

Dependence of Carrier Doping on the Impurity Potential in Transition-Metal-Substituted FeAs-Based Superconductors

S. Ideta,¹ T. Yoshida,^{1,2} I. Nishi,¹ A. Fujimori,^{1,2} Y. Kotani,³ K. Ono,³ Y. Nakashima,⁴ S. Yamaichi,⁴ T. Sasagawa,⁴ M. Nakajima,^{1,2,5} K. Kihou,^{2,5} Y. Tomioka,^{2,5} C. H. Lee,^{2,5} A. Iyo,^{2,5} H. Eisaki,^{2,5} T. Ito,^{2,5} S. Uchida,^{1,2} and R. Arita^{2,6}

¹Department of Physics, University of Tokyo, Bunkyo-ku, Tokyo 113-0033, Japan

²JST, Transformative Research-Project on Iron Pnictides (TRIP), Chiyoda, Tokyo 102-0075, Japan

³KEK, Photon Factory, Tsukuba, Ibaraki 305-0801, Japan

⁴Materials and Structures Laboratory, Tokyo Institute of Technology, Yokohama, Kanagawa 226-8503, Japan

⁵National Institute of Advanced Industrial Science and Technology, Tsukuba 305-8568, Japan

⁶Department of Applied Physics, University of Tokyo, Bunkyo-ku, Tokyo 113-8656, Japan

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In order to examine to what extent the rigid-band-like electron doping scenario is applicable to the transition metal-substituted Fe-based superconductors, we have performed angle-resolved photoemission spectroscopy studies of $\text{Ba}(\text{Fe}_{1-x}\text{Ni}_x)_2\text{As}_2$ (Ni-122) and $\text{Ba}(\text{Fe}_{1-x}\text{Cu}_x)_2\text{As}_2$ (Cu-122), and compared the results with $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$ (Co-122). We find that Ni 3d-derived features are formed below the Fe 3d band and that Cu 3d-derived ones further below it. The electron and hole Fermi surface (FS) volumes are found to increase and decrease with substitution, respectively, qualitatively consistent with the rigid-band model. However, the total extra electron number estimated from the FS volumes (the total electron FS volume minus the total hole FS volume) is found to decrease in going from Co-, Ni-, to Cu-122 for a fixed nominal extra electron number, that is, the number of electrons that participate in the formation of FS decreases with increasing impurity potential. We find that the Néel temperature T_N and the critical temperature T_c maximum are determined by the FS volumes rather than the nominal extra electron concentration or the substituted atom concentration.

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Carrier doping plays an essential role in a variety of correlated electron systems such as the high- T_c cuprates as well as the newly discovered ion-based high- T_c superconductors. For example, one of the parent compounds AFe_2As_2 ($\text{A} = \text{Ba}, \text{Sr}$) abbreviated as “122” is an antiferromagnetic metal but becomes superconducting (SC) by substitution of monovalent metal atoms for divalent Ba or Sr at the A site, which obviously dopes the Fe-As layer with holes [1,2]. Superconductivity is also realized via partial substitution of transition-metal atoms such as Co, Ni, and Cu for Fe [3–6]. According to the rigid-band model, the substitution leads to electron doping and the doped electron number in $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$ (Co-122), $\text{Ba}(\text{Fe}_{1-x}\text{Ni}_x)_2\text{As}_2$ (Ni-122), and $\text{Ba}(\text{Fe}_{1-x}\text{Cu}_x)_2\text{As}_2$ (Cu-122) is expected to be x , $2x$, and $3x$, respectively, while it is x for Co-122. This is a remarkable phenomenon given the fact that the substitution of transition-metal atoms for Cu in the CuO_2 plane of the cuprate superconductors quickly kills the superconductivity [7].

