Possible unconventional superconductivity in substituted BaFe$_2$As$_2$ revealed by magnetic pair-breaking studies

P. F. S. Rosa$^{1,2}$, C. Adriano$^1$, T. M. Garitezi$^1$, M. M. Piva$^{1,4}$, K. Mydeen$^4$, T. Grant$^2$, Z. Fisk$^2$, M. Nicklas$^4$, R. R. Urbano$^1$, R. M. Fernandes$^3$ & P. G. Pagliuso$^1$

$^1$Instituto de Física “Gleb Wataghin”, UNICAMP, Campinas-SP, 13083-859, Brazil, $^2$University of California, Irvine, California 92697-4574, USA, $^3$School of Physics and Astronomy, University of Minnesota, Minneapolis, MN 55455, USA, $^4$Max Planck Institute for Chemical Physics of Solids, Nöthnitzer Str. 40, D-01187 Dresden, Germany.

The possible existence of a sign-changing gap symmetry in BaFe$_2$As$_2$-derived superconductors (SC) has been an exciting topic of research in the last few years. To further investigate this subject we combine Electron Spin Resonance (ESR) and pressure-dependent transport measurements to investigate magnetic pair-breaking effects on BaFe$_{1.9}$M$_{0.1}$As$_2$ ($M = $ Mn, Co, Cu, and Ni) single crystals. An ESR signal, indicative of the presence of localized magnetic moments, is observed only for $M = $ Cu and Mn compounds, which display very low SC transition temperature ($T_c$) and no SC, respectively. From the ESR analysis assuming the absence of bottleneck effects, the microscopic parameters are extracted to show that this reduction of $T_c$ cannot be accounted by the Abrikosov-Gorkov pair-breaking expression for a sign-preserving gap function. Our results reveal an unconventional spin- and pressure-dependent pair-breaking effect and impose strong constraints on the pairing symmetry of these materials.

The Fe-based superconductors (SC) RFeAsO ($R = $ La-Gd) and AFe$_2$As$_2$ ($A = $ Ba, Sr, Ca, Eu) have been a topic of intense scientific investigation since their discovery$^{1,2}$. In particular, the semi-metal member BaFe$_2$As$_2$ (Ba122) displays a spin-density wave (SDW) phase transition at 139 K which can be suppressed by hydrostatic pressure and/or chemical substitution (e.g. K, Co, Ni, Cu, and Ru) inducing a SC phase. Although the proximity to a SDW state suggests a magnetic-mediated pairing mechanism$^{4,5}$, the precise nature and symmetry of the SC state, as well as the microscopic mechanism responsible for driving the SDW phase towards a SC state, remain open questions begging for further investigation. Importantly, suppressing the SDW phase – either via applied pressure or chemical substitution – is not sufficient for SC to emerge$^{16,20}$. Furthermore, when SC is found, the achieved optimal $T_c$ differs dramatically depending on the particular chemical substitution. This difference may be related to the pair-breaking effect associated with substitutions, which create local impurity scatterers, particularly when introduced in the FeAs planes.

A complete understanding of the impurity pair-breaking (IPB) effect in the Fe-pnictides is hindered, however, by their multi-band character and by the absence of quantitative information about the impurity potential. Indeed, the suppression of $T_c$ by impurities has been used as an argument in favor of both a sign-preserving $s^+$ state$^{22,23}$ and a sign-changing $s^-$ state in Ba122-derived materials$^{25-28}$. In these analyses, the impurity potential is usually estimated by the changes in the residual resistivity. However, the latter is sensitive to the transport scattering rate, which may differ from the quasi-particle scattering rate related to the suppression of $T_c$. Furthermore, using optimally-doped (OPD) compositions to study the effects of impurities on $T_c$ may introduce additional complications, since any kind of perturbation will likely drive the system away from the vicinity of the SDW phase and suppress SC by diminishing the strength of the pairing interaction instead of breaking the Cooper pairs$^{25,27}$.

