Effects of Disordered Ru Substitution in $BaFe_2As_2$: Possible Realization of Superdiffusion in Real Materials

Limin Wang (王莉敏),[1] Tom Berlijn,[1] Yan Wang (王彦),[2] Chia-Hui Lin (林佳輝),[1,3] P. J. Hirschfeld,[2] and Wei Ku (顧威)[1,3]

[1]Condensed Matter Physics and Materials Science Department, Brookhaven National Laboratory, Upton, New York 11973, USA
[2]Department of Physics, University of Florida, Gainesville, Florida 32611, USA
[3]Physics Department, State University of New York, Stony Brook, New York 11790, USA
(Received 12 September 2012; published 14 January 2013)

An unexpected insensitivity of the Fermi surface to impurity scattering is found in Ru substituted $BaFe_2As_2$ from first-principles theory, offering a natural explanation of the unusual resilience of transport and superconductivity to a high level of disordered substitution in this material. This robustness is shown to originate from a coherent interference of correlated on-site and intersite impurity scattering, similar in spirit to the microscopic mechanism of superdiffusion in one dimension. Our result also demonstrates a strong substitution dependence of the Fermi surface and carrier concentration and provides a resolution to current discrepancies in recent photoelectron spectroscopy. These effects offer a natural explanation of the diminishing long-range magnetic, orbital, and superconducting orders with high substitution.

DOI: 10.1103/PhysRevLett.110.037001 PACS numbers: 74.70.−b, 71.15.−m, 71.18.+y, 71.23.−k

Chemical substitution is the most widely employed technique to induce high-temperature superconductivity [1–5]. The most obvious effects of substitution are carrier doping and chemical pressure. On the other hand, such substitution should also introduce disordered impurity scattering, an effect mostly unexplored in the studies of the electronic structure of real materials due to its complexity. Recently, owing to an advances in first-principles theoretical methods [6,7], various novel and surprising physical effects of disorder were found in the new Fe-based superconductors containing transition metal dopants [8–10] and Fe vacancies [11]. Naturally, one would wonder whether there are also unexpected disorder effects in isovalent substitution. An ideal candidate to investigate is the Ru substituted Fe-based superconductor $Ba(Fe_{1-x}Ru_x)_2As_2$ (Ru122) [12–20]. Unlike other existing cases with isovalent substitution at the anion sites, Ru atoms replace the essential Fe atoms. Given that Ru is a $4d$ element, it must be quite different chemically from $3d$ Fe and therefore must introduce a strong impurity scattering potential.

One obvious physical puzzle regarding Ru122 is the resilience of its superconductivity and transport against a large concentration of disordered impurities. Indeed, samples are found to retain their superconductivity even with 40% Ru substitution of Fe [13,15]. Given the current proposal that the superconducting order parameter is most likely of $s_\pm$ symmetry [4], it is extremely puzzling how a sign-changing order parameter can survive such a large concentration of strong impurities, from the standard pair-breaking consideration. Similarly, given that Ru is more distinct from Fe than Co is, it is quite unexpected that Ru substituted samples exhibit a residual resistivity comparable to an 8% Co substituted system [5] at a much higher 35% substitution level.

Another important current issue is the Ru substitution dependence of the electronic structure. Qualitatively similar to the Co substituted systems, Ru substitution at high enough level systematically suppresses the magnetic, orbital, and then superconducting orders. For Co substituted systems, this behavior can be understood from the weakening of the nesting between the electron and hole pockets since the former grow in size while the latter shrink, responding to the additional doped carriers [10]. For Ru substitution, however, the size of the electron and hole pockets should remain balanced (and approximately nested) since Ru is supposed to be isovalent to Fe. It is thus not as obvious what substitution-dependent features in the electronic structure suppress the long-range order in this case.

