The dual nature of As-vacancies in LaFeAsO-derived superconductors: magnetic moment formation while preserving superconductivity

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Although the general features of the superconducting (SC) and magnetic states in the Fe pnictides and chalcogenides are experimentally well-documented and theoretical models convincingly outline a predominantly non-phononic pairing, including multiband effects and unconventional pairing symmetries, the detailed mechanism of Cooper pairing in these materials still awaits elucidation. From a general point of view, the study and control of magnetic and non-magnetic defects can be helpful in this respect since the way in which they affect the Cooper pairs depends directly on the pairing interactions and symmetries in these multiband systems. In the pronounced multiband situation with unconventional SC as considered in the Fe-pnictides, point-defects/impurities that affect the nonmagnetic interband scattering will be detrimental for SC and is in no manner expected to strengthen it. Note several counterintuitive experimental observations related to the presence of As-vacancies (V\textsubscript{As}): (i) a significantly improved upper critical field slope near a slightly enhanced $T_{c}$ but Pauli-limiting behavior above 30 T and a lacking thereof in "clean" samples, (ii) a strongly enhanced spin susceptibility pointing at the formation of magnetic moments localized in the vicinity of V\textsubscript{As} and (iii) a steepened descend of the NMR relaxation rate in the SC state as compared with "clean" non-deficient As systems. Here we show that from a theoretical standpoint these observations can be understood in terms of a highly unconventional role that V\textsubscript{As} play in magnetic and SC properties of the As-deficient, optimally doped LaFeAs\textsubscript{1−δ}O\textsubscript{1−x}F\textsubscript{x}. From the Anderson-Wolff model\cite{10.1103/PhysRevLett.111.257002,10.1103/PhysRevB.86.104514} that we apply, it turns out that a nominally non-magnetic V\textsubscript{As} creates a local magnetic moment due its breaking of four strong, covalent Fe-As bonds. This moment formation gives rise to the observed strongly enhanced paramagnetic susceptibility in both the normal and SC state. At the same time, however, the presence of V\textsubscript{As} does not deteriorate SC properties and might even strengthen them.

An V\textsubscript{As} in the anisotropic FeLaAs\textsubscript{1−x}OF system can be considered as a dangling-bond (DB) defect in its Fe-As triple layers, which electronically can be viewed as single layers (see Fig. 1). The V\textsubscript{As}, treated as a missing As\textsuperscript{3−}, generates DB with 4 neighboring Fe ions in the central square plane and 4 neighboring As ions in tetrahedral coordination. In a minimal tight binding model these bonds are formed by the $p_{x,y}$ and $d_{xz,yz}$ orbitals. The corresponding $dp$ and $pp$ hopping integrals are denoted as $W_{1}$ and $W_{2}$, respectively. This model reflects the basic features of the band structure of LaFeAsO (see, e.g.,\cite{10.1103/PhysRevB.86.104514}). According to density functional theory combined with a tight binding analysis (DFT-TB), the Fe-related $3d$ bands range from $-2$ eV to $+2$ eV around the Fermi level $\varepsilon_{F} = 0$. The bonding and antibonding $4p_{x,y}$ states contribute to As-related bands deep below $\varepsilon_{F}$ and the nearly empty bands above it. The partial density of states (DOS) for these states is shown schematically.

![FIG. 1: Bonds around a single As vacancy V\textsubscript{As} in a Fe-As layer. Fe ions: ●. As ions above and below the Fe plane: solid and dashed ○, respectively. The $dp$-dangling bonds (DB) between the V\textsubscript{As} and its 4 Fe NN neighbors forming the orbital $\beta$ are labeled as $W_{1}$; $pp$-DB between V\textsubscript{As} orbital $\alpha$ and its 4 neighbors in As tetrahedra are labeled as $W_{2}$. Inset: fragment of the BZ for a single FeAs layer (dashed lines) and the folded BZ for the Fe sublattice (full lines). The axes for full lattice and Fe sublattice are denoted as (x,y) and (x’,y’), respectively.](image-url)
in Fig. 2. The empty states in the very vicinity of $\varepsilon_F$ correspond to hole ($\hbar$) and electron ($e\ell$) pockets, and the pronounced step in the DOS at the upper band edges arises due to the nearly 2D character of these $dp$-bands.

