Pressure-induced magnetic transition and volume collapse in FeAs superconductors: an orbital-selective Mott scenario

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Abstract. Motivated by pressure experiments on CaFe\textsubscript{2}As\textsubscript{2}, we propose a scenario based on local-moment physics to explain the simultaneous disappearance of magnetism, reduction of the unit cell volume, and decrease in resistivity. In this scenario, the low-pressure magnetic phase derives from Fe moments, which become screened in the paramagnetic high-pressure phase. The quantum phase transition can be described as an orbital-selective Mott transition, which is rendered first order by coupling to the lattice, in analogy to a Kondo volume collapse. Spin-fluctuation driven superconductivity competes with antiferromagnetism and may be stabilized at low temperatures in the high-pressure phase. The ideas are illustrated by a suitable mean-field analysis of an Anderson lattice model.
1. Introduction

The discovery of superconductivity in the iron pnictides [1]–[3], with the maximum reported transition temperature over 50 K [4], has spurred intense activities in both experiment and theory. While the initial research has mainly concentrated on compounds with $P4/nmm$ structure, e.g. LaFeAsO$_{1-x}$F$_x$, superconductivity was later also found in oxygen-free materials with $I4/mmm$ structure [5], with examples being CaFe$_2$As$_2$ and BaFe$_2$As$_2$. According to their chemical composition, the two groups have been dubbed 1111 and 122 compounds, respectively. In both cases, the structure consists of FeAs layers, which are believed to be responsible for the low-energy electronic properties.

The temperature-doping phase diagram of LaFeAsO$_{1-x}$F$_x$ has been mapped out in some detail [6]. At $x = 0$ the material undergoes a structural transition into an orthorhombic phase upon cooling, closely followed by a magnetic transition. Neutron diffraction shows that the order is of layered antiferromagnetic type, with an in-plane ordering wavevector $(\pi, 0)$ [7]. With increasing $x$, magnetism disappears abruptly at $x \approx 4.5\%$ and gives way to superconductivity, with $T_c$ having little doping dependence up to $x = 0.2$.

This phase diagram suggests interesting similarities to the high-$T_c$ cuprates, where a doping-driven transition from an antiferromagnet (AFM) to a superconductor (SC) is found as well. However, a number of differences between the FeAs compounds and the cuprates are apparent. (i) The ‘undoped’ FeAs materials are not Mott (or charge-transfer) insulators, but may be characterized as bad metals. (ii) The FeAs magnetism is not fully consistent with a local-moment picture, as the size of the ordered moment is unexpectedly small, in the range of $0.25\mu_B$ [8] to $0.36\mu_B$ [7], whereas a local moment on Fe is expected to have at least $2\mu_B$. Although magnetic frustration has been identified as a relevant ingredient [9], this alone is not enough to explain the experimental data. (iii) In the doping regime, where superconductivity occurs at low temperatures in the FeAs materials, the signatures of magnetism appear to be weak, although the magnetic susceptibility is larger than in a conventional metal [10], and a magnetic ‘resonance’ mode has been reported below $T_c$ in Ba(Fe, Co)$_2$As$_2$ [11].

From first-principles calculations [12], the most important bands in the iron arsenides are of Fe 3d character, with sizeable admixtures of As p states. Importantly, all Fe 3d orbitals appear to contribute to the low-energy properties. In contrast, in the cuprates only the Cu 3d$_{x^2-y^2}$
orbital (together with O 2p_{x,y}) contributes. Thus, orbital degeneracy and strong hybridization likely play an important role in the iron arsenides. (It should be noted that the reported results of first-principles calculations are partially contradictory, in particular regarding the magnetic properties, see [13].)