Currently, this issue is quite controversial in the field due to seemingly contradictory experimental observations. Some angular-resolved photoemission spectroscopy (ARPES) experiments [15] reported a nearly substitution-independent Fermi surface and suggested that superconductivity emerges from dilution of the magnetism, in contrast to other doped 122 systems. Other ARPES measurements, on the other hand, reported a large increase of the number of carriers [14] with increasing Ru concentration and a crossover from two-dimensional to three-dimensional structure of some of the holelike Fermi surfaces [16]. Similar contradictions also emerge in current first-principles computations. Some concluded that Ru substitution induces no doping [18] and no changes in the low energy band structure [19], while others [20] found large changes. It is thus timely to investigate the substitution dependence of the electronic structure of Ru122 with a proper account of the disorder effects to resolve the current debates and, if possible, to offer an explanation for the suppression of long-range magnetic, orbital, and superconducting orders upon increased substitution levels.

In this Letter, we address these important issues by studying the electronic structure of $Ba(Fe_{1-x}Ru_x)_2As_2$ over the full range of substitution ($0 \leq x \leq 1$), taking into account the realistic disorder effects in first-principles calculation. This is made possible via the recently developed Wannier-function-based effective Hamiltonian method for disordered systems [6]. Surprisingly, while large scattering is found on the entire Fe band complex, for all substitution levels, the states near the chemical potential remain very sharp and coherent. This unexpected insensitivity of the quasiparticles to impurity scattering is here traced back to a coherent interference between on-site and off-site impurity effects. In spirit, this mechanism is very similar to the microscopic mechanism that gives rise to superdiffusion in 1D theory [21], and our observation may be the first realization of this exotic phenomenon in real materials.

This insensitivity to impurity scattering provides a natural explanation of the amazing resilience of transport and superconductivity in the presence of a high level of Fe site substitution in this specific material. In addition, our results reproduce the measured spectral functions and resolve the current controversy in the interpretations of the Ru substitution dependence. We find a systematic reduction of carrier density upon Ru substitution accompanied by an enhanced 3D character of the Fermi surface. These effects lead naturally to the suppression of long-range magnetic and superconducting orders at a high substitution level. Our findings highlight the general need to incorporate disorder effects in most chemically substituted systems.

We first evaluate the configuration-averaged spectral function $\langle A_n(k, \omega)\rangle$ of Wannier orbital n, frequency ω, and crystal momentum k, within the approach of Ref. [6] and with the help of the band structure unfolding method [7]. The resulting $\langle A_n(k, \omega)\rangle$ is found converged within the resolution of the plots after averaging over 10 large randomly shaped supercells containing 400 atoms on average with random Ru substitutions. The influence of Ru substitution on the Hamiltonian is extracted from the results of several density functional theory calculations: the undoped $BaFe_2As_2$ or $BaRu_2As_2$ as well as the impurity supercells of $Ba_2Fe_3RuAs_4$ or $Ba_2FeRu_3As_4$. The low energy Hilbert space is taken within $[-6, 4]$ eV consisting of Wannier orbitals of Fe-d, Ru-d, and As-p characters. Careful benchmarks of the quality of our effective Hamiltonian are conducted against full density functional theory calculations using stoichiometric ordered "impurity lattice" test cases [22]. The entire study is conducted using the 2-Fe Brillouin zone required by the symmetry [23] and unfolded to the 1-Fe zone [7,23] when direct comparison with ARPES spectra is needed.

Figure 1 summarizes our resulting spectral functions over the entire range of substitution for $Ba(Fe_{1-x}Ru_x)_2As_2$ ($x = 0.0, 0.21, 0.38, 0.55, 0.75$, and 1.0). A clear broadening of quasiparticle spectral lines in both momentum and frequency is observed over the entire Fe d-band complex, reflecting the finite mean free path and lifetime of carriers in these states due to disorder. The broadening is naturally the strongest for the $x = 0.55$ case since it is the most disordered one shown. (As x approaches 0 or 1, the system starts to become cleaner, approaching the pure end compounds.) Such a strong impurity scattering is expected since the $4d$ level of Ru is about 0.8 eV lower in energy than the $3d$ level of Fe, and the different spatial extent of the orbitals also implies large changes in their hopping strength.

