Where Are the Extra *d* Electrons in Transition-Metal-Substituted Iron Pnictides?

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Transition-metal substitution in Fe pnictides leading to superconductivity is usually interpreted in terms of carrier doping to the system. We report on a density functional calculation of the local substitute electron density and demonstrate that substitutions like Co and Ni for Fe do not carrier dope but rather are isovalent to Fe. We find that the extra *d* electrons for Co and Ni are almost totally located within the muffin-tin sphere of the substituted site. We suggest that Co and Ni act more like random scatterers scrambling momentum space and washing out parts of the Fermi surface.

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The discovery of superconductivity in layered Fe pnictides [1] is attracting a lot of interest because their transition temperatures up to $T_c = 56$ K [2] are the highest except for cuprates. The $A\mathrm{Fe}_2\mathrm{As}_2$ (A denotes alkaline-earth-metal atoms such as Ca, Sr, and Ba) systems are in a spin-density-wave state at low temperatures [3]. Upon hole doping by the chemical substitution of A^{2+} ions with potassium ions (K^+) superconductivity appears [4]. This is reminiscent of the cuprates where the introduction of charge carriers via doping indeed seems to control the phase diagram. It is surprising that the substitution of Co or Ni for divalent Fe also leads to superconductivity [5,6], which by analogy is also mostly ascribed to electron doping with the explanation that the extra *d* electrons in Co and Ni are donated to the system. One should note this implies that Co and Ni would behave like Co^{3+} or Ni^{4+}. Chemical intuition, on the other hand, advocates the isovalent nature of the substitution with the extra *d* electrons bound to the higher nuclear charge, but then leads to questions regarding the role of these substitutions for Fe. In this Letter we study the local electron-density distribution in the vicinity of the substitutes, Co, Ni, Cu and Zn, using density functional (DFT) methods.

Recent theoretical density functional theory studies of the changes in the density of states close to the Fermi energy of the Co substituted materials [5] suggest a shift in the density of states qualitatively consistent with a so-called virtual crystal approach in which basically the extra nuclear charge on Co is in effect averaged over the whole crystal. The net result of the virtual crystal approach is to good approximation a rigid shift of the Fermi level. It is also important to recognize that the density of states is actually not a ground-state property and therefore perhaps a less reliable quantity to look at within DFT. It is interesting therefore to look at the actual charge density distribution in the substituted material with DFT methods to see where the extra *d* electrons actually reside. By looking at the charge density distribution we are looking at a quantity that is a ground-state property and therefore at least in principle exact in a DFT framework. Recent reports of a periodic impurity model in DFT studied the spin density distribution and found that the excess spin density is indeed localized at Co sites in Co-substituted $\mathrm{BaFe}_2\mathrm{As}_2$ [7]. In this Letter, we report on the results of a detailed DFT study of a similar periodic impurity model of various substitutes (Co, Ni, Cu, Zn, Ru, Rh, and Pd) in $\mathrm{BaFe}_2\mathrm{As}_2$ and FeSe. The main reasons for including the FeSe substituted system is to demonstrate the insensitivity of our conclusions to the details of the chemical composition of the host material and, secondly, to be able to handle a larger supercell and lower concentration in FeSe to demonstrate the insensitivity to the "impurity" concentration for concentrations below 12.5%. We report a study of the electron-density spatial distribution which is a basic property of DFT. We show that the extra *d* electrons are almost totally concentrated within the muffin-tin (MT) sphere of the substitute atoms consistent with an isovalent scenario rather than a virtual crystal scenario.

The band-structure calculations were performed using the linearized augmented plane wave method implemented in the WIEN2K package [8]. The exchange and correlation effects were treated within the generalized gradient approximation [9]. As for $\mathrm{BaFe}_2\mathrm{As}_2$, we considered the tetragonal $I4/mmm$ structure, where we used lattice constants $a = 3.9625$ Å and $c = 13.0168$ Å as obtained in Ref. [10]. The lattice constants of FeSe were taken from Ref. [11] as $a = 3.7734$ Å and $c = 5.5258$ Å. The effect of substitution was taken into account with the supercells of $\mathrm{Ba}_8\mathrm{Fe}_{14}M_2\mathrm{As}_{16}$ (12.5%) and $\mathrm{Fe}_{17}M\mathrm{Se}_{18}$ (5.6%) ($M =$ Co, Ni, Cu, Zn, Ru, Rh, or Pd), as shown in Fig. 1. We adopt the crystallographic notation for the directions (11) and (01) in the Fe plane of the pure material.