Pressure experiments on CaFe\textsubscript{2}As\textsubscript{2} have provided interesting additional information [14]–[19]. Starting from the undoped magnetically ordered compound in the orthorhombic phase, the application of hydrostatic pressure induces a first-order transition at around 0.4 GPa into a (compressed) tetragonal phase, where magnetism disappears. Remarkably, there is also a pressure-driven structural transition at elevated temperatures, from the ambient-pressure tetragonal phase into the compressed high-pressure tetragonal phase. This transition is accompanied by a drop in the resistivity, i.e. the high-pressure phase appears to be a better conductor [15]. Band-structure calculations suggest that the disappearance of magnetism is intimately connected to the pressure-induced volume collapse [14, 16, 20]. The high-pressure phase was reported to be superconducting [14, 15] with a \( T_c \) of about 12 K over a significant range of pressures, however, subsequent experiments [17, 19] with optimized hydrostatic pressure conditions did not detect superconductivity down to 4.2 K, suggesting that the earlier reports were related to strain-induced superconductivity. Nevertheless, all measurements agree on the volume collapse and the concomitant loss of magnetism and drop of resistivity. In addition, superconductivity under high pressures has also been reported [21] in SrFe\textsubscript{2}As\textsubscript{2} and BaFe\textsubscript{2}As\textsubscript{2}.

The purpose of this paper is to propose a phenomenological local-moment-based scenario for the physics of the FeAs compounds, with the primary goal of explaining the pressure experiments on CaFe\textsubscript{2}As\textsubscript{2} [14]–[16], [19]. Our scenario is based on the assumption that bands with more itinerant electrons co-exist and interact with more localized (i.e. moderately to strongly correlated) ones, which renders the problem similar to Kondo or Anderson models for heavy-fermion metals. (We note that related ideas on localized and itinerant electrons in iron arsenides have been put forward in a few recent theory papers [22]–[25] which appeared while this work was being completed.) Our analysis will draw analogies to recent developments in heavy-fermion physics, particular, we shall associate the pressure-induced transition in CaFe\textsubscript{2}As\textsubscript{2} with a variant of the Kondo volume-collapse transition, driven by a large increase of the hybridization between the itinerant and localized electron bands, which in turn quenches the magnetism.

The remainder of the paper is organized as follows. In section 2, we sketch our general ideas and point out similarities and differences between the iron arsenides and classical heavy-fermion materials. We then illustrate the proposal by a simple mean-field calculation in section 3, which we believe captures important parts of the relevant physics of the CaFe\textsubscript{2}As\textsubscript{2} pressure experiments. A discussion of implications will wrap up the paper.

2. Local moments in a correlated Anderson lattice

Our proposal is based on the assertion that electronic correlations in the iron arsenides are sizeable [9, 22, 26, 27]. Then, the magnetism is not purely of weak-coupling type, but instead local-moment physics is relevant\(^4\). This view appears consistent with the results of neutron

\(^4\) Itinerant and local-moment antiferromagnetism are not necessarily distinct, but can be adiabatically connected as, e.g. in the insulating phase of a single-band Hubbard model, see [28].
scattering experiments, which find spin-wave excitations in the antiferromagnetic ground state of CaFe$_2$As$_2$, that are well described by an anisotropic 3d Heisenberg model, at least for long wavelengths [29].

To explain the fact that the antiferromagnetic phase of FeAs compounds is neither an insulator nor a good metal, we invoke the existence of (at least) two types of electrons, one more localized and one more itinerant species. In the spirit of a Kondo or Anderson lattice model, we shall adopt here the language of ‘local-moment’ and ‘conduction’ electrons. In the antiferromagnetic phase, the local-moment electrons carry the magnetism, and the residual interaction between local-moment and itinerant electrons provides sizeable scattering, leading to both bad-metal behavior and reduced moment amplitudes [28]$^5$. In the paramagnetic phase, the local-moment electrons are strongly hybridized with the conduction electrons (i.e. the moments are Kondo-screened), leading to good metallic behavior. Provided that spin fluctuations are still sizeable, spin-fluctuation-mediated superconductivity can arise at low temperatures.

How does this phenomenological picture tie in with microscopic considerations? The most plausible scenario is that both types of electrons are primarily of Fe 3d character, with strong admixtures of As 2p. As detailed in [22], the interplay of p–d hybridization, spin–orbit coupling and crystal-field splitting can lead to the two highest occupied FeAs levels being filled with one electron, but with different correlation strengths. The electrons in the lower level are more localized, providing a natural basis for our phenomenological approach$^6$.