Strikingly, the bands near the Fermi level (shown in the second panel of Fig. 1) remain very sharp, as if carriers occupying states near the Fermi level do not scatter from the impurity. Correspondingly, the configurational-averaged spectral function [Fig. 2(a)] exhibits a very sharp peak at the Fermi level with a well-defined dispersion. (In comparison, around -1 eV, the spectral function shows a much broader peak, reflecting strong impurity scattering effects.) Therefore, the puzzling resilience of transport and superconductivity against a high substitution level in Ru122 is now understandable simply from the lack of net impurity scattering for states near the Fermi level.

Figures 2(b)–2(d) give further insights into the microscopic origin of this unusual insensitivity to disorder near the Fermi level. Here, we compare spectral functions under the influence of different partial components of the impurity potential in the Wannier-function basis. With only the diagonal impurity potential (on-site disorder), Fig. 2(c) shows a strong smearing of the entire d-band complex, including states near the Fermi level. On the other hand, with only the off-diagonal impurity potential (off-site disorder), Fig. 2(d) shows a well-structured smearing of the band structure: The farther away they are from the center of the d bands, the more the states are affected by the impurity. In particular, near the center of the band, the effects of the off-site impurity potential diminish. This is understandable since the off-site terms of the Hamiltonian are responsible for the band dispersion, and their effects are at their maximum at the band edges. One would expect a similar structure for the effectiveness of the off-site impurity potential, particularly positive (negative) above (below) the center of the band. (The Ru orbital is bigger than Fe, so the impurity potential tends to enhance the band width.) A similar conclusion can be reached by imagining the band structure interpolated between pure $BaFe_2As_2$ and pure $BaRu_2As_2$.

Upon combining both the on-site and off-site disorder potentials, Fig. 2(b) shows that the energy range with weak impurity scattering moves up, close to the Fermi level. This can now be understood as a consequence of the cancelation of the (negative) on-site and (positive) off-site impurity

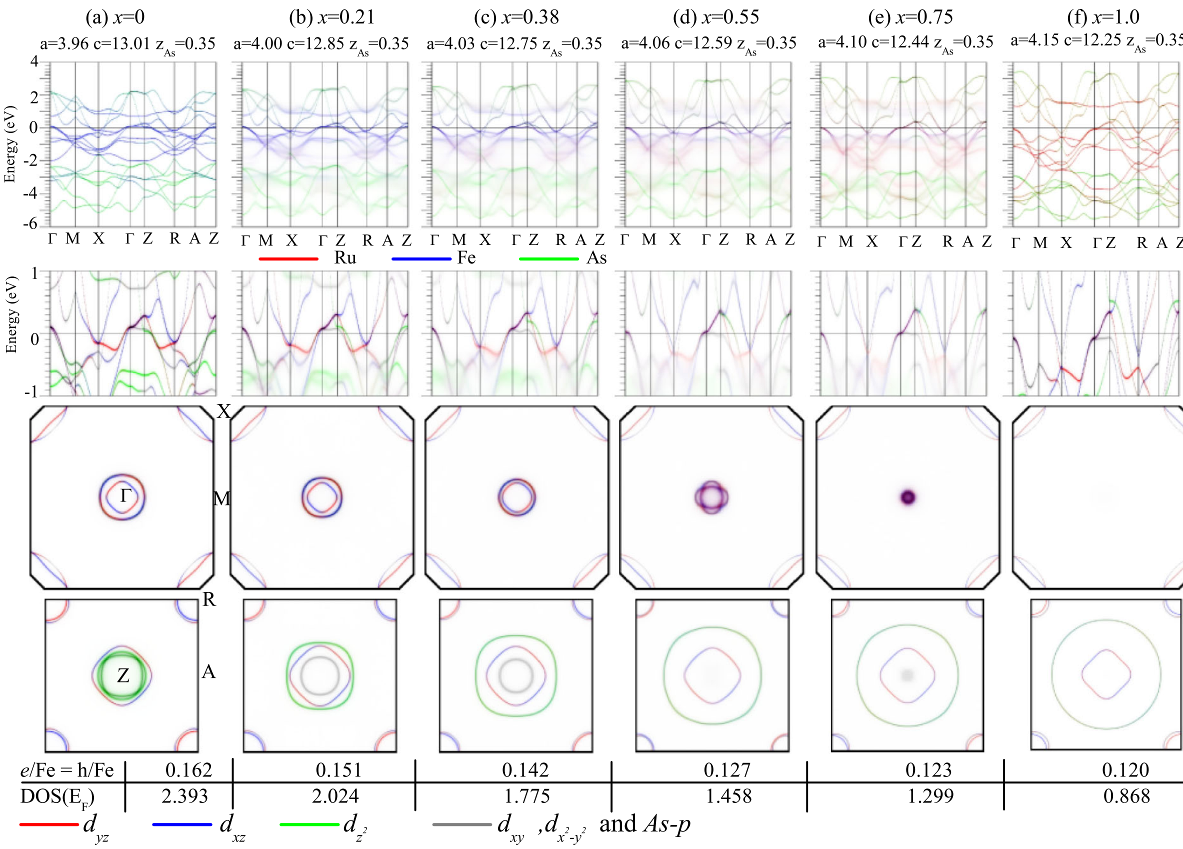
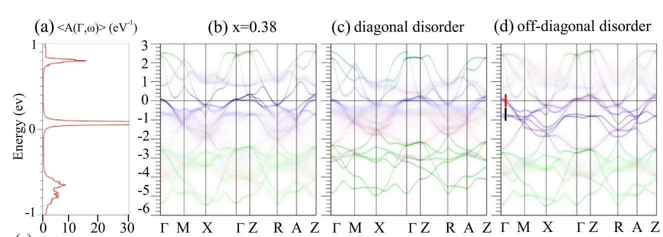