The phase diagrams of the transition metal-doped BaFe_2As_2 are reported by Canfield *et al.* [4] and Ni *et al.* [5]; however, they exhibit complex behavior as shown in Fig. 1, where the SC transition temperatures T_c s and the Néel temperatures T_N s of Co-, Ni-, and Cu-122 are plotted as functions of substituted atom concentration x [panel (a)] and nominal extra electron concentration [panel (b)]. The T_c of Co-122 reaches the maximum 24 K at $x \sim 0.06$. As for

Ni-122, the maximum T_c of ~ 18 K is reached at $x \sim 0.05$, but the T_c drops more rapidly with Ni substitution than Co substitution. Cu-122 is largely non-SC except for $x \sim 0.044$, where a very low T_c of ~ 2 K has been reported [4,5,8]. The nearly coinciding T_c domes of Co- and Ni-122 in panel (b) (plotted against the nominal extra electron number) suggest that Fermi surfaces (FSs) follow the rigid-band model, but that the small but distinct mismatch of the two T_c domes suggests that there are some changes in the electronic structure beyond the rigid-band model, that is, the impurity potential of the substituted atoms are likely to

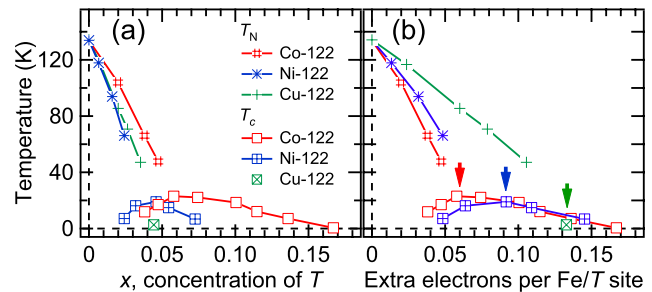


FIG. 1 (color online). Superconducting and magnetic transition temperatures (T_c and T_N) of $\text{Ba}(\text{Fe}_{1-x}\text{T}_x)_2\text{As}_2$ (T -122: $\text{T} = \text{Co}, \text{Ni}, \text{Cu}$) reported in Refs. [4,5]. (a) Plotted as functions of the number of substituted transition-metal atoms per Fe site, x . (b) Plotted as functions of nominal extra electron number per Fe sites x , $2x$, and $3x$ for Co-, Ni-, and Cu-122, respectively.

influence the electronic structure and hence T_c . For Cu-122, the T_c is strongly suppressed, and the T_c “maximum” occurs at a much higher nominal extra electron concentration of ~ 0.13 than Co- (~ 0.06) and Ni-122 (~ 0.10) [5], suggesting that its electronic structure is strongly deviated from that expected from the rigid-band model. Contrary to T_c , the drop of the T_N with doping is determined by the substituted atom concentration x rather than the number of extra electrons, as seen from the relatively well overlapping T_N curves in Fig. 1(a) (although the T_N curve for Co-122 is somewhat deviated from the other curves).

So far, a large number of angle-resolved photoemission spectroscopy (ARPES) studies have been made on the Co-122. The results have shown that there are two hole FSs and two electron FSs at the two-dimensional Brillouin zone center and corner, respectively [9–13]. The SC gaps [14,15] and the three dimensionality [12,13,16] of the hole and electron FSs have also been identified. The FSs evolve following the rigid-band model with electron doping, that is, the volumes of the FSs change according to the number of extra electrons x and the chemical potential is shifted accordingly [13,17,18]. However, according to a recent density functional theory calculation on supercells [19], the extra electronic charges are largely distributed on the substituted Co, Ni, or Cu atoms, apparently contradicting the rigid-band model [13,20]. On the other hand, another supercell calculation has indicated that the total electron number enclosed by the FSs changes in proportion to the dopant concentration in Co and Ni-doped LaFeAsO [21].

In this Letter, we have performed an ARPES experiment on Ni- and Cu-122, and investigated the evolution of the electronic structure with the strength of impurity potential in going from Co-, Ni-, to Cu-122. We find that the number of doped electrons in Ni- and Cu-122 estimated from the FS volumes is smaller than the value expected from the simple rigid-band model, and decreases in going from Co-, Ni-, to Cu-122 for a fixed nominal doped electron number.