In this paper, we circumvent these issues by combining macro and microscopic experiments, namely pressure-dependent transport measurements and electron spin resonance (ESR) in order to investigate the magnetic IPB effects in BaFe$_{0.9}$M$_{0.1}$As$_2$ ($M = $ Mn, Co, Cu, and Ni) single crystals slightly below the OPD concentration. A sizeable ESR signal for $M = $ Mn, Cu samples provides not only direct evidence for their role as local magnetic impurities, but it also allows us to extract the averaged exchange coupling $\langle J^x(q) \rangle$ between them and the Fe 3$d$
conduction electrons. The estimated suppression of $T_c$ derived from this quantity, which plays the role of the magnetic impurity potential in the Abrikosov-Gor’kov (AG) formalism, is found to be significantly smaller than the observed one, in sharp contrast to the excellent agreement found previously in borocarbides – multi-band compounds that display conventional sign-preserving SC states. Furthermore, we find that pressure strongly enhances $T_c$ of the $M$ = Cu sample, presumably by promoting stronger Cu-Fe hybridization and consequently suppressing the IPB effect. Our findings impose strong constraints on the mechanism responsible for SC and provide a strong evidence for an unconventional gap symmetry in these materials.

Fig. 1 displays the in-plane electrical resistivity, $\rho_{ab}$ ($T$), at ambient pressure for the selected single crystals. A linear metallic behavior is present at high-$T$ and the SDW phase transition of the parent compound is suppressed for all substitutions. A slight upturn is still present (arrows in Fig. 1), as typically found for substituted samples of Ba122 slightly below the OPD concentration. As $T$ is further decreased, SC emerges with the onset of $T_c$, defined as the temperature at which $d\rho_{ab}/dT = 0$, at 26.1 K, 22.2 K, and 3.8 K for Co, Ni, and Cu substitutions, respectively. On the other hand, no $T_c$ is observed for $M$ = Mn.

Figs. 2a–b show $\rho_{ab}$ ($T$) as a function of pressure for Co and Ni-substituted compounds. A small increase of $T_c$ is observed, as expected for nearly OPD samples. For instance, $T_c$ reaches 28.6 K at 18 kbar for $M$ = Co, whereas the self-flux OPD compound reaches a maximum $T_c$ of ~23 K in the same pressure range, suggesting that the In-flux samples are of high quality. On the other hand, for $M$ = Ni, $T_c$ only reaches 24.7 K. One can speculate that the reason the Ni-OPD sample does not achieve $T_c$ ~ 29 K is that it introduces more disorder than cobalt.

Now we turn our attention to the striking behavior of Mn- and Cu-substituted compounds, shown in Figs. 2c–d. First, we observe a substantial unexpected enhancement of $T_c$ by a factor of ~2.5 ($T_c$ = 10 K at 24 kbar) for the Cu-substituted compound. Although an increase of $T_c$ is expected for undoped samples, the maximum $T_c$ achieved is also expected to be roughly the same as in the OPD sample at ambient pressure. Surprisingly, this is not the case for the studied Cu-substituted compound, which presents $T_c$ = 4.2 K for the OPD crystal. On the other hand, SC does not emerge for $M$ = Mn up to $P$ = 25 kbar, in agreement with previous reports. In addition, there is a drastic decrease of $\rho_{ab}(T)$ with pressure by a factor of ~3 for $M$ = Cu and of ~1.5 for $M$ = Mn over all $T$ range (see Fig. 1 for a comparison), suggesting a possible decrease of the impurity scattering potential. These results seem to be consistent with a magnetic IPB mechanism since – unlike their Co and Ni counterparts – Mn and Cu substitutions are expected to introduce local moments. In many compounds, pressure is well known to enhance the hybridization between the local moments and the conduction electrons. Such enhancement would suppress the magnetic IPB effect and, consequently, increase $T_c$. As Mn$^{2+}$ has a much higher spin ($S = 5/2$) than Cu$^{2+}$ ($S = 1/2$), it is not surprising that the magnetic IPB is larger for $M$ = Mn, which in turn does not display SC.