Assuming the applicability of an Anderson lattice picture, let us further develop our ideas, concentrating on the transition between the antiferromagnetic and paramagnetic phases. In fact, many qualitative results can be borrowed from recent theoretical work on heavy-fermion materials. There, the zero-temperature transition between a paramagnetic heavy Fermi liquid (FL) and an antiferromagnetic metal can be a standard spin-density-wave transition of a FL, described by a Landau–Ginzburg–Wilson theory of Hertz–Millis type, or involve the breakdown of Kondo screening [31]. For the latter scenario, a number of theoretical descriptions have been put forward [32]–[36]. Within the Kondo-breakdown scenario of Senthil $et$ $al$ [35], the coupling to lattice degrees of freedom has been investigated recently [37]. If the electron–lattice coupling is sufficiently strong, then the Kondo-breakdown transition is rendered first order and accompanied by an isostructural volume change, which is a zero-temperature variant [38] of the classical Kondo volume-collapse transition [40]–[43]. This first-order transition extends to finite temperatures and masks an otherwise existing magnetic quantum critical point. (A first-order transition removes the sharp distinction between the Kondo-breakdown and spin-density-wave transition scenarios.)

In a situation with intermediate correlations, where valence fluctuations are not fully quenched, it is useful to think about the Kondo-breakdown transition as an orbital-selective Mott transition [36]: In the non-magnetic FL phase, the local-moment electrons become itinerant and strongly hybridized with the conduction electrons, whereas they undergo Mott localization in the magnetic phase. In fact, such orbital-selective Mott transition have been studied extensively in two-band Hubbard models [44]. Based on the cited works, we propose that the pressure-driven transition in CaFe$_2$As$_2$ can be described as orbital-selective Mott transition, which becomes strongly first order due to electron–lattice coupling. The low-pressure phase displays partial

$^5$ In heavy-fermion metals, itinerant and local-moment antiferromagnetism are not qualitatively distinct phases, see [30].

$^6$ For our phenomenological model, the precise orbital character of itinerant and localized electrons is of little relevance.
Mott localization, leading to local-moment magnetism, whereas in the high-pressure phase strong hybridization quenches the moments and leads to a conventional paramagnetic FL. The pressure-driven isostructural lattice transition at elevated temperatures is then the analogue of a Kondo volume collapse.

It is important to point out that our scenario is not in contradiction with itinerant spin-density-wave descriptions of magnetism in the FeAs compounds. In the Kondo-lattice context, itinerant and local-moment magnetism can be adiabatically connected (apart from transitions involving changes of the Fermi surface (FS) topology) (see footnote 5). Therefore, a system at intermediate coupling can in principle be described using both itinerant and localized electron concepts. Here, we find it advantageous to employ a strong-coupling language in order to highlight the nature of the volume collapse transition. Independent of the language, the driving force of the volume collapse is the energy gain due to an increasing in the effective hybridization between the bands.

Let us note that there are a few important differences between our envisioned scenario for the FeAs materials and the phenomenology of heavy-fermions compounds. (i) The local-moment electrons in the iron arsenides are probably far from the Kondo limit. Then valence fluctuations are sizeable, and the picture of Kondo screening does not literally apply. The coherence temperature on the high-pressure side of the transition is not small, and the quasiparticles are not very heavy, in contrast to that of typical heavy fermions. (ii) The character of the \((\pi, 0)\) magnetic order is important to understand the details of the phase diagram.

The magnetism deserves a few further comments: in order to explain the magnetic order at wavevector \((\pi, 0)\), both local-moment and itinerant scenarios have been invoked (which are not mutually exclusive (see footnotes 4 and 5)). In a local-moment picture, the exchange interactions \(J_1\) and \(J_2\) on the square lattice of Fe atoms (between nearest and next-nearest neighbors, respectively) have been deduced to be both antiferromagnetic with \(J_1 \lesssim J_2\) [9, 12]. In this regime, the \(J_1-J_2\) square-lattice Heisenberg antiferromagnet (AFM) is known to have a ‘layered’ antiferromagnetic ground state with \((\pi, 0)\) order [45, 46]. In contrast, in an itinerant picture the \((\pi, 0)\) order arises from nearly nested Fermi surface pieces. Independent of whether the magnetism is better described in an itinerant or localized picture, magnetic ordering at \((\pi, 0)\) in an originally tetragonal environment breaks the 90° lattice rotation symmetry. This induces an orthorhombic distortion inside the antiferromagnetic phase. However, the lattice rotation symmetry may also be broken at a higher temperature than the spin symmetry, in which case the orthorhombic distortion occurs before the magnetic order [47, 48]. This is indeed what happens experimentally, i.e. magnetic fluctuations are likely the driving force of the structural phase transition.