High-quality single crystals of $\text{Ba}(\text{Fe}_{1-x}\text{Ni}_x)_2\text{As}_2$ with $x = 0.02, 0.0375$ ($T_c \sim 16$ K), 0.05 ($T_c \sim 18$ K), and 0.08 ($T_c \sim 5$ – 10 K), and $\text{Ba}(\text{Fe}_{1-x}\text{Cu}_x)_2\text{As}_2$ with $x = 0.04, 0.07, 0.09$, and 0.14 were grown by the self-flux method. The Ni and Cu concentrations were determined by x-ray fluorescence analysis and energy dispersive x-ray analysis, respectively. ARPES measurements were carried out at beam line 28 A of Photon Factory (PF) using circularly polarized light ranging from $h\nu = 34$ to 88 eV and a Scienta SES-2002 analyzer with the total energy resolution of ~ 15 – 25 meV. The crystals were cleaved *in situ* at $T = 10$ K in an ultrahigh vacuum less than 1×10^{-10} Torr. ARPES measurements on Ni-122 ($x = 0.02$, $T_N \sim 90$ K) and Cu-122 ($x = 0.04$, $T_N \sim 50$ K) were performed at temperatures above T_N , $T = 110$ and 60 K, respectively. The other samples were measured at $T = 10$ K.

Figure 2 shows angle-integrated photoemission spectra of Ni-122 and Cu-122 in the entire valence-band region. Ni

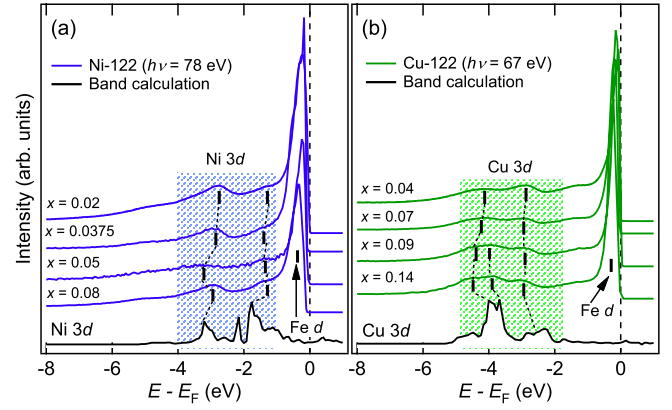


FIG. 2 (color online). Angle-integrated photoemission spectra of Ni-122 [panel (a)] and Cu-122 [panel (b)]. Partial density of states for Ni and Cu 3d orbitals obtained by band-structure calculation [19] are also plotted. The shaded area shows the energy region dominated by Ni and Cu 3d-derived states.

3d-derived emission is located ~ 2 – 4 eV below the Fermi level (E_F), and overlaps with the Fe 3d band. The Cu 3d-derived emission is located at higher binding energies of ~ 4 – 5 eV. This indicates that the impurity potential of the substituted transition metal atoms becomes stronger in going from Co, Ni, to Cu. The spectra are consistent with the density of state given by the supercell band-structure calculation [19] shown in the same figure.

Figure 3 shows the summary of FS mapping in $k_{||}$ - k_z space for the hole and electron FSs of Ni- and Cu-122. Raw data of hole and electron bands near E_F are shown in Fig. S2 of the Supplemental Material [22]. While the two hole FSs around the Z point are always observed, the hole FS around the Γ point shrinks and disappears with increasing Ni concentration, resulting in three-dimensional hole FSs [23,24]. On the other hand, the volumes of the electron FSs around the X point become larger with increasing Ni concentration, indicating electron doping. All the FSs show warping along the k_z direction and the electron FS is less warped than the hole FS. For Ni- and Cu-122, we could not resolve the two electron bands, and therefore, we consider that the two bands are almost degenerate. As a whole, the hole and electron FSs are similar to those of Co-122 [12]. In the case of Cu-122, the hole FSs were observed only for $x = 0.04$ as shown in Fig. 3(b1), and we show only the electron FSs for $x = 0.07, 0.09$, and 0.14 in Figs. 3(b2)–3(b4) (see Figs. S1 and S2 and the text of [22]).