To investigate such magnetic IPB scenario, we performed ESR – a powerful spin probe technique sensitive to the presence of local moments and their coupling to the conduction electrons. In agreement with the expectation that Cu and Mn ions have local moments, our ESR data reveal an intense resonance line for $M$ = Cu and Mn, but not for $M$ = Co and Ni. Fig. 3 shows the $X$-Band ESR lines normalized by the concentration of paramagnetic ions at $T$ = 150 K for fine powders of gently crushed single crystals. The Lorentzian fitting of the spectra reveals a linewidth of $\Delta H = 600(60)$ G and a $g$-value of $g = 2.08(3)$ for $M$ = Cu. For $M$ = Mn, $g = 2.04(3)$ and the linewidth is slightly larger, $\Delta H = 750(80)$ G, indicating stronger Mn-Mn interactions. Finally, for $M$ = Mn and Co, $g = 2.05(3)$ and $\Delta H = 670(70)$ G. For all samples, the calibrated number of resonating spins at room-$T$ is in good agreement with the concentrations obtained from Energy Dispersive Spectroscopy (EDS). As expected, the ESR intensity, which is proportional to $S(S + 1)$, was found to be roughly twelve times larger for $M$ = Mn samples, as compared to the $M$ = Cu sample. These results also indicate that the oxidation states of Cu and Mn are indeed Cu$^{2+}$ ($S = 1/2$) and Mn$^{2+}$ ($S = 5/2$). In the former case, Cu$^{2+}$ (3$d^9$ state) would not display an ESR resonance line since it is not a paramagnetic ion. In the case of copper, Cu$^{2+}$ (3$d^9$ state) would not display an ESR resonance line since it is not a paramagnetic probe with unpaired electrons. In the case of manganese, for Mn$^{2+}$ ($S = 2$) and Mn$^{2+}$ ($S = 3/2$) ions, one would expect a distinct ESR response (i.e., different $g$-value and calibrated signal intensity). Consequently, one can infer that there is no effective charge doping into the system, as suggested previously both experimentally and theoretically. Furthermore, our ESR results agree with other indirect probes that also suggest localized Cu$^{2+}$ and Mn$^{2+}$ moments in chemically-substituted Ba122.

Now let us turn to the question of what mechanism gives rise to such large and unexpected spin-polarization effects. To probe into such magnetic IPB scenario, we performed ESR – a powerful spin probe technique sensitive to the presence of local moments and their coupling to the conduction electrons. In agreement with the expectation that Cu and Mn ions have local moments, our ESR data reveal an intense resonance line for $M$ = Cu and Mn, but not for $M$ = Co and Ni. Fig. 3 shows the $X$-Band ESR lines normalized by the concentration of paramagnetic ions at $T$ = 150 K for fine powders of gently crushed single crystals. The Lorentzian fitting of the spectra reveals a linewidth of $\Delta H = 600(60)$ G and a $g$-value of $g = 2.08(3)$ for $M$ = Cu. For $M$ = Mn, $g = 2.04(3)$ and the linewidth is slightly larger, $\Delta H = 750(80)$ G, indicating stronger Mn-Mn interactions. Finally, for $M$ = Mn and Co, $g = 2.05(3)$ and $\Delta H = 670(70)$ G. For all samples, the calibrated number of resonating spins at room-$T$ is in good agreement with the concentrations obtained from Energy Dispersive Spectroscopy (EDS). As expected, the ESR intensity, which is proportional to $S(S + 1)$, was found to be roughly twelve times larger for $M$ = Mn samples, as compared to the $M$ = Cu sample. These results also indicate that the oxidation states of Cu and Mn are indeed Cu$^{2+}$ ($S = 1/2$) and Mn$^{2+}$ ($S = 5/2$). In the former case, Cu$^{2+}$ (3$d^9$ state) would not display an ESR resonance line since it is not a paramagnetic ion. In the case of copper, Cu$^{2+}$ (3$d^9$ state) would not display an ESR resonance line since it is not a paramagnetic probe with unpaired electrons. In the case of manganese, for Mn$^{2+}$ ($S = 2$) and Mn$^{2+}$ ($S = 3/2$) ions, one would expect a distinct ESR response (i.e., different $g$-value and calibrated signal intensity). Consequently, one can infer that there is no effective charge doping into the system, as suggested previously both experimentally and theoretically.