FIG. 1 (color online). The lattice constants (Å) [13,29,30], band structure (the top panel), low energy band structure (the second panel), the Fermi surface around the Γ point with $k_z = 0$ (the third panel), and the Fermi surface around the Z point with $k_z = 2\pi/c$ (the bottom panel) for $Ba(Fe_{1-x}Ru_x)_2As_2$ with different Ru concentrations $x = 0$ (a), 0.21 (b), 0.38 (c), 0.55 (d), 0.75 (e), and 1.0 (f). The orbital characters of Fe, Ru, and As are distinguished by the colors given in the legends. The resulting carrier density per Fe and density of states at the Fermi level $N(E_F)$ per (eV Fe) are given below the plots.

potentials above the center of the band. Indeed, Fig. 2(e) gives an example of the net coupling involving the 8th/7th and 9th/10th bands near the Γ point resulting from a single impurity for all three cases. One sees that, near the Fermi level, the impurity scattering between the 9th and 10th bands has a large on-site contribution (similar to that between the 8th and 7th bands), but it is almost entirely canceled by the equally large off-site scattering. It is important to note that such coherent interference can only take place because the positions of the on-site and off-site impurity potentials are always correlated: Both are associated with the location of the Ru substitution. Therefore, moving the impurity position only adds the same overall phase to both of the terms but does not affect their interference.

This effect is in spirit very similar to the microscopic mechanism that gives rise to the unusual lack of localization in certain very special 1D models [21], referred to as "superdiffusion." In general, disordered 1D systems are known to be insulating because any disorder would localize all the states. However, an exceptional situation can take place, in which a subset of the states in the system would propagate superdiffusively. This has been demonstrated in a specially constructed first-neighbor-only tight-binding model with the values of on-site energies and the hopping matrix elements correlated in a specific way [21]. What we find here in Ru122 is probably a more general (and



(e)

k	j	k'	j'	<kj|Δ|k'j'>	<kj|Δ_D|k'j'>	<kj|Δ_OD|k'j'>
Γ	9	0.3ΓM	10	-0.0578	-0.3023	0.2445
Γ	8	0.3ΓM	7	-0.2938	-0.3316	0.0378