Last not least, we discuss the possible emergence of superconductivity. For the Kondo-breakdown scenario, magnetically mediated pairing has been argued to be a generic instability of the FL [34], with the maximum \(T_c\) near the continuous Kondo-breakdown transition. In the present situation of intermediate correlations, the absolute value of \(T_c\) will depend strongly on microscopic details, e.g. of the band structure. Moreover, if the lattice coupling renders the transition strongly first order, the system will effectively ‘jump’ over the parameter region with large \(T_c\). Thus, while both pressure-induced volume collapse and loss of magnetism are integral and robust parts of the proposed scenario, superconductivity with a sizeable \(T_c\) is more fragile.
3. Mean-field theory

We now illustrate the ideas described in the last section by a simple model calculation. We shall refrain from using a realistic band structure with five or more bands, but instead employ a two-band Anderson lattice model which is sufficient to capture most of the qualitative physics.

3.1. Anderson–Heisenberg lattice model

The starting point of our analysis is an Anderson lattice model, describing delocalized conduction (c) electrons on a lattice which hybridize with correlated and more localized f electrons on the same lattice. (Despite the labels c and f, both bands may have primarily Fe 3d character.) To simplify the approximate treatment of magnetism, we supplement our model by an explicit Heisenberg exchange interaction between the local moments. The resulting Hamiltonian reads

\[
\mathcal{H} = \sum_{k\sigma} \varepsilon_k c^\dagger_k c_k + \sum_{i\sigma} \varepsilon_f f^\dagger_i f_i + U \sum_i n^c_i n^f_i + \frac{1}{\sqrt{N}} \sum_{k\sigma} (V_k e^{-ikR} c^\dagger_k f_i + H.c.) + \sum_{ij} J_H(i, j) \mathbf{S}_i \cdot \mathbf{S}_j
\]

in standard notation. The first term describes conduction electrons with band filling \( n_c \), \( \varepsilon_f^0 \) (U) is the bare f electron energy (Coulomb repulsion), \( V_k \) the hybridization matrix element, and \( N \) the number of unit cells. \( \mathbf{S}_i = f^\dagger_i \mathbf{\sigma} f_i / 2 \) is the operator for the spin moment of the f electrons on site \( i \). Although the system is three-dimensional, we shall neglect the electronic coupling between the layers for simplicity, hence the model (1) will be treated on a 2d square lattice. Further we shall assume \( V_k \equiv V^0 \), and take the Heisenberg interaction \( J_H(i, j) \) to be nonzero for nearest and next-nearest neighbors, with values \( J^0_1 < J^0_2 \). Note that the Kondo limit will not be taken.

3.2. Lattice distortions and electron–lattice coupling

Elastic energy changes of the lattice under application of hydrostatic pressure depend on the lattice distortion. For tetragonal lattice symmetry, the most general form of the elastic contribution to the free enthalpy is [39]

\[
G_{\text{lat}}(\epsilon_x, \epsilon_y, \epsilon_z) = \frac{1}{2} v_0 c_{33} \epsilon_z^2 + \frac{1}{2} v_0 c_{11} (\epsilon_x^2 + \epsilon_y^2) + c_{12} \epsilon_x \epsilon_y + v_0 c_{13} \epsilon_z (\epsilon_x + \epsilon_y) + p v_0 (\epsilon_x + \epsilon_y + \epsilon_z).
\]

Here, the dimensionless \( \epsilon_{x,y,z} \) are the diagonal entries of the strain tensor, i.e. the relative changes of the lattice parameters of the tetragonal unit cell. The elastic constants \( c_{ij}, c_{ij} \), and the reference volume \( v_0 \) depend on the material at hand. Below, we shall choose values for the \( c_{ij} \), \( c_{ij} \) such that the experimentally observed lattice distortions of CaFe\(_2\)As\(_2\) [14] are approximately reproduced. Importantly, the largest pressure-induced change is the collapse of \( \epsilon_z \), whereas \( \epsilon_{x,y} \) even increase slightly at the collapse.