Now, we estimate the total hole and electron FS volumes in order to discuss to what extent the electron-doped system can be understood within the rigid-band model. First, let us estimate the volume of each hole and electron FS from the result of the FS mapping shown in Fig. 3. For the “rugby ball”-like hole FSs of Ni-122, we have estimated the volumes assuming two degenerate inner ($x = 0.02, 0.0375$, and 0.05) and one outer ($x = 0.02, 0.0375, 0.05$, and 0.08) hole FSs [13] (see also Fig. S3 in the

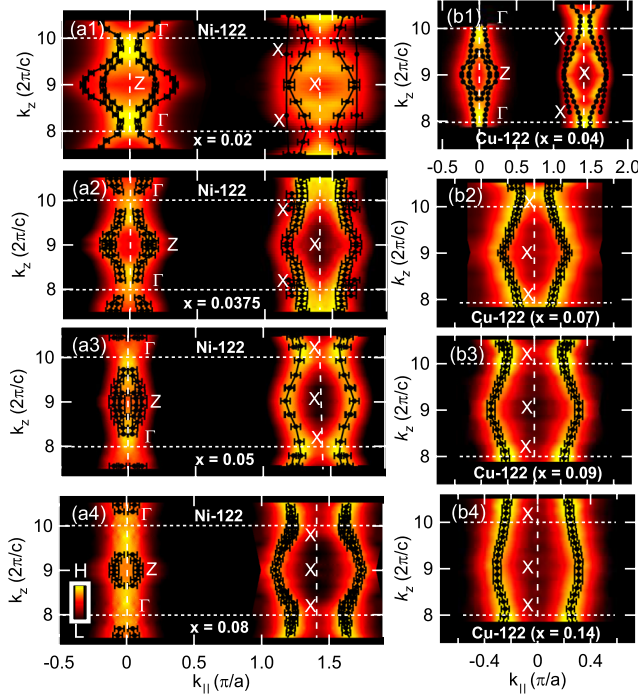


FIG. 3 (color online). ARPES intensity plot in k_{\parallel} - k_z momentum space for Ni-122 and Cu-122 obtained by $h\nu$ -dependent ARPES measurements. (a1)–(a4) Hole and electron FSs for Ni-122. (b1)–(b4) Hole and electron FSs for Cu-122. k_F points of the hole and electron FSs are plotted by black dots. The ARPES intensity plots have been symmetrized with respect to symmetry lines.

Supplemental Material [22]). For the hole FS of Cu-122 with $x = 0.04$, we applied the same method. For the electron FSs, we have also estimated the volumes assuming that two FSs are nearly degenerate as in the case of Co-122 [25]. The total volume of the hole FSs, n_h , that of the electron FSs, n_{el} , and the total FS volume, namely, the difference $n_{el} - n_h$, are plotted as functions of nominal extra electron number in Fig. 4. In order to compare the present ARPES result with the previous studies of Co-122 [12,13], n_h and n_{el} are plotted as functions of the nominal electron number, x for Co, $2x$ for Ni, and $3x$ for Cu in Figs. 4(a) and 4(b). (Data for Co-122 with $x < 0.05$ are not plotted here because of the antiferromagnetic band folding and hence the difficulty in estimating n_h and n_{el} .) In the previous ARPES result on Co-122 [12,13], the plots of n_h from the nondoped to overdoped samples decreases gradually with increasing Co concentration as shown in Fig. 4(a). The n_h of Ni-122 exhibits the same behavior. In Fig. 4(c), one finds that $n_{el} - n_h$ for Co-122 [13] is proportional to x for $x \geq 0.07$, where the antiferromagnetic order disappears. On the other hand, the value of $n_{el} - n_h$ for Ni-122 increases, but seems to be slightly deviated downwards from the linear relationship predicted by the rigid-band model, indicating that signature of the deviation from the rigid-band model starts to be seen from Ni-122. As for Cu-122, $n_{el} - n_h$ is even smaller than that of Ni-122 in the entire doping range. The present

ARPES result suggests that although most of the doped electrons participate in the formation of FSs, part of them may be partially localized and do not fill the energy bands as predicted by the rigid-band model. Recent neutron scattering study has also reported that the electron counting based on the rigid-band model is inappropriate [26].

The plots of n_h for Co-, Ni-, and Cu-122 shown in Fig. 4(a) almost coincide with each other. On the other hand, the n_{el} curve shown in Fig. 4(b) is shifted toward higher electron concentrations in going from Co, Ni, to Cu. This means that in going from Co-, Ni-, to Cu-122, the hole bands are shifted away from E_F by the same ratio, and that the relative positions of the electron and hole bands change (see Figs. S4 and S5 of the Supplemental Material [22]), indicating that the nonrigid band effect clearly exists.

