d states.

Representative examples of Mn $L_{2,3}$ edges taken in surface-sensitive TEY and bulk-sensitive FY mode are compared in Fig. 3(a). To extract reliable estimates for the valence state from the TM spectra, multiplet calculations have been performed (displayed as lines in the figures). While the TEY data show that there is Mn$^{2+}$ at the sample’s surface (most probably from a thin oxidic-related surface layer, cf. surface iron oxide in Sr(Fe$_{1-x}$Co$_x$)$_2$As$_2$ Ref. [6]), it is evident from the FY data that there exists only monovalent Mn in the bulk of the samples. Mn$^{2+}$ implies that one hole per Mn is donated to the system. Yet as discussed for the Fe $L_3$ data of Fig. 2(b), the donated holes are not found on Fe 3d states. Assuming that Ba$^{2+}$ behaves ionic and since no spectral changes are observed at the As $L_3$ edge upon Fe-site substitution, this suggests that the doped holes merely have a localized character around the Mn impurity.

Regarding the Fe/Co substitution, the Co $L_{2,3}$ and Ba $M_{1,5}$ edges almost coincide for Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ and, thus, we refer to the Co $L_{2,3}$ edges of Sr(Fe$_{1-x}$Co$_x$)$_2$As$_2$ of Ref. [6] where it was also demonstrated that both Co and Fe remain effectively divalent. Nevertheless, in all energy ranges of the Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ spectrum where the Co $L_{2,3}$ edge can be separated from the strong Ba absorption (not shown) it is apparent that the Co $L_{2,3}$ signals of these two families closely resemble each other. As a consequence of the observed isovalence of Co$^{2+}$ and Fe$^{2+}$ no effective electron doping is observed for Fe/Co replacement (Fig. 2 and Ref. [6]).

Examples of Ni $L_{2,3}$ edge spectra measured in bulk-sensitive FY are displayed in Fig. 3(b). A small normal-
grazing electronic anisotropy (similar to the anisotropy observed for Fe and Co) remains also for Ni. Comparing the measured spectra with our multiplet calculations it is obvious that Ni appears as trivalent. Consequently, and consistent with the strong reduction of $h_{As,Fe}^{-}$ in Fig. 1(a), Ni$^{3+}$ effectively donates one electron more to the system than Co$^{2+}$ does. Surprisingly, (but similar to the Fe$^{3+}$/Mn$^{+}$ replacement,) no energy shift is observed for Fe$^{2+}$/Ni$^{3+}$ substitution in the Fe $L_3$ data of Fig. 2(b). This again reflects that the electrons doped by Ni$^{3+}$ are not found on Fe 3d orbitals and again seem to have a limited extension around the Ni impurity. The character of these “localized” impurity states will be discussed together with the XRD results in more detail below.

The Cu $L_{2,3}$ edge of Ba(Fe$_{0.93}$Cu$_{0.07}$)$_2$As$_2$ is illustrated in Fig. 3(c). Normal and grazing incidence data show that while there is only a negligible anisotropy at the $L_3$ edge, the anisotropy observed at the $L_2$ edge is quite obvious. This anisotropy together with the quite small but still visible multiplet structures at the $L_{2,3}$ data might be a fingerprint for a certain degree of hybridization between Cu 3d and Cu 4s/4p orbitals. Yet more importantly, the small $L_{2,3}$ peak-to-edge jump ratio unequivocally resembles the absorption edge of Cu metal and signals that the Cu 3d shell is almost completely filled. Consistent with photoemission data a predominant part of Cu 3d states is found to be located below the Fermi level $E_F^{Fe}$ [18, 22] and, thus, does not contribute to the density of states at $E_F$. Furthermore, significant Cu$^{2+}$ contributions (3d$^9$4s$^0$ configuration) can be excluded as well since the corresponding multiplet spectrum (without taking 4s/4p hybridization with the 3d orbitals into account) consists of only a single peak at the $L_3$ edge and is structureless at the $L_2$ edge. Hence Cu has an (almost) closed 3d shell and a formal valence around $\approx 0$ (a valence of up to $\approx +1$ cannot be completely ruled out). In other words - and fully consistent with the previously inexplicable increase of $h_{As,Fe}^{-}$ in Fig. 1(a) for Cu substitution - Cu definitely donates holes to the system. Yet again, no energy shift is observed for Fe/Cu substitution in the Fe $L_3$ data of Fig. 2(b) and, therefore, the doped holes are again expected to have local character around the impurity.

These results already give a rather comprehensive overview if and how charge carriers are doped to the system. Yet in many cases, the equally important question remains on which states the “doped” carriers reside. To answer this point we combine our electronic (NEXAFS) and structural (XRD) results and find five distinct categories:

(i) Ba/K substitution for which the $<Fe-Fe>$ bond length is drastically reduced. This leads to a widening of the Fe bands at $E_F$ and, simultaneously, holes are doped directly to the Fe 3d states of the system as demonstrated by the energy shift of the $L_3$ maxima in Fig. 2(b). The $<Fe-As>$ distances, on the other hand, remain almost unaffected upon hole doping of the 3d-derived bands reflecting an unchanged Fe 3d-As 4p hybridization.