FIG. 2 (color online). (a) Spectral function and (b) band structure for a system with two types of disorder, (c) with only the diagonal disorder and (d) with only the off-diagonal disorder for disordered $Ba(Fe_{0.62}Ru_{0.38})_2As_2$. (e) Single-impurity induced coupling between the Bloch orbitals near and far from the chemical potential, indicated by the red (upper) and black (lower) segments in (d).

realistic) case, in which the interference takes place at a single impurity between on-site and off-site contributions. While the real system with longer-range hopping matrix elements is beyond the scope of the original superdiffusion model, it seems intuitively reasonable that the same cancelation of scattering processes (which leads to a divergence of the localization length in the latter case) will lead to dramatically more coherent behavior even if the cancelation is not quite exact. From this point of view, Ru122 may thus be considered the first realization of such an exotic superdiffusion mechanism in real materials. This effect results in the survival of superconductivity to a high substitution level due to the insensitivity of states near the chemical potential to the impurity scattering. In general, similar interference should occur in some other materials with disordered impurities as well since realistic impurity induced on-site and off-site effects are always correlated in position. This might also explain why metallic transport can often be found in some thin nanowires [24,25] and quasi-1D materials [26,27], despite the unavoidable occurrence of disorder.

Next, considering the Ru substitution dependence of the electronic structure, Fig. 1 shows several clear trends. First, the hole pockets in the center of the Brillouin zone become more three-dimensional, shrinking significantly in size in the $k_z = 0$ plane and eventually disappearing, while surviving in the $k_z = 2\pi/c$ plane. Specifically, the pocket with large z^2 character shows the strongest 3D dispersion, growing in size in the $k_z = 2\pi/c$ plane. On the other hand, the electron pockets near the corner of the zone show only a slight substitution dependence. This large change is quite consistent with the recent ARPES observation [16] but *seems* to contradict the earlier observation of a substitution-independent Fermi surface [15].

This discrepancy can, in fact, be easily resolved by accounting for the matrix element of the incident photon in the experiment [28]. The photon polarization used in Ref. [15] is along the y direction, which couples mostly to the yz orbitals. Figure 3 shows the yz character of our theoretical unfolded band structure [7], showing little change upon Ru substitution at the $k_z = 2\pi/c$ plane, in excellent agreement with the experiment.

The second physical effect of Ru substitution revealed in Fig. 1 is a physical reduction of carrier density, a real doping effect, and correspondingly a reduction of the density of states (DOS) at the chemical potential. In typical systems with only one sign of carriers, carrier doping is typically achieved via substitution of a different valence. Here, Ru substitution, while typically considered isovalent, actually decreases the carrier concentration significantly, from 0.16/Fe at $x = 0$ to 0.12/Fe at $x = 1$, about a 25% reduction (cf. the bottom of Fig. 1). This takes places through reducing the 3D volume of both the electron and the hole pockets (while keeping charge neutrality), as if the system is being depleted of both electrons and holes

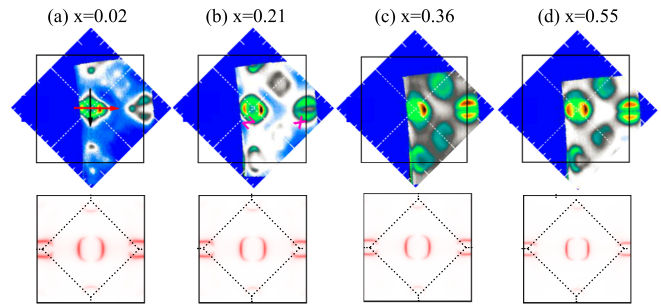


FIG. 3 (color online). Comparison of the Fermi surface at the $k_z = 2\pi/c$ plane between the ARPES results [15] (top panel) and our results (bottom panel) in the 1-Fe zone for different Ru concentrations $x = 0.02$ (a), 0.21 (b), 0.36 (c), and 0.55 (d). The dashed lines mark the true 2-Fe Brillouin zone boundaries.

simultaneously. Microscopically, this originates from a larger splitting between the conduction and valence bands due to the enhanced hopping via Ru substituted sites. Such chemical "pressure" effects should survive the mass renormalization observed in real materials.