In view of this structure of the energy spectrum, the experimentally reported influence of $V_{\text{As}}$ defects on the magnetic properties of doped LaFeAsO looks especially puzzling. Indeed, the overlap between the $p_{x,y}$ states and $d_{yz,xz}$ state is noticeable only near $\varepsilon_F$. The mechanism, which may be responsible for the formation of local magnetic moments in defect cells is the influence of broken $dp$ valence bonds described by the transfer integral $W_1$ (Fig. 1) on the states near $\varepsilon_F$. We conclude from the geometry of the DB and the structure of the band spectrum that the $V_{\text{As}}$-related defect potential disrupts mainly the hybridization with the $d_{yz,xz}$ partial component of the $d$ states and note that this transfer integral should mainly contribute to the intraband scattering within the $h$-pocket of the Fermi surface (FS), which is formed mainly by the $d_{yz,xz}$ states.

The resulting Hamiltonian of this minimal model is

$$H = H_d + H_p + H_{dp} + H_{vd} = \sum_{k,\sigma} \varepsilon_{k,d} d_{k,\sigma}^\dagger d_{k,\sigma} + \sum_{k,\sigma} \varepsilon_{k,p} P_{k,\sigma} + \sum_{k,\sigma} \left( V_{dp}(k) d_{k,\sigma}^\dagger P_{k,\sigma} + \text{H.c.} \right) + W_1 \sum_{j,}\left( d_{j,\sigma}^\dagger P_{0,\sigma} + \text{H.c.} \right).$$

(1)

The first three terms describe the nearly filled $d_{x^2-y^2}$ band $\varepsilon_{k,d}$, the nearly empty $p_{x,y}$ band $\varepsilon_{k,p}$, and the hybridization between them, respectively. $H_{vd}$ is the $V_{\text{As}}$-induced hybridization between the Wannier $p$-state in the defect cell labeled as "0" and the $d$-band. An orbital splitting will be irrelevant in what follows and we do not account for it here. It results in a double degeneracy of each band. The defect potential is given by the $dp$-DB characterized by the coupling constant $W_{\beta\sigma} = \langle \beta \rvert W_1 \lvert \sigma \rangle$ (see Fig. 1).

The energy spectrum of defect related states is determined by the secular equation (see also Ref. 13)

$$1 - \sum_{\alpha} W_{\beta\alpha} G_{\alpha\alpha}^0(\omega) W_{\alpha\beta} G_{\beta\beta}^0(\omega) = 0,$$

(2)

The local Green’s functions (LGF) are defined as $G_{\alpha\alpha}^0(\omega) = \sum_{k} \langle \alpha(k) \rvert \omega - \varepsilon_{k,p} \rangle$ and $G_{\beta\beta}^0(\omega) = \sum_{k} \langle \beta(k) \rvert \omega - \varepsilon_{k,d} \rangle$. The $T$-matrix for the scattering in the $d$-band is $T_{kk'} = F_{\beta}(k) W_{\beta}(\omega) F_{\beta}(k') / 1 - W_{\beta}(\omega) G_{\beta\beta}^0(\omega)$, with the structure factor $F_{\beta}(k) = \langle kd|\beta \rangle$ and $W_{\beta} = \sum_{\alpha} W_{\beta\alpha} G_{\alpha\alpha}^0(\omega) W_{\alpha\beta}$.