We now construct a model for the electron–lattice coupling, combining the results from different approaches with simple theoretical arguments. We start with the strain dependence of the magnetic couplings \( J_1 \) and \( J_2 \) that are responsible for the ambient-pressure magnetism, and will also be relevant for spin-fluctuation-mediated superconductivity. In experiment, antiferromagnetic ordering at wavevector \((\pi, 0)\) is energetically stabilized by an orthorhombic
distortion with $\epsilon_x > \epsilon_y$. Additional evidence is the strong dependence of $J_1$ and $J_2$ on the strain $\epsilon_z$, as shown in band structure calculations [49]. In addition, it has been shown [53] that changes in the Fe–As bond angle stabilize antiferromagnetic ordering at wavevector $(\pi, 0)$, providing an additional hint towards the importance of coupling all strain directions to the exchange couplings. We therefore parameterize

$$
\begin{align*}
J_{1x} &= J_1^0 (1 + \gamma_{1x}^\perp \epsilon_x + \gamma_{1z}^\perp \epsilon_z), \\
J_{1y} &= J_1^0 (1 + \gamma_{1y}^\perp \epsilon_y + \gamma_{1z}^\perp \epsilon_z), \\
J_{2} &= J_2^0 \left[ 1 + \gamma_{2x}^\perp (\epsilon_x + \epsilon_y) + \gamma_{2z}^\perp \epsilon_z \right].
\end{align*}
$$

(3)

From neutron scattering data and local density approximation (LDA) calculations for the orthorhombic phase of CaFe$_2$As$_2$ [29] a rough estimate of $\gamma_{1}^\perp$ can be obtained. For $S = 1/2$, we plug the LDA values $J_{1x} = 82$ meV and $J_{1y} = 20$ meV from [29] into the parameterization of equation (3) and set $\epsilon_x - \epsilon_y = 0.01$, as observed in the orthorhombic phase of CaFe$_2$As$_2$ [14]. This calculation yields the estimate $\gamma_{1x}^\perp \approx 70$. The size and sign of $\gamma_{1}^\perp$ might well account for the observed orthorhombic distortion and the $(\pi, 0)$ ordering vector, as argued in [12].

From band-structure calculations for LiFeAs [49] it is suggested that $\gamma_{1x}^\perp$ and $\gamma_{2x}^\perp$ are numbers of $O(10)$, whereas their signs turn out to depend on pressure. To account for the vanishing superconductivity at high pressures, we chose their sign to be positive, since $\gamma_{1}^\perp$ and $\gamma_{2}^\perp$ dominate the changes in $J_1$ and $J_2$ at high pressures [7]. Finally, $\gamma_{2}^\perp$ is of subleading influence within our calculation as long as it is of $O(10)$ or smaller, which is suggested by the order of magnitude of $\gamma_{1}^\perp$ and $\gamma_{2}^\perp$.

A crucial ingredient for our model is the strain dependence of the hybridization, which we assume to be the dominant mechanism to drive the volume collapse, as observed in the Kondo volume collapse in Cerium and other materials. In general, the mechanism for the Kondo volume collapse transition is a gain in hybridization energy via a structural distortion. A plausible parameterization is

$$
V = V_0^0 \left[ 1 + \gamma^\perp_z (\epsilon_x + \epsilon_y) + \gamma^\perp_z \epsilon_z \right].
$$

(4)

As our model is to be understood as an effective model, $V$ is related to actual band structure parameters in a likely complicated fashion, and information about its strain dependence is not available. From the Kondo volume collapse model it is known [38, 41] that $\gamma^x$, $\gamma^z$ should be chosen of $O(1)$ to reproduce volume collapses of $O(10\%$). Given the experimental behavior of the CaFe$_2$As$_2$ lattice constants [14], $\gamma^z < 0$ is crucial. We shall also take $\gamma^\perp > 0$, but this is subdominant.