(ii) Fe/Cu substitution for which the $<Fe-Fe>$ bond length is increased and where the doped holes are assumed to have local character around the impurity. Since density-functional calculations predict the end member...
BaCu$_2$As$_2$ to be an $sp$-band metal [21], our data suggest that the holes introduced by Fe/Cu substitution reside on 4$s$/4$p$-dominated states of the impurity. These states are localized with the observed (almost) closed 3$d$ shell character, and explain the increased $\langle$Fe-Fe$\rangle$ bond length. For higher substitution levels these hybrids will overlap on adjacent sites and a (3$d$-)4$s$/4$p$-band metal can start to develop. Apparently, “doped charge carriers” on such states weaken the TM 3$d$-As 4$p$ hybridization and lead to an enlarged $\langle$Fe-As$\rangle$ distance.

(iii) Independent of the sample’s individual composition, Fe/Mn replacement behaves quite similar to Fe/Cu substitution. “Doped holes” seem to be again localized at 4$s$/4$p$ hybrids of the impurity and, consequently, $\langle$Fe-Fe$\rangle$ and $\langle$Fe-As$\rangle$ distances are increased. Despite a different amount of 3$d$ electrons, the atomic configurations of Cu$^0$ (3$d^{10}$4$s^1$) and Mn$^+$ (3$d^5$4$s^1$) have an equivalent electron count on the 4$s$ states. Upon substitution (hole doping) occupied 4$s$-derived bands are expected to be pushed towards $E_F$ to overlap with the respective 3$d$ states accommodating the additional hole introduced by the TM impurity. Although it is established that such states significantly contribute to the density of states around $E_F$ for elemental systems like Mn, Fe, Co, Ni or Cu they are usually neglected for band structure calculations in the case of the pnictides.

(iv) For Fe/Co substitution, the Co content-dependent changes in $\langle$h$_{As,Fe}\rangle$ indicate electron doping whereas the NEXAFS spectra clearly point to an effective isovalence (+2) of Fe and Co. Consistent with previous work this suggests that Fe/Co replacement indeed introduces electrons to the system; the ensemble of all $d$ electrons, however, screens the extra positive charge of the Co impurity on such a short length scale that the total electron density peaks around the impurity and the TM atom appears isovalent to Fe [6, 8–11]. Since Fe/Co substitution has no significant impact on the $\langle$Fe-Fe$\rangle$ bond length we conclude that TM 4$s$/4$p$ states play only a minor role in this case and remain separated from $E_F$. The reduced $\langle$Fe-As$\rangle$ bond distance points to an enhanced Fe 3$d$-As 4$p$ hybridization of the states at $E_F$ by which the topology of the Fermi surface can be slightly modified [6].

(v) For Fe/Ni substitution Ni appears as trivalent. Hence, Ni$^{3+}$ effectively donates one electron more than Co$^{2+}$ but otherwise behaving somewhat similarly. More precisely, the decrease of $\langle$h$_{As,Fe}\rangle$ and $\langle$Fe-As$\rangle$ supports the fact that, at least at low substitution levels, for Fe/Ni replacement all 3$d$ electrons of the system screen the impurity. For higher Ni concentration, however, the discrepancies between $\langle$Fe-As$\rangle$ of Fe/Co and Fe/Ni substitution and, particularly, of $\langle$Fe-Fe$\rangle$ together with the absent shift of the Fe $L_3$ peak signal that 4$s$/4$p$ states have to play an important role at $E_F$ as well. The structural data even indicate that the end member BaNi$_2$As$_2$ is a good candidate for a (3$d$-)4$s$/4$p$-band metal, similar to BaCu$_2$As$_2$. Corresponding to the “electron doping” and the atomic 3$d^7$4$s^0$ configuration of Ni$^{3+}$, unoccupied 4$s$-derived bands are expected to be pushed downwards to $E_F$ upon Fe/Ni substitution to accommodate the additional electron introduced by the impurity.

To summarize, our NEXAFS and XRD data evidence that only Ba/K substitution leads to a significant doping of charge carriers directly to the Fe 3$d$ states. In contrast, for Fe-site replacement no charge carriers are doped to the Fe 3$d$ states which is a strong deviation from the rigid-band model. In the case of Fe/Co substitution the “Co 3$d$ electrons” behave very comparably to the “Fe 3$d$ electrons” and the ensemble of all $d$ states seems to screen the extra positive charge of the impurity. For the replacement of Fe by Mn, Ni or Cu, on the other hand, occupied and unoccupied 4$s$/4$p$ impurity states become quite important for the electronic structure of Fe-site substituted BaFe$_2$As$_2$ and accommodate the additional charge carriers introduced by the TM impurity. For low substitution levels, these charge carriers remain localized at the TM site. In this “doping” regime the impurity states may act as strong scatterers and induce a topological change of the Fermi surface while the same states can form metallic 4$s$/4$p$ bands for higher substitution content. The 4$s$/4$p$ states themselves, however, do not directly contribute to superconductivity.

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