From general properties of the LGF, we conclude that for repulsive vacancy potential $W_1 > 0$ the effective potential $U_{\beta}(\omega)$ is also positive for $\omega$ close to the top of the band $\varepsilon_{\alpha}$. Then we anticipate strong intraband scattering in the $h$-pocket of the FS due to the nearly 2D electronic structure. In this case the DOS at the top $\varepsilon_t$ of the $h$-band is constant $\nu_0$, and this step-like singularity results in the logarithmic divergence of the LGF.

$$\text{Re} G_{\beta\beta}^0(\omega \to \varepsilon_t) \propto \nu_0 \ln |\omega - \varepsilon_t|/D.$$

(3)

Here $D$ is an effective bandwidth (see e.g. Ref. 5). Such an edge-singularity of the LGF means that the resonance (the zero in the denominator of the $T$-matrix should appear near $\varepsilon_t$, even if the scattering potential is weak (Fig. 3 middle panel) so that in any case the impurity scattering in the $h$-pocket is close to the unitarity limit: the scattering phase $\delta(\varepsilon_F)$ is close to $\pi/2$. Thus, the DB induce a scattering in the $(xz, yz)$ channel, which generates mainly intraband scattering in the $h$-pocket.

Now we turn to the magnetic structure of a $[V_{\text{As}}, Fe_4]$ defect. The $V_{\text{As}}$ itself is not magnetically active, but involving its four Fe NN and possibly also four NNN in the complex defect shown in Fig. 1 changes the situation dramatically. Indeed, the necessary precondition for the formation of localized magnetic states in a system with itinerant electrons is the presence of a noticeable short-range spin-dependent interaction which may overcome the kinetic energy of the electrons. Fe ions bound with $V_{\text{As}}$ may be the source of such interactions due to the on-site Hubbard repulsion $U_0$ in their 3$d$ shells. To model this effect, one has to add the term $U n_{\beta\sigma}\bar{n}_{\beta\sigma}$ to the Hamiltonian (1). Here $U$ is the intrcell Coulomb repulsion integral for the "molecular orbital" $|\beta\rangle$ (see Fig. 1). We expect $U_b \lesssim U \lesssim U_0$ due to the slight delocalization of the 3$d$ wave functions because of $dp$-mixing and a reduced screening due to the missing $V_{\text{As}}$-bond, where $U_b$ denotes the Coulomb repulsion on bulk Fe-sites. Treating this interaction in a mean-field manner results in an additional spin-dependent term in the local scattering potential so that $W_{\beta} \to W_{\beta\sigma} = W_{\beta} + U n_{\beta\sigma}$.

One may expect that the broken $dp$-valence bonds in the presence of a short range Coulomb repulsion in the
As the spin susceptibility of the pristine La-1111 compound, χ/χ₀ explains the substantially enhanced paramagnetic susceptibility, one might expect that with respect to SC, the defect-related narrow peaks arise in the DOS near ε₁ (see also Ref. [13]). This means that two δ₁(ε₁) > δ₂(ε₁). Both phases δ₁ < π/2, which means that the magnetic scattering is strong and not too far from the unitarity limit.

Thus, we have found that the nominally nonmagnetic Vₐs defect can give rise to the appearance of localized moments formed by states in the h-pocket due to the quasi-2D character of the electronic band spectrum in ferropnictides. This explains the observed strong enhancement of the magnetic susceptibility χ(0) in an As-deficient La-1111 system, with an enhancement factor of χ/χ₀ = 1 ≈ cUₓP₁/(1 − Uₓ₁), where P₁ is the Pauli-spin susceptibility of the pristine La-1111 compound, c denotes the Vₐs concentration, and χ₁ = ⟨S₁, S₃⟩ is the local susceptibility at the defect site.