Furthermore, our ESR results agree with other indirect probes that also suggest localized Cu$^{2+}$ and Mn$^{2+}$ moments in chemically-substituted Ba122. The detailed analysis of the ESR data confronted with Eu-substituted BaFe$_2$M$_{0.1}$As$_2$ ($M$ = Co, Ni, Cu, Mn, and Ru) requires further technical discussion. Therefore, it will be the focus of a separated report.

Besides revealing the presence of localized moments, ESR also allows us to extract the averaged squared exchange coupling ($\langle J^2(q) \rangle$) between the localized moments and the conduction electrons from the linear increase of the linewidth with temperature (Korringa behavior) (see Table I) $^{12,13,15,31,37,38}$. In a general approach for single-band metals, the thermal broadening $b$ of the ESR linewidth $\Delta H$ $\approx 1/T_c$ is the linear well-known Korringa relaxation defined as $b = d(\Delta H)/dT = \pi k_B g \mu_B \langle J^2(q) \rangle \eta(E_F) K(x) (1-x)^{-1}$. Here, $\langle J^2(q) \rangle^{3/2}$ is the effective exchange interaction between the local moment and the conduction electrons ($c$) in the presence of $c$ momentum transfer averaged over the whole Fermi surface (FS), $\eta(E_F)$ is the “bare” density of states (DOS) for one spin direction at the Fermi level, $g$ is the local moment $g$-value and $K(x)$ is the Korringa exchange enhancement factor due to electron-electron exchange interaction. In the present analysis, we found empirically that “bottleneck” and “dynamic” effects are not present. When “dynamic” effects are present the $g$-values are usually strongly $T$-dependent, which is not observed in our experimental data. Moreover, when “bottleneck” effects are relevant the Korringa rate $b$ decreases with increasing concentration of the magnetic ions. However, in our data, we observe that spin-spin interaction dominates the entire temper-
nature range for dilute concentrations of Mn and Cu ions. In addition, bottleneck effects are not observed in Eu-substituted BaFe$_2$As$_2^{1,2}$, indicating that FeAs-based compounds are intrinsically unbottlenecked systems likely due to fast relaxation rates between the 3d conduction electrons and the lattice. In fact, recent ultrafast spectroscopy measurements have found a very large spin-lattice coupling in BaFe$_2$As$_2^{28}$. Finally, even if bottleneck effects were present, they alone would hardly be able to account for the enormous difference between $I_{\text{ESR}}$ and $I_{\text{AC}}$ observed here.

The key point here is that this parameter $\langle F(q) \rangle$ is the same one determining the suppression of $T_c$ by magnetic impurities within the AG formalism$^{29,30}$. To estimate whether the extracted value of $\langle F(q) \rangle_{\text{ESR}}$ for $M = \text{Cu}$ and Mn compounds can account for the observed suppression of $T_c$ in this formalism, we consider the “conventional case”, where the gap function has the same amplitude and sign across the entire Brillouin zone. This is the scenario in which magnetic impurities have the strongest effect on $T_c$ — in fact, introducing anisotropies in the gap function would make the magnetic pair-breaking effect weaker$^{24,31}$. In this situation, we have$^{30}$:

$$\ln \left( \frac{T_{c,0}}{T_c} \right) = \psi \left( \frac{1}{2} + \frac{1}{2\pi T_c \tau_\text{c}} \right) - \psi \left( \frac{1}{2} \right),$$

where $\psi(x)$ is the digamma function, $T_{c,0}$ is the transition temperature in the absence of magnetic impurities, and $\tau_\text{c}^{-1} = \frac{\pi}{2} \Delta c \eta(E_F)$.