So far, we have shown that electrons are indeed doped in the transition metal-substituted BaFe_2As_2 , but the deviation from the rigid-band model exists in the band structure and the FS volumes and increases with increasing strength of the impurity potential. As shown in Fig. 1(b), the extra doped electron concentration determines the T_c better than the impurity concentration, but the $T_{c,\text{max}}$ for Co-, Ni-, and Cu-122 are still significantly deviated from each other in this plot. As for T_N , the same plot fails, particularly in

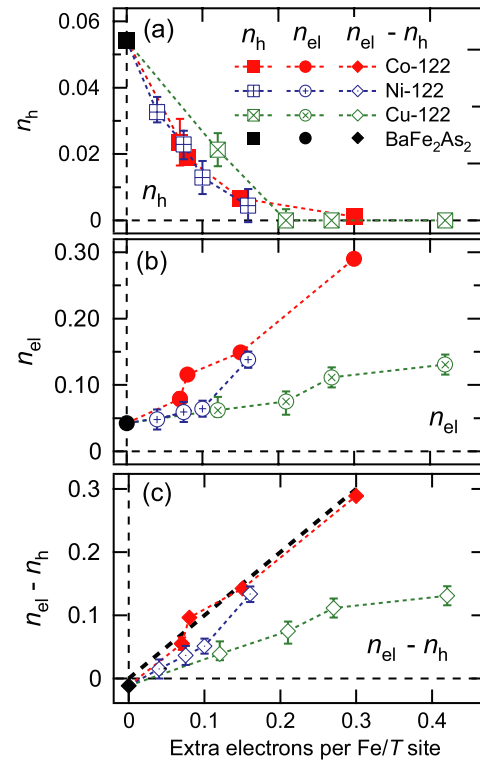


FIG. 4 (color online). Hole and electron FS volumes from the ARPES data of BaFe_2As_2 , Co-122, Ni-122, and Cu-122 plotted as functions of the nominal extra electron number. (a) Hole FS volume n_h . (b) Electron FS volume n_{el} . (c) Total FS volume $n_{el} - n_h$. Black dashed line shows the behavior ($n_{el} - n_h = x$) expected from the rigid-band model. BaFe_2As_2 and Co-122 data are taken from [12,13].

Cu-122. On the other hand, if the T_c and T_N for Co-, Ni-, and Cu-122 are plotted as functions of $n_{\text{el}} - n_h$ deduced from the ARPES data [27], in Fig. 5 the T_N for Co-, Ni-, and Cu-122 coincides with each other, and the T_c maximum occurs at nearly the same $n_{\text{el}} - n_h$ value of ~ 0.06 for all the systems [8]. This means that the T_N values as well as the optimal composition of T_c in the electron-doped BaFe_2As_2 are controlled by $n_{\text{el}} - n_h$ relatively well. Since the $T_{c,\text{max}}$ varies between the systems, the absolute T_c values should be controlled not only by $n_{\text{el}} - n_h$, but also by other parameter(s) such as n_h , n_{el} , or the band structure. Since the energy position of the impurity 3d level is lowered in going from Co, Ni, to Cu, it is natural to consider that the strong impurity potential suppresses the T_c value.

Recently, Haverkort *et al.* [28] and Berlijn *et al.* [29] have studied how the electronic structure is affected by impurity potential when host atoms are substituted by other atoms. It has been shown that the hole-FS volume increases with increasing impurity potential [21]. For strong impurity potentials, substitution creates an impurity band split-off below the original host band [19,30,31]. The impurity band removes electrons from the host band, leading to an apparent decrease in the electron occupation. This calculated result can be compared with the FS volume changes in the series $T = \text{Co, Ni, and Cu}$ for the same number of extra electrons estimated in the present ARPES study. In going from Ni to Cu, the impurity potential becomes stronger as demonstrated in Fig. 2 and the hole-FS volume decreases. However, since the total electron number estimated from the FS volumes show a smaller value than that expected from the rigid-band model, both the calculation and experimental results show decrease in the electron occupation. For Co-122, the electronic structure almost

follows the rigid-band model, because the Co 3d level is near the Fe 3d level.