Figure 2 shows the partial Fe *d* density of states in the pure material and the partial Co, Ni, Cu, or Zn *d* density of states in 12.5% substituted $\mathrm{BaFe}_2\mathrm{As}_2$ [2(a)] and 5.6% substituted FeSe [2(b)]. The zero of energy is at the

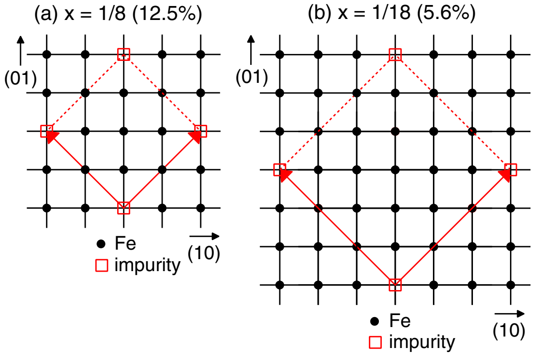

FIG. 1 (color online). Supercells used for 12.5% (a) and 5.6% (b) substitution as used in the calculation. The arrows define the unit vectors for the supercell. The filled circles and open squares denote Fe and impurity sites, respectively.

Fermi energy. The density of states of the substituted materials clearly shows a shift relative to the pure material, but this shift is not uniform. Clearly there is a substantial change in the shape itself of the density of states indicating a strong influence of the changed local potential produced by the substitutes. This is clearest in comparing the local projected density of states for the Ni, Cu, and Zn cases with that of the Fe local projected density of states in the pure material. In the extreme and as yet experimentally unstudied case of Zn, the Zn 3*d* states form a very narrow impurity band at ~8 eV, resembling what is often referred to as a shallow core level. The whole evolution of the substitute density of states with increasing nuclear charge is qualitatively what is expected for isovalent substitution. We also note that the results for 12.5% $BaFe_2As_2$ and 5.6% FeSe are almost the same, demonstrating that the impurity-impurity interaction is already small for the fifth nearest-neighbor distances. This also demonstrates that the major part of the action is confined to the Fe plane being rather insensitive to replacing Se with As.

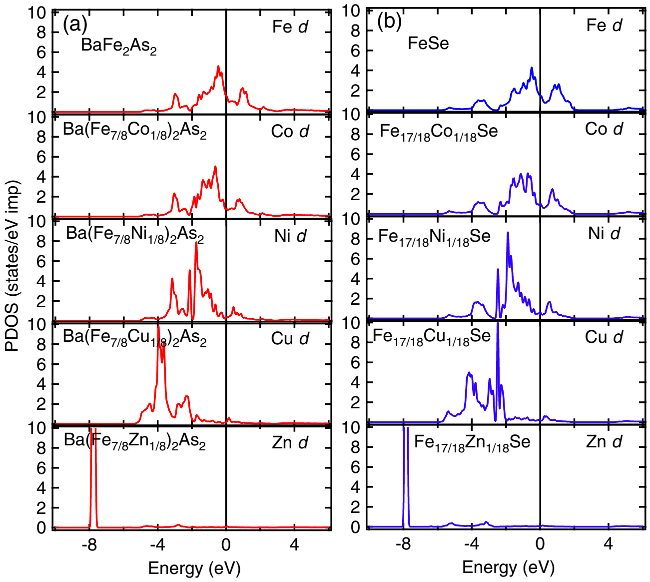

FIG. 2 (color online). Partial Fe *d* density of states in the pure material and the partial Co, Ni, Cu, or Zn *d* density of states in 12.5% substituted $BaFe_2As_2$ (a) and 5.6% substituted FeSe (b). The zero of energy is at the Fermi energy.