Figure 2 | $\rho_{\text{ap}}(T)$ vs. $T$ for BaFe$_{1.8}$M$_{0.1}$As$_2$ ($M = \text{Co, Cu, Ni, and Mn}$) single crystals for $P = 5$–25 kbar. The insets show the evolution of $T_c$ with pressure.

Figure 3 | X-Band ESR lines at $T = 150$ K for powdered crystals of BaFe$_{1.8}$M$_{0.1}$As$_2$ ($M = \text{Co, Mn}$) and BaFe$_{1.85}$M$_{0.05}$Co$_{0.1}$As$_2$. The spectra were normalized by the concentration of paramagnetic probes in order to clearly compare their intensities. The solid lines are Lorentzian fits to the spectra (sample grain size smaller than the skin depth$^{32}$). It is worth mentioning that, in order to obtain the ESR signal, the sample surface must be completely clean and free of In-flux. The ESR signals for both samples were calibrated at 300 K using a strong pitch standard sample with $4.55 \times 10^{15}$ spins/cm.
For these materials, as discussed in Refs. [31, 37], the calculated magnitude depends on the ratio between intra and inter-band scattering. 25,56

Equation 1 by replacing $S_{1}$ segments, one needs to properly rewrite the Abrikosov-Gor'kov formalism is valid and (ii) similar normal-state phase diagrams displays a superconducting transition temperature of 26 K.

With these assumptions, we can thus estimate the magnetic pair-breaking impurity potential ($\langle F(q)\rangle_{AG}$) that would be necessary to cause the observed suppression of $T_c$ for three different samples, namely, BaFe$_{1.88}$Cu$_0.1$As$_2$, BaFe$_{1.88}$Mn$_{0.12}$As$_2$, and the mixed doping BaFe$_{1.895}$Co$_0.1$Mn$_{0.005}$As$_2$ compounds. The results are shown in Table I, and reveal a remarkable disagreement (of two orders of magnitude) between the results for the mixed doping BaFe$_{1.895}$Co$_0.1$Mn$_{0.005}$As$_2$ compounds.

The huge difference between $\langle F(q)\rangle_{AG}$ and $\langle F(q)\rangle_{ESR}$ is clearly robust against small variations of $T_{c,0}$ and $\eta(E_F)$.

Finally, we comment on the effects of pressure on $T_c$, summarized in Fig. 4. For the Co and Ni substitutions, the rate $dT_c/dP$ is ~0.1 K/kbar and the application of pressure has little effect on $T_c$. Strikingly, this rate is three times larger for the $M = Cu$ sample, while for $M = Mn$, no SC is observed. We argue that these results are linked to the magnetic pair-breaking discussed above. In particular, because pressure increases the hybridization between the Cu 3d bands and conduction electron bands, the copper bands become more itinerant, progressively losing their local moment character and consequently suppressing the magnetic IPB effect. Therefore, it is not surprising that the pure BaCu$_2$As$_2$ is a Pauli paramagnet with completely delocalized Cu 3d bands and no phase transition. Within this scenario, the fact that the Mn compounds do not display SC would follow from the fact that Mn$^{2+}$ has a spin value five times larger than Cu$^{+}$. Interestingly, if the magnetic IPB mechanism is suppressed by pressure, $T_c$ is, in principle, unconstrained to increase up to a maximum defined by the local distortions that the M-substitution creates. For Cu-substituted samples, it remains to be confirmed whether applying higher pressures with Diamond Anvil Pressure cells would further enhance or even suppress $T_c$ in the impurity pair-breaking regime.