While the magnetic moment formation around Vₐs sites explains the substantially enhanced paramagnetic susceptibility, one might expect that with respect to SC, it opens up a Pandora’s box. Why is the magnetic moment formation in the h-pockets not detrimental for SC? The most straightforward explanation should be related to cases when a competing or coexisting commensurate stripe-like spin density wave (CS-SDW) phase or its short-range fluctuations are still present which detrimental effect on SC is well-known. Then, the strongly enhanced scattering of itinerant electrons from the h-pockets in their intraband channel found above, will help to suppress further its influence and enhance Tc. This effect becomes weaker in the strongly overdoped region where the SDW suppression by the doping itself is more and more pronounced. Obviously, also the appearance of relatively large magnetic defects with ferromagnetically ordered large local moments provides a strong perturbation for such a CS-SDW found in undoped clean samples. As a result at low Vₐs concentrations its transformation to an inhomogeneous magnetic state with discommensurations, or to a spin-glass type phase are expected. For them it is much easier to establish a coexistence of magnetism and SC. The next intriguing puzzle is then why is the formation of a magnetic moment in the h-pockets not detrimental for the SC as in usual s+SC? The possibility for a qualitatively new solution to this paradox relies on the observation that neither the standard theory of doped single-band SC, nor the available approaches to imperfect multiband SC can be used to address this issue in Fe-pnictide superconductors. Since the mechanism of SC in Fe-pnictides is not established as yet, we start with general remarks on the role of Vₐs related defects in our SC for which actually also the symmetry of the order parameter is under debate, which may in principle be different in different Fe-based materials and even depend on the doping type. To be definite, we will consider here only the most with a nodeless order parameter Δₕ having opposite signs for the h- and the d-pockets. In accordance with the theory of s± multiband SC in pnictides the pairing is mainly given by the anomalous vertices shown in Fig. 4 containing the T-matrix (see the text for a more detailed explanation).

![FIG. 3: Upper: DOS near ε₁. Middle: Graphical solution of Eq. U⁺₁⁺(ω) = ReG₀(ω) for spin ↑ (solid line) and spin ↓ (dashed line). Lower: Frequency dependent phase shifts δ₁(ω) and δ₂(ω) (solid and dashed curves, respectively). The energies ω₁ mark the positions of resonances δ₁ = π/2.](image)

![FIG. 4: Diagrammatic representation for the anomalous vertex Γ (a), the susceptibility χ₋₋ responsible for the SDW fluctuations (b) and defect related corrections to χ₋₋ (c). Dashed and solid lines correspond to the el- and h-propagators, respectively. circle stands for the the anomalous Coulomb vertices t₀₃ (in notations of Ref. [23]). Shaded circle stands for the T-matrix (see the text for a more detailed explanation).](image)
of attractive interactions within $el$- and $h$-pockets of the BZ. This means that the main contribution of the magnetic scattering to the $h$-propagator comes in via $\chi_{sdw}$ (Fig. 4c), represented by the intraband $T$-matrix $T_{pp}$. It is seen from this diagram that we deal with magnetic scattering without spin flips, which creates narrow local resonance levels below and above $\varepsilon_p$ in the $h$-pockets and modifies the $h$-propagators in the bubble $\chi_{sdw}(q, \omega)$.

Significantly SDW-affected Cooper pairing may be realized due to the almost singular behavior of $\chi_{sdw}(Q, \omega) \propto \nu_0 \ln[D/\max(\omega, \epsilon, \gamma)]$, where $D$ is the energy interval where the nesting conditions are approximately satisfied, $\epsilon$ and $\gamma$ are parameters characterizing the imperfection of nesting (including modifications of the magnetic response due to the presence of the $V_{As}$) and the electron damping due to imperfection of a real crystal. The contribution of $V_{As}$ defects to $\epsilon$ are $\propto \Re T(\omega)$. Besides, As vacancies can act as dopants. The net result of changed $\epsilon$ is not known a priori: based on the interplay between these physical effects the nesting conditions may either slightly improve or worsen, or just remain unaltered. The damping $\gamma \lesssim c |\varepsilon_p - \omega_p|$ is efficient only provided $\gamma > \epsilon$. The main point is that either of these mechanisms cannot radically reduce the SC $T_c$. Besides, magnetic resonances give their own contribution $\delta \chi_{sdw}(q, \omega)$ not related to the nesting. Transitions from the local states in the $h$-pocket to the empty states in the $el$-pocket result in $\delta \chi_{sdw}(q, \omega) \propto c \nu_0 \ln[D/(\omega_p - \omega_p)]$. This contribution favors $s_{+}\text{-pairing}$. To summarize, from an analysis of the consequences of $V_{As}$ defects and their magnetic moment formation on the SC Fe-pnictides, it follows that their presence can even be more constructive than detrimental for $s_{+}$ SC that is mediated by SDW fluctuations. In this context it is interesting to note the related conclusions on the role of intraband magnetic scattering. The arguments given above are also in the spirit of the “Swiss cheese” model, which presumes that the defect related bound states contribute to the subgap DOS and do not suppress $T_c$ completely.