Finally, we neglect any dependence of the $c$ dispersion $\epsilon_k$ and the $f$ energy $\epsilon_0$ on lattice strain. While such a dependence certainly exists, it will not qualitatively change our picture, which is dominated by the effects parameterized in equations (3) and (4); moreover, a pressure dependence of the bandwidth can be absorbed in a pressure dependence of the reference energy scale of our calculation.

3.3. Fermionic mean-field theory

Model (1) will be solved using a standard mean-field theory, with a fermionic representation of the local moments and slave bosons to deal with strong local repulsions. Theories of this type

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The strain-induced changes of $J_{1,2}$ are likely dominated by changes in the bond angles [12].

New Journal of Physics 11 (2009) 055064 (http://www.njp.org/)
have been extensively used in the study of the Kondo and Anderson lattice and also allow one to deal with the magnetic exchange term in equation (1) \[35, 36, 50, 51\].

In the limit of infinite Coulomb repulsion \(U\), the physical electron can be represented by a spinless boson \(r_i\) and an auxiliary fermion \(\bar{f}_{i\sigma}\), \(\bar{f}_{i\sigma} = r_i \pi f_{i\sigma}\), together with the constraint
\[
r_i^\dagger r_i + \bar{f}_{i\sigma}^\dagger \bar{f}_{i\sigma} = 1. \tag{5}
\]
The auxiliary bosons \(r_i\) will be treated on the mean-field level. The Heisenberg part of the Hamiltonian, represented in pseudo-fermions \(\bar{f}_{i\sigma}\), has to be decoupled. Guided by the presence of potential magnetic and superconducting instabilities, we introduce mean fields according to
\[
\hat{M}_r = \frac{1}{2} (\bar{f}_{i\sigma}^\dagger \bar{f}_{j\sigma} - \bar{f}_{j\sigma}^\dagger \bar{f}_{i\sigma}), \quad \Delta_{ij} = -(\bar{f}_{i\uparrow} \bar{f}_{j\downarrow} - \bar{f}_{i\downarrow} \bar{f}_{j\uparrow}) \tag{6}.
\]
The decoupling of the quartic interaction takes the form (additional constants omitted):
\[
\bar{S}_i \cdot \bar{S}_j = x \left[ \frac{1}{4} \hat{M}_i \cdot \bar{f}_{j\sigma}^\dagger \bar{f}_{j\sigma}^\dagger + (i \leftrightarrow j) \right] + (1 - x) \left[ \frac{1}{2} \Delta_{ij}(\bar{f}_{i\uparrow} \bar{f}_{j\downarrow} - \bar{f}_{i\downarrow} \bar{f}_{j\uparrow}) + \text{h.c.} \right]. \tag{7}
\]
We have introduced an additional decoupling parameter \(x \in (0, 1)\), where \(x = 0\) corresponds to an \(\text{Sp}(N)\) large-\(N\) limit \[34\] and \(x = 1/2\) to unrestricted Hartree–Fock. Physically, \(x\) regulates the balance between ordered magnetism and superconductivity, and we shall choose \(x = 0.3\) and 0.4 below.

It remains to specify the spatial dependence of the mean-field parameters. The obvious parameterization for the magnetization \(\hat{M}_r\) is \(\hat{M}_r = m_s \exp(i \vec{Q} \cdot \vec{r})\) with \(\vec{Q} = (\pi, 0)\). The complex pairing fields \(\Delta_{ij}\) live on the nearest-neighbor and next-nearest-neighbor bonds of the square lattice. In the general orthorhombic case, we focus on saddle points with \(\Delta_x\) on horizontal bonds, \(-\Delta_y\) on vertical bonds, and \(\pm \Delta_{xy}\) on diagonal bonds, such that the pairing term in \(k\)-space reads \(\Delta_k = \Delta_x \cos k_x - \Delta_y \cos k_y + 2 \Delta_{xy} \sin k_x \sin k_y\). For a tetragonal lattice, \(\Delta_x = \Delta_y\), and the pairing is a mixture of \(d_{z^2-r^2}\) and \(d_{xy}\) symmetric terms (see footnote 8). Finally, the slave boson is chosen to be uniform, \(r_i \equiv r_0\).