To make this reasoning more quantitative, we assume that the enhancement of $T_c$ caused by the magnetic IPB suppression with pressure follows a phenomenological expression of the form $\Delta T_c$. The dotted lines are guide to the eyes for $T_{c,0}$ and $\eta(E_F)$.
existence of a Cu$_2$

overcome the latter linear increase of fluctuation suppression starts to play an important role and would overcome the latter linear increase of T$_c$. A detailed study on the effects of Cu substitution in critical current measurements is presented in Ref. [14]. Now, by constraining the same linear dependence for M = Mn and changing only the spin value to S = S/2, we obtain a lower limit for the critical pressure $P_c \approx 66$ kbar necessary for the emergence of SC (dashed line in Fig. 4). This $P_c$ value is in good agreement with the experimental absence of SC in the M = Mn compounds up to 25 kbar (see Fig. 2d), also in agreement with previous reports.

In conclusion, we have demonstrated the contrasting behavior of hydrostatic pressure effects on nearly OPD BaFe$_{2-x}$M$_x$As$_2$ (M = Co, Cu, and Ni) high-quality single crystals grown from In-flux method. The striking enhancement of $T_c$ with pressure for M = Cu and the existence of a Cu$^{5+}$ ESR line provide strong evidence of a spin-dependent pair-breaking mechanism strongly suppressed by pressure, suggesting an increase of hybridization between the Cu 3d bands and the conduction electron bands. More interestingly, by using the magnetic impurity potential extracted from the ESR analysis in the absence of bottleneck effects, we find that the Abrikosov-Gor'kov pair-breaking mechanism, applied to a conventional sign-preserving pairing state, cannot account for the observed suppression of $T_c$ in the Cu and Mn-substituted compounds. This result not only implies that the suppression of $T_c$ in these samples is due to other mechanisms, but also that an unconventional pairing state is more likely to be realized.

**Methods**

Single crystals of BaFe$_{2-x}$M$_x$As$_2$ (M = Mn, Co, Cu, and Ni) were grown using In-flux as described elsewhere. The crystals were checked by x-ray powder diffraction and submitted to elemental analysis using a commercial EDS microprobe. In-plane electrical resistivity measurements were performed using a standard four-probe method and a self-contained piston-cylinder type Be-Cu pressure cell, with a core of hardened NiCrAl alloy. ESR spectra were taken in a commercial ELEXSYS 500 X-band (v = 9.5 GHz) spectrometer equipped with a continuous He gas-flow cryostat.