The spin susceptibility $\chi_{\omega}(\omega)$, is responsible also for the $1/T_1$ NMR spin-lattice relaxation rate, which changes from a nearly power-law dependence $\sim T^3$ in As stoichiometric samples to more steep and close to an exponential one in As-deficient samples. The analysis above suggests that these changes relate to the interplay between the mid-gap states stemming from non-magnetic scattering induced by $P$ doping and those inserted by magnetic defects $V_{As}$ (cf. Ref. 22). The interplay of magnetic vortices with both kinds of impurities, will affect the $1/T_1$ rate. A detailed analysis will be published elsewhere.

We have shown, in conclusion, that As-vacancies form highly nontrivial defects in 1111 Fe-pnictide superconductors which strongly modify their physical properties in both the normal and the SC states. Being nominally non-magnetic in nature, they are nevertheless responsible for the formation of relatively large local magnetic moments on the Fe-sites surrounding the vacancies, which give rise to enhanced spin susceptibility in the normal state and Pauli-limiting behavior in the SC state. The behavior at low fields is unusual too, due to scattering properties remarkably different from those of usual magnetic impurities in standard single band and dirty multiband $s_{+}$ SC. Controlling these defects can be helpful to improve the understanding of real $s_{+}$ systems, the electronic structure, and correlation effects in the pnictides, in general. In particular, for 122-pnictides with As vacancies and Fe-chalcogenides one expects a similar but somewhat weaker scattering effect due to the larger electronic dispersion perpendicular to the FeAs planes. An analysis on various types of point-defects will also be of considerable interest, since our results imply that they may strongly affect the physical properties of real pnictide materials even at small defect concentrations.

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1 D.C. Johnston, Adv. Phys. 59, 803 (2010).
2 J. Paglione et al., Nature Physics 6, 645 (2010).
3 O.K. Andersen and L. Boeri, Annalen der Physik 258, 8 (2011).
4 G. Fuchs, et al, Phys. Rev. Lett. 101 237003 (2008); G. Fuchs, et al, New J. Phys. 11 075007 (2009).
5 V. Grinenko et al., Phys. Rev. B 84, 134516 (2011).
6 F. Hammerath, et al., Phys. Rev. B 81 140504(R) (2010).
7 P.W. Anderson, Phys. Rev. 124, 41 (1961).
8 P.A. Wolff, Phys. Rev. 124, 1030 (1961).
9 D.J. Mills and P. Lederer, Phys. Rev. 160, 590 (1967).
10 G.A. Sawatzky, et al., Europhys. Lett. 86, 17006 (2009)
11 H. Eschrig and K. Koepernik, Phys. Rev. B 80, 104503 (2009).
12 Y. Yanagi, et al, Phys. Rev. B 81, 054518 (2010).
13 See EPAPS Document No. [] for more information on EPAPS, see [http://www.aip.org/pubservs/epaps.html](http://www.aip.org/pubservs/epaps.html)
14 E.N. Economou, Green’s Functions in Quantum Physics, 3rd Edition (Springer, 2006).
15 In the two-orbital model the exchange $J$ should also taken into account. However, since $U > J$, it is enough to consider the Coulomb intraband scattering in order to detect a magnetic solution. The interband exchange gives only small corrections to this result.
16 M.G. Vavilov and A.V. Chubukov, Phys. Rev. B, 84, 214521 (2001).
17 M.V. Sadovskii, Diagrammatics (World Sci, 2006), Ch. 5
18 V. Grinenko et al., arXiv:1203.1585, attributed to few % excess Fe in KFe$_2$As$_2$.
19 G. Preosti and P. Muzikar, Phys. Rev. B 54, 3489 (1996).
20 D. Parker, et al., ibid. 78, 134524 (2008).
21 T.K. Ng and Y. Avishai, ibid. 80, 104504 (2009).
22 D. Zhang, Phys.Rev. Lett. 103, 186402 (2009).
In our minimal model the doping effect is compensated by the levels split off the top of hole band, but the third orbital \( p_z \) may become the source of \( cl \)-doping and/or even contribute to the large local moment of 3.2 \( \mu_B \) per \( V_{\text{As}} \) according to Ref. 5.