Our result, which is perfectly consistent with the recent ARPES measurement [16], suggests a more complex picture. Indeed, we found that the green z^2 pocket increases in size at $k_z = 2\pi/c$ upon Ru substitution, as observed experimentally [16]. However, the total volume of the hole pockets (or equivalently that of the electron pockets) actually reduces, as reflected in the corresponding carrier density shown at the bottom of Fig. 1.

The above substitution dependence of the electronic structure corresponds nicely to the overall features in the phase diagram of this material. Both the enhanced 3D nature and the reduced DOS tend to suppress the long-range magnetic or orbital order and eventually the superconductivity with a sufficiently high substitution level (the "overdoped" regime). Indeed, the enhanced 3D band structure weakens the nesting condition for magnetic or orbital correlation and therefore presumably the pairing correlations as well in the "overdoped" regime. This is true not only in the weak-coupling Fermi surface instability point of view (through a phase-space argument) but also in the strong-coupling perspective (through stiffness of transverse or phase fluctuations). The smaller DOS has a similar effect, either reducing the Fermi surface instability or weakening the stiffness of the magnetic, orbital, and pairing channels. In essence, the case of Ru substitution offers a unique test case with strong substitution dependence of the electronic structure but without tipping the balance between electron and hole pockets. This unique feature of Ru122 should serve as a good qualitative benchmark for all proposed theories of magnetic or orbital order and superconductivity.

In summary, a remarkable insensitivity of the states near the chemical potential to disordered impurity scattering is found in $Ba(Fe_{1-x}Ru_x)_2As_2$ despite the strong impurity potential of Ru. This offers a natural explanation of the unusual resilience of transport and superconductivity against a high impurity level. This exotic behavior originates from a coherent interference of on-site and off-site disorder potentials and thus may be considered the first realization of a superdiffusion mechanism in real materials. Our result, which is well consistent with existing ARPES measurements, resolves a few current discrepancies in the field and leads to new physical conclusions. Specifically, Ru substitution is found to physically reduce the carrier density instead of being "isovalent." Our findings offer a natural explanation of the diminishing long-range magnetic, orbital, and superconducting orders at a high substitution level.

The authors thank Vladimir Dobrosavljevic for pointing out the similarity of our mechanism to that of the superdiffusion. This work is funded by the U.S. Department of Energy, Office of Basic Energy Sciences, under Grants No. DE-AC02-98CH10886, No. DE-FG02-05ER46236, and No. DOE-CMCSN.