By computing the configuration-averaged spectral function of disordered Co/Zn substituted BaFe_2As_2 , Berlijn *et al.* [29] have estimated the hole and electron volumes. For Co-122, the FS volume of Co-122 follows the Luttinger theorem, that is, the system follows the rigid-band model. On the other hand, for Zn-122, the Luttinger theorem breaks down. The result also indicates that the FS volume is smaller than that expected from the rigid-band model. Therefore, the increased deviation from the rigid-band model becomes stronger in going from Co, Ni, to Cu-122 is consistent with the calculated result for Zn-122. Thus, to understand the effect of the transition-metal atom substitution for Fe atoms on the electronic structure, the strength of the impurity potential should be taken into account. The calculations have also shown that all the spectral features of Zn-122 are broadened compared to Co-122. In fact, the hole and electron bands for Ni- and Cu-122 are not clearly resolved into multiple bands, whereas those of Co-122 and BaFe_2As_2 have been clearly resolved. In the studies of conventional binary random alloys, photoemission spectroscopy and theoretical calculation by the coherence potential approximation (CPA) [32–37] have shown that the rigid-band model breaks down when the potential difference between two constituent atoms is comparable to or exceeds the bandwidths. In the latter case of alloys, characteristic features in the densities of states of the two constituent materials survive. In this sense, the present ARPES result may be understood in analogy of the conventional binary alloys.

In conclusion, we have performed an ARPES study of the transition metal-substituted $\text{Ba}(\text{Fe}_{1-x}\text{T}_x)_2\text{As}_2$ ($T = \text{Ni, Cu}$) to investigate the validity of and the deviation from the rigid-band model, which has been usually assumed for Co-122. We find that, although the rigid-band model works qualitatively and electrons are indeed doped, the electron FS volumes in Ni- and Cu-122 are smaller than the value which is expected from the rigid-band model. This result suggests that part of electrons doped by substitution of Ni or Cu preferentially occupy the Ni 3d or Cu 3d states, or are trapped around the impurity sites, and do not behave like a mobile carrier. We found that the T_N in the electron-doped BaFe_2As_2 is determined by $n_{\text{el}} - n_h$, while T_c is determined by both $n_{\text{el}} - n_h$, the band structure, and chemical disorder, which are affected by the impurity potential.

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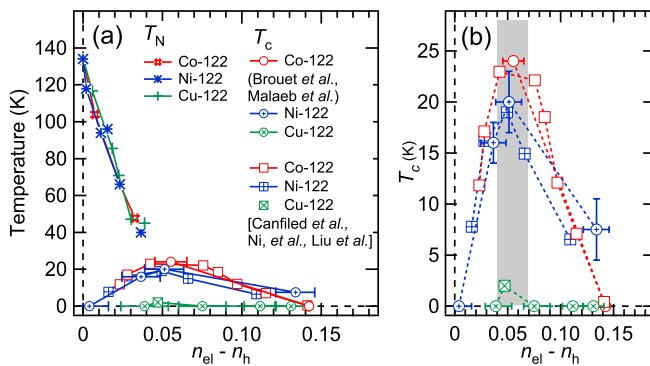


FIG. 5 (color online). T_c and T_N of $\text{Ba}(\text{Fe}_{1-x}\text{T}_x)_2\text{As}_2$ ($T = \text{Co, Ni, Cu}$) plotted as functions of the total FS volume $n_{\text{el}} - n_h$ evaluated by ARPES. The data for Co-122 are taken from [4,5]. (b) is a magnified plot of T_c . The T_c values for Co-, Ni-, and Cu-122 are taken from [4,5,12,13,38]. The $n_{\text{el}} - n_h$ of Co-, Ni-, and Cu-122 for small x 's has been estimated by linear interpolation between the lowest $n_{\text{el}} - n_h$ data and $n_{\text{el}} - n_h = 0$. T_N for Ni-122 with $x = 0.02$ and Cu-122 with $x = 0.04$ are also plotted.

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