The Green’s functions for the band Hamiltonian form the matrix \( G(\omega) \):

\[
G(\omega) = \begin{pmatrix} G_{dd}(\omega) & 0 \\ 0 & G_{pp}(\omega) \end{pmatrix}
\]

(here the spin index is temporarily omitted). The perturbation \( \sim W_1 \) is nonzero in a limited space around an As-vacancy. The states within this cluster are described in a local basis \( (\alpha, \beta) \) formed by projecting the states \( (p, d) \) onto the perturbed region. Then the perturbation is described by the matrix \( W \),

\[
W = \begin{pmatrix} 0 & W_{\beta \alpha} \\ W_{\alpha \beta} & 0 \end{pmatrix}
\]

so that only the \( dp \) bonds are broken in the defect cluster.

The local basis obeys the point symmetry of the 2D lattice. In the simplest tight-binding approximation the states \( |\alpha\rangle \) are the orbital states \( p_x, p_y \) centered at the As-vacancy site “0”. Then the states \( |\beta\rangle \) are the “molecular” orbitals
formed by \( d_{xz,xy} \) orbitals centered at the sites 1,2,3,4 surrounding the As-vacancy site “0” and transforming along the same irreducible representation of the point group as the states \(|\alpha\rangle\), namely the combinations

\[
|\beta\rangle = |d_1\rangle - |d_2\rangle + |d_3\rangle - |d_4\rangle,
\]

where the Fe-sites in the first coordination sphere around the vacancy are enumerated as 1,2,3,4. Next we construct the secular matrix \( Q(\omega) = 1 - WG(\omega) \) and project this matrix on the local basis \( \{\alpha, \beta\} \), \( Q \rightarrow \tilde{Q} \).

\[
\tilde{Q}(\omega) = \begin{pmatrix}
1 & -W_{\alpha\beta}G^0_{\beta}\omega \\
-W_{\beta\alpha}G^0_{\alpha\omega} & 1
\end{pmatrix}.
\]  

(S4)

We derive from (S4) the secular equation \( \det \tilde{Q}(\omega) = 0 \). Since we are interested in the scattering in the band \( \beta \) related to the \( d \)-states, we project this secular equation on the subset \( \langle \beta | \ldots | \beta \rangle \).

\[
1 - \sum_{\alpha} W_{\beta\alpha}G^0_{\alpha\omega}(\omega)W_{\alpha\beta}G^0_{\beta\omega}(\omega) = 0.
\]  

(S5)

\( W_{\beta\alpha} = \langle \beta | W_1 | \alpha \rangle \). Comparing Eq. (S5) with a Slater-Koster-like equation \( 1 - WG^0 = 0 \) for a single band defect characterized by the local potential \( W \) we note that in our problem this potential is substituted for the non-local potential \( W_{\beta} \):

\[
1 - W_{\beta}(\omega)G_{\beta\beta}(\omega) = 0
\]  

(S6)

\[
W_{\beta}(\omega) = \sum_{\alpha} W_{\beta\alpha}G^0_{\alpha\omega}(\omega)W_{\alpha\beta}.
\]