[1] Y. Kamihara, T. Watanabe, M. Hirano, and H. Hosono, J. Am. Chem. Soc. **130**, 3296 (2008).
[2] D.C. Johnston, Adv. Phys. **59**, 803 (2010).
[3] G.R. Stewart, Rev. Mod. Phys. **83**, 1589 (2011).
[4] P.J. Hirschfeld, M.M. Korshunov, and I.I. Mazin, Rep. Prog. Phys. **74**, 124508 (2011).
[5] P.C. Canfield and S.L. Bud'ko, Annu. Rev. Condens. Matter Phys. **1**, 27 (2010).
[6] T. Berlijn, D. Volja, and W. Ku, Phys. Rev. Lett. **106**, 077005 (2011).
[7] W. Ku, T. Berlijn, and C.-C. Lee, Phys. Rev. Lett. **104**, 216401 (2010); For other unfolding methods, see V. Popescu and A. Zunger, Phys. Rev. Lett. **104**, 236403 (2010); M.W. Haverkort, I.S. Elfimov, and G.A. Sawatzky, arXiv:1109.4036.
[8] H. Wadati, I. Elfimov, and G.A. Sawatzky, Phys. Rev. Lett. **105**, 157004 (2010).
[9] A.F. Kemper, C. Cao, P.J. Hirschfeld, and H.-P. Cheng, Phys. Rev. B **80**, 104511 (2009).
[10] T. Berlijn, C.-H. Lin, W. Garber, and W. Ku, Phys. Rev. Lett. **108**, 207003 (2012).
[11] T. Berlijn, P.J. Hirschfeld, and W. Ku, Phys. Rev. Lett. **109**, 147003 (2012).
[12] S. Sharma, A. Bharathi, S. Chandra, V.R. Reddy, S. Paulraj, A.T. Satya, V.S. Sastry, A. Gupta, and C.S. Sundar, Phys. Rev. B **81**, 174512 (2010).
[13] F. Rullier-Albenque, D. Colson, A. Forget, P. Thuéry, and S. Poissonnet, Phys. Rev. B **81**, 224503 (2010).
[14] V. Brouet, F. Rullier-Albenque, M. Marsi, B. Mansart, M. Aichhorn, S. Biermann, J. Faure, L. Perfetti, A. Taleb-Ibrahimi, P. Le Fèvre, F. Bertran, A. Forget, and D. Colson, Phys. Rev. Lett. **105**, 087001 (2010).
[15] R.S. Dhaka, C. Liu, R.M. Fernandes, R. Jiang, C.P. Strehlow, T. Kondo, A. Thaler, J. Schmalian, S.L. Bud'ko, P.C. Canfield, and A. Kaminski, Phys. Rev. Lett. **107**, 267002 (2011).
[16] N. Xu, T. Qian, P. Richard, Y.-B. Shi, X.-P. Wang, P. Zhang, Y.-B. Huang, Y.-M. Xu, H. Miao, G. Xu, G.-F. Xuan, W.-H. Jiao, Z.-A. Xu, G.-H. Cao, and H. Ding, Phys. Rev. B **86**, 064505 (2012).
[17] R.S. Dhaka, S.E. Hahn, E. Razzoli, R. Jiang, M. Shi, B.N. Harmon, A. Thaler, S.L. Bud'ko, P.C. Canfield, and A. Kaminski, arXiv:1205.6731.
[18] L. Zhang and D.J. Singh, Phys. Rev. B **79**, 174530 (2009).
[19] K. Nakamura, R. Arita, and H. Ikeda, Phys. Rev. B **83**, 144512 (2011).
[20] G. Wang, L. Zheng, M. Zhang, and Z. Yang, Phys. Rev. B **81**, 014521 (2010).
[21] D.H. Dunlap, K. Kundu, and P. Phillips, Phys. Rev. B **40**, 10999 (1989); D.H. Dunlap, H.-L. Wu, and P.W. Phillips, Phys. Rev. Lett. **65**, 88 (1990).
[22] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevLett.110.037001 for computational details.
[23] The 2-Fe Brillouin zone has been shown as physically necessary by C.-H. Lin, T. Berlijn, L. Wang, C.-C. Lee, W.-G. Yin, and W. Ku, Phys. Rev. Lett. **107**, 257001 (2011).
[24] R. Rurali, Rev. Mod. Phys. **82**, 427 (2010).
[25] A. Del Maestro, B. Rosenow, J.A. Hoyos, and T. Vojta, Phys. Rev. Lett. **105**, 145702 (2010).
[26] B.J. Kim, H. Koh, E. Rotenberg, S.-J. Oh, H. Eisaki, N. Motoyama, S. Uchida, T. Tohyama, S. Maekawa, Z.-X. Shen, and C. Kim, Nat. Phys. **2**, 397 (2006).
[27] N. Wakeham, A.F. Bangura, X. Xu, J.-F. Mercure, M. Greenblatt and N.E. Hussey, Nat. Commun. **2**, 396 (2011).
[28] X.-P. Wang, P. Richard, Y.-B. Huang, H. Miao, L. Cevey, N. Xu, Y.-J. Sun, T. Qian, Y.-M. Xu, M. Shi, J.-P. Hu, X. Dai, and H. Ding, Phys. Rev. B **85**, 214518 (2012).
[29] M. Rotter, M. Tegel, D. Johrendt, I. Schellenberg, W. Hermes, and R. Pöttgen, Phys. Rev. B **78**, 020503 (2008).
[30] R. Nath, Y. Singh, and D.C. Johnston, Phys. Rev. B **79**, 174513 (2009).