The electron-density distribution in the ground state has a sounder theoretical basis in DFT than does the density of states since the latter is not a ground-state property, so we will focus on the electron density here. In Fig. 3(a), we show the valence electron-density distribution in the *ab* plane after integration along the *c*-axis direction and after subtracting off that of the pure material. The valence electron density is defined as the density of electrons in the states situated between −8 eV and the Fermi energy. Figure 3(b) is the same as 3(a) but for FeSe and 5.6% substitution. Both the pure and substituted material were treated with identical unit cells. Aside from the strong increase in the electron density close to the substituents, there is a quite minor density change in the rest of the unit cell. A more detailed picture of the change in the charge density is shown in Fig. 4. Here we plot the change in the charge density again integrated over the *c* direction with a cut along the (11) and (10) directions. This figure shows the monotonic increase in the local impurity charge density as we go from Fe to Co, Ni, Cu, and Zn. One can see that the excess electrons from the impurity are concentrated at the impurity site, and there is little effect on the electron-density distribution in the rest of the material. For example, there is no observable offset of the electron density as would have been expected from a rigid Fermi level shift.

To determine the number of electrons within the MT containing mainly 3*d* electrons in the valence-band region, we show in Fig. 5 the integral over the colored disk with a radius *R* and integrated also over the *c* axis (as shown in the inset). The result is the radial dependence of the electron density. Again here the vertical axis is the difference between the pure material with Fe at the origin and the substituted material with the substitute at the origin. This plot clearly demonstrates that for Co one extra electron is located inside the MT radius, and for Ni it is 2, for Cu it is 3, and for Zn it is 4, consistent with isovalent substitution.

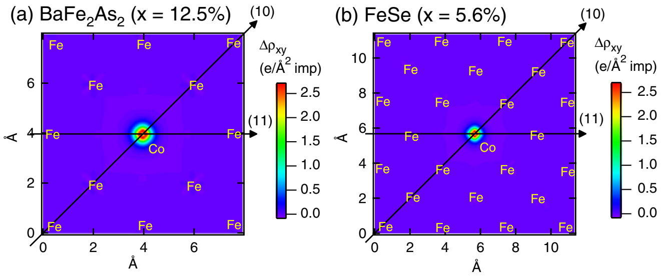

FIG. 3 (color online). (a) A contour plot of the difference in valence electron density integrated along *c*-axis direction between 12.5% Co substituted and pure $BaFe_2As_2$. (b) The same as (a) but for FeSe and 5.6% substitution.

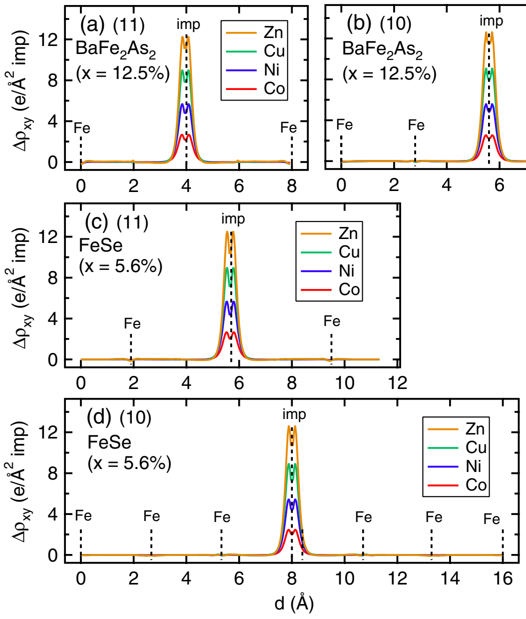

FIG. 4 (color online). The difference in valence electron density integrated along c-axis direction between 12.5% Co substituted and pure BaFe$_2$As$_2$ with a cut along (11) (a) and (10) (b) direction. Panels (c) and (d) are the same as (a) and (b), respectively, but for FeSe and 5.6% substitution.