The solution of Eq. (S6) provides us with the information about the scattering phase \( \delta_{\beta}(\omega) \)

\[
\tan \delta_{\beta}(\omega) = -\frac{\text{Im det} \tilde{Q}(\omega)}{\text{Re det} \tilde{Q}(\omega)}.
\]  

(S7)

which characterizes the strength of the defect potential at the Fermi level \( \omega = \varepsilon_F \). The \( T \)-matrix for the scattering in the \( d \)-band is

\[
T_{kk'} = \frac{F_{\beta}(k)W_{\beta}(\omega)F_{\beta}(k')}{1 - W_{\beta}(\omega)G_{\beta\beta}(\omega)}.
\]  

(S8)

with the structure factor \( F_{\beta}(k) = \langle k d | \beta \rangle \). Due to the predominantly \( d \)-character of the hole band, it is convenient to treat the problem in the square lattice with a folded Brillouin zone (see Fig. 1 in the main text). Then the structure factor is \( F_{\beta}(k) \approx 2(\cos k_x/2 - \cos k_y/2) \).

Next we estimate the contribution of the dangling bonds in the band \( \varepsilon_{kp} \) neglected in the above calculations. This contribution would result in a modification of the local Green’s function \( G^0_{\alpha\beta}(\omega) \) in the effective potential (S6). Instead of the form \( \langle \alpha | G_{kk'} | \alpha \rangle \) used in the right hand side of Eq. (S4), one should project the Green’s function on the subset \( \langle \beta | \ldots | \beta \rangle \) with the Slater-Koster defect in this band, namely, change

\[
\langle \alpha | G_{kk'} | \alpha \rangle \rightarrow \langle \alpha | G_{kk'} \left( 1 + \frac{W_2G_{kk}}{1 - W_2G^0_{\alpha\alpha}} \right) | \alpha \rangle
\]  

(S9)

(see Fig. 1 in the main text for the definition of \( W_2 \)).

The first term in the right hand side of Eq. (S9) is the Green’s function projected onto the local \( p \)-orbitals \(|\alpha\rangle\). Corrections due to the contribution of dangling bond states in the \( p \)-band would be important only for those energies where \( 1 - W_2G^0_{\alpha\alpha}(\omega) \sim 0 \). However, it is seen from Eqs. (S8) and (S9) and from the shape of the DOS in Fig. 2 that the function \( G^0_{\alpha\alpha}(\omega) \) is smooth in the region of overlap with the partial \( d \) component of the DOS, and the singularities in the Green’s function reflecting the 2D van Hove singularities in the DOS are located around the top of the \( p \) band in the region of unoccupied states. In other words, \( W_2G^0_{\alpha\alpha}(\omega) \ll 1 \) around the Fermi level, and the \( p \) wave in Eq. (S9) is represented by the unperturbed orbital \(|\alpha\rangle\).

**Search for magnetic solutions**

In order to find a magnetic solution, the Coulomb interaction is included in the scattering potential, \( W_{\beta} \rightarrow W_{\beta\sigma} = W_{\beta} + \tilde{n}_{\beta\sigma} \). The average \( \tilde{n}_{\beta\sigma} \) is given by

\[
\tilde{n}_{\beta\sigma} = \frac{1}{4\pi N} \sum_{k_1,k_2} \text{Im} \int_{-\varepsilon_F}^{\varepsilon_F} F_{\beta}(k_1)F_{\beta}(k_2)G_{k_1,k_2,d\sigma}(\omega)d\omega = \frac{1}{4\pi} \int_{-\varepsilon_F}^{\varepsilon_F} G_{\beta\sigma}(\omega)d\omega.
\]  

(S10)
Its defect related part reads\textsuperscript{S1}

\[
n_{\beta\sigma}' = \frac{1}{i\pi u_{\beta\sigma}} \int_{\varepsilon_F}^{\varepsilon_F} \text{Im} \left[ \frac{1}{1 - W_{\beta\sigma} G_{\beta\sigma}(\omega)} \right] d\omega. \tag{S11}
\]