1. Kamihara, Y., Watanabe, T., Hirano, M. & Hosono, H. Iron-based layered superconductor LaOFeAs, J. Am. Chem. Soc. 130, 3929 (2008).
2. Rotter, M. et al. Spin density wave anomaly at 140 K in the ternary iron arsenide BaFe$_2$As$_2$, Phys. Rev. B 78, 020503(R) (2008).
3. Ishida, K., Nakai, Y. & Hosono, H. To What Extent Iron-Pnictide New Superconductors Have Been Clarified: A Progress Report. J. Phys. Soc. Japan 78, 062001 (2009).
4. Hirschfeld, P. J., Korshunov, M. M. & Mazin, I. I. Gap symmetry and structure of Fe-based superconductors. Rep. Prog. Phys. 74, 124508 (2011).
5. Chubukov, A. V. Pairing Mechanism in Fe-Based Superconductors. Annu. Rev. Cond. Mat. Phys. 3, 57 (2012).
6. Bittar, E. M. et al. Co-Substitution Effects on the Fe Valence in the BaFe$_2$As$_2$ Superconducting Compound: A Study of Hard X-Ray Absorption Spectroscopy. Phys. Rev. Lett. 107, 267202 (2011).
7. Granado, E. et al. Pressure and chemical substitution effects in the local atomic structure of BaFe$_2$As$_2$, Phys. Rev. B 83, 184508 (2011).
8. Wadati, H., Elfmor, I. & Sawatzky, G. A. Where Are the Extra Electrons in Transition-Metal-Substituted Pnictides? Phys. Rev. Lett. 105, 157004 (2010).
9. Ieda, S. et al. Dependence of Carrier Doping on the Impurity Potential in Transition-Metal-Substituted FeAs-Based Superconductors. Phys. Rev. Lett. 110, 107007 (2013).
10. Berlijn, T., Lin, C.-H., Garber, W. & Ku, W. Do Transition-Metal Substitutions Dope Carriers in Iron-Based Superconductors? Phys. Rev. Lett. 108, 207003 (2012).
46. Ramos, S. M. et al. Superconducting Quantum Critical Point in CeCoIn$_{5-\delta}$Sn$_\delta$. Phys. Rev. Lett. **105**, 126401 (2010).
47. Heréz, E. N. et al. Pressuréatemperaturecomposition phase diagram of Ce$_2$Mn$_{1-x}$Sn$_x$. Physica B: Cond. Matt. **378** (2006).
48. Dyson, F. J. Electron Spin Resonance Absorption in Metals. II. Theory of Electron Diffusion and the Skin Effect. Phys. Rev. **98**, 349 (1955).
49. Texier, Y. et al. Mn local moments prevent superconductivity in iron pnictides Ba(Fe$_{1-x}$Mn$_x$)$_{2}$As$_2$. Physica B: Cond. Matt. **378** (2006).
50. Kim, M. G. et al. Effects of Transition Metal Substitutions on the Incommensurability and Spin Fluctuations in BaFe$_2$As$_2$ by Elastic and Inelastic Neutron Scattering. Phys. Rev. Lett. **109**, 167003 (2012).
51. Openov, L. A. Combined effect of nonmagnetic and magnetic scatterers on the critical temperatures of superconductors with different anisotropies of the gap. JETP Lett. **66**, 661 (1997).
52. Efremov, D. V. et al. Disorder-induced transition between $s$ and $s_{\pm}$ states in two-band superconductors. Phys. Rev. B **84**, 180512(R) (2011).
53. Chi, S. et al. Sign inversion in the superconducting order parameter of LiFeAs inferred from Bogoliubov quasiparticle interference. arXiv:1308.4413v1 (2013).
54. Johnston, D. C. Adv. Phys. **59**, 803 (2010); Paglione, J. & Greene, R. L. High-temperature superconductivity in iron-based materials. Nature Phys. **6**, 645 (2010).
55. Openov, L. A. Combined effect of nonmagnetic and magnetic scatterers on the critical temperatures of superconductors with different anisotropies of the gap. JETP Lett. **66**, 661 (1997).
56. Efremov, D. V. et al. Disorder-induced transition between $s$ and $s_{\pm}$ states in two-band superconductors. Phys. Rev. B **84**, 180512(R) (2011).
57. Tucker, G. S. et al. Competition between stripe and checkerboard magnetic instabilities in Mn-doped BaFe$_2$As$_2$. Phys. Rev. B **86**, 020503(R) (2012).
58. Fernandez, R. M. & Millis, A. J. Suppression of Superconductivity by Neel-Type Magnetic Fluctuations in the Iron Pnictides. Phys. Rev. Lett. **110**, 117004 (2013).
59. Chi, S. et al. Sign inversion in the superconducting order parameter of LiFeAs inferred from Bogoliubov quasiparticle interference. arXiv:1308.4413v1 (2013).
60. Johnston, D. C. Adv. Phys. **59**, 803 (2010); Paglione, J. & Greene, R. L. High-temperature superconductivity in iron-based materials. Nature Phys. **6**, 645 (2010).
61. Wen, H. H. & Li, S. Materials and Novel Superconductivity in Iron Pnictide Superconductors. Annu. Rev. Cond. Mat. Phys. **2**, 121 (2011).