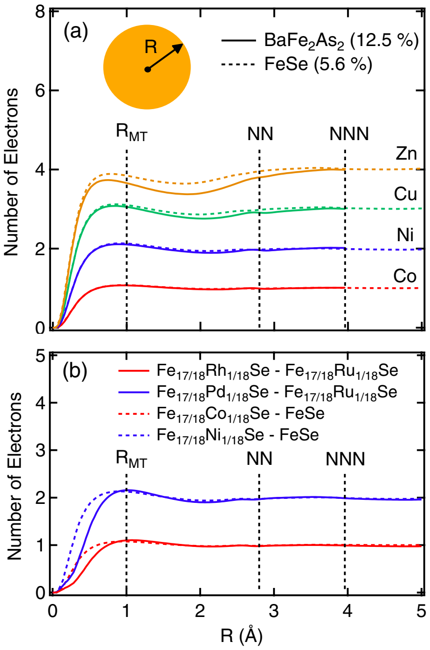

FIG. 5 (color online). (a) The integrated change in the electron density as a function of the distance R from the impurity in 12.5% substituted BaFe$_2$As$_2$ and 5.6% substituted FeSe. As shown in the inset, the integration is over the colored disk with a radius R and over the c axis. (NN denotes nearest neighbor and NNN denotes next-nearest neighbor.) (b) A comparison between 3d and 4d substitutions in FeSe. The changes in the electron density for the Rh and Pd cases are calculated with respect to Ru substitution.

This strongly suggests that these substituents bind locally the number of d electrons needed to compensate for the change in the nuclear charge.

To study the distribution of the excess d electrons in the case of 4d substitutes, we calculate the change in the electron density of FeSe upon Rh or Pd substitution. There is an issue with doing a simple direct difference density with pure Fe because the 4d orbitals have an extra radial node and are more extended than the 3d wave functions of Fe and Co or Ni. This causes a relative transfer of charge density from small radii to larger radii for the 4d's, and because there are 6 or more 4d occupied orbitals, each of which have this contribution, it tends to overwhelm the contribution from the single extra electron. Rather than comparing these charge densities with pure FeSe, we use FeSe substituted with Ru which is isovalent with Fe and which would also have the extended wave functions for all the occupied orbitals. Using otherwise the same procedure as above, we get the plots shown in Fig. 5. One can see that Rh is very similar to Co and Pd to Ni in that they both have the same number of extra electrons, i.e., 1 and 2, respectively, as the 3d substitutions. The somewhat larger orbital radius for Rh and Pd as compared to Co and Ni is also evident from the initial slops.

Summarizing, we studied the effects on the electron density of various substitutes (Co, Ni, Cu, Zn, Ru, Rh, and Pd) in BaFe$_2$As$_2$ and FeSe using density functional theory. The partial substitute d density of states exhibits a strong change compared to that of the projected Fe density of states in the pure material over a wide energy range. This change is strongly different from that obtained by a rigid shift of the Fe projected density of states of the pure material. We also presented a DFT calculation of the electron-density distribution in the unit cell of a superlattice of substitutes. This clearly demonstrates that the excess d electrons are concentrated within the MT sphere at the substitute sites compensating for the increased nuclear charge. The charge density in the rest of the unit cell is hardly affected. This result strongly suggests that Co, Ni, Cu, Zn, Ru, Rh, and Pd substitutes for Fe should not be considered as "dopants" because they are isovalent with Fe.

The question then remains, What is the physical origin of the strong influence on T_c? In answering this, we should not forget that these "impurities" are located in the Fe plane and therefore will be strong scatterers especially for electrons in narrow bands. We should also remember that in the real material these impurities are randomly distributed and so will tend to scramble k space. This could have the influence of "washing out" (parts of) the Fermi surface. The parts most strongly effected would be those for which the Fermi velocity measured along the band dispersion is the smallest. In other words, the rather flat band contributions to the total Fermi surface would be washed out first. This could destabilize competing phases based on the Fermi surface nesting in favor of superconductivity.

In fact, there are potential experiments that can prove or disprove the importance of impurity scattering in these systems. In a recent angle-resolved photoemission spectroscopy paper [12], the authors demonstrate very narrow momentum space widths for the pure nonpolar material LiFeAs. All other pnictides and FeSe materials exhibit extremely wide momentum space widths. Therefore, LiFeAs provides an ideal platform for studying momentum space broadening as a function of various substitutions. Such experiments would be able to distinguish accurately between the doping and the impurity scattering effects.

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