It is known\textsuperscript{S1 \textbf{\textit{\&}} S2}, that a magnetic solution \(n_{\beta\uparrow} \neq n_{\beta\downarrow}\) exists provided the repulsive potential exceeds some critical value, \(W_{\beta c} > 1/J_c\) given by

\[
J_c = \frac{1}{i\pi} \int_{\varepsilon_F}^{\varepsilon_F} \text{Im} \left\{ \frac{|-G_{\beta\beta}^0(\omega)|^2}{[1 - W_{\beta c} G_{\beta\beta}^0(\omega)]^2} \right\} d\omega. \tag{S12}
\]

Such a magnetic solution is expected to be realized due to the logarithmic singularity of \(G_{\beta\beta}^0(\omega)\) in the very vicinity of \(\varepsilon_F\), shown in Eq. (5) in the main text. Due to this singularity in the denominator of the integrand in the r.h.s. of Eq. (S12) the factor \(J_c\) is strongly enhanced. This enhancement favors magnetic solutions.

The electron-band may be easily included in this calculation scheme, and the corresponding secular matrix may be constructed in the same way as it was done above for the hole-band. In order to describe the states in the electron pockets (as well as the interband scattering), one should add at least one more orbital, namely the \(d_{xy}\) one, to this minimal model\textsuperscript{S3 \textbf{\textit{\&}} S4 \textbf{\textit{\&}} S5}. However, the real part of the local Green’s function \(G^0(\omega) < 0\) near the bottom of the conduction band is negative\textsuperscript{S6}, so the intraband scattering in the electron pocket is expected to be weak. Thus, we conclude that a \(V_{\text{As}}\) defect influences mainly the states in the hole pocket, leaving the electron pockets practically the same as in perfect samples.

**Few remarks on As-vacancies and spin-density wave states**

Finally, we would like to mention an additional challenging problem closely related to that of As-vacancies in a paramagnetic enviroment considered above: namely, the perturbational effect of As-vacancies on a surrounding spin density wave (SDW) to be investigated in more detail elsewhere. From a general point of view it is however already clear that sizable effects of common interest can be expected. Indeed, since the competing spin-stripe SDW phase may be schematically represented by a frustrated 2D \(J_1-J_2\) or closely related spin model Hamiltonians with an essential antiferromagnetic next nearest neighbor exchange coupling \(J_2\) microscopically mediated by the superexchange involving the As-4p states, the presence of an As-vacancy will locally eliminate this antiferromagnetic coupling \(J_2\) even in the case of a nonmagnetic bound or resonance state discussed above. Moreover, in case that the SDW (or its by doping weakened corresponding SDW-magnetic state) will not prevent the ferromagnetic polarization effect for the four surrounding Fe sites, the presence of such a local ferromagnetic ”mini”-cluster as an extended magnetic defect will obviously cause an additional weakening or destruction of the SDW or its fluctuations probably present even in the ”non-magnetic” superconducting state mentioned above. This effect might explain the observed slight \(T_c\)-enhancement of about 2 to 3 K after creating As-vacancies within an optimal doped system (see Ref. 4 of the main text). Within a broader context magnetic defects under control and As-vacancies in particular should provide a new tool to probe various SDW states and this way give more insight into the complex interplay of various competing ground states of Fe pnictides in general.

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\textsuperscript{S1} D.J. Mills and P. Lederer, Phys. Rev. \textbf{160}, 590 (1967).
\textsuperscript{S2} P.A. Wolff, Phys. Rev. \textbf{124}, 1030 (1961).
\textsuperscript{S3} Y. Yanagi, \textit{et al}, Phys. Rev. B \textbf{81}, 054518 (2010).
\textsuperscript{S4} S. Graser, \textit{et al.}, New J. Phys. \textbf{11}, 025016 (2009).
\textsuperscript{S5} T.A. Maier, \textit{et al}, Phys. Rev. B \textbf{79}, 224510 (2009).
\textsuperscript{S6} E.N. Economou, \textit{Green’s Functions in Quantum Physics}, 3-rd Edition (Springer, 2006).