The mean-field amplitudes are obtained from the saddle-point equations
\[
\tilde{\Delta}_x = \frac{2}{N} \sum_k \langle \bar{f}_{k\uparrow}^\dagger \bar{f}_{-k\downarrow}^\dagger \rangle \cos k_x,
\]
\[
\tilde{\Delta}_y = -\frac{2}{N} \sum_k \langle \bar{f}_{k\uparrow}^\dagger \bar{f}_{-k\downarrow}^\dagger \rangle \cos k_y,
\]
\[
\tilde{\Delta}_{xy} = \frac{4}{N} \sum_k \langle \bar{f}_{k\uparrow}^\dagger \bar{f}_{-k\downarrow}^\dagger \rangle 2 \sin k_x \sin k_y, \tag{8}
\]
\[
m_s = \frac{1}{4N} \sum_k \langle \bar{f}_{k\uparrow}^\dagger \bar{f}_{k+Q\uparrow} - \bar{f}_{k\downarrow}^\dagger \bar{f}_{k+Q\downarrow} \rangle + \text{h.c.},
\]
\[
1 - r_0^2 = \frac{1}{N} \sum_{k\sigma} \langle \bar{f}^\dagger_{k\sigma} \bar{f}_{k\sigma} \rangle,
\]
where \(\tilde{\Delta}\) denotes the complex conjugate of \(\Delta\).

\[\text{Footnote 8}\] For our parameter values, we have checked that saddle points with magnetic order at \((\pi, \pi)\) as well as those with \(s\)-wave-like pairing have a higher free energy.

New Journal of Physics 11 (2009) 055064 (http://www.njp.org/)
3.4. Phases and electronic phase diagram

The electronic mean-field theory specified above can display the following phases (not all of which will appear for our choice of parameters):

- Decoupled, with \( r_0 = 0, m_s = 0, \Delta = 0 \), describing a paramagnetic high-temperature regime with localized \( f \) electrons.
- Fractionalized FL\(^*\), with \( r_0 = 0, m_s = 0, \Delta \neq 0 \). This is a paramagnetic phase, where conduction electrons alone form a ‘small’ FS and are decoupled from a fractionalized spin liquid of paired spinons. This phase was introduced in [34], but will not play a role here.
- Local-moment AFM, with \( r_0 = 0, m_s \neq 0 \). Here, \( \Delta \) may be zero or finite, the latter case reflecting residual spinon pairing.
- Paramagnetic FL, with \( r_0 \neq 0, m_s = 0, \Delta = 0 \) with itinerant \( f \) electrons and a ‘large’ FS.
- Antiferromagnetic FL, with \( r_0 \neq 0, m_s \neq 0, \Delta = 0 \) with itinerant \( f \) electrons.
- Paramagnetic SC, with \( r_0 \neq 0, m_s = 0, \Delta \neq 0 \), obtained from pairing in the large-FS FL.
- Antiferromagnetic SC, with \( r_0 \neq 0, m_s \neq 0, \Delta \neq 0 \).

A zero-temperature transition from a phase with \( r_0 \neq 0 \) to \( r_0 = 0 \) is associated with Mott localization of the \( f \) electrons, i.e. an orbital-selective Mott transition. A continuous \( T = 0 \) transition of this type will survive beyond mean-field in the paramagnetic case [34, 35], whereas it becomes a crossover in the antiferromagnetic case (see footnote 4).

For the numerical calculations, serving as an illustration of our ideas from section 2, we choose parameters as follows: the \( c \) electron dispersion consists of nearest-neighbor hopping, \( \varepsilon_k = -2t (\cos k_x + \cos k_y) \), with \( t = 0.5 \text{ eV} \) and filling \( n_c = 0.8 \). The resulting band width is comparable to the energy range where the Fe DOS is sizeable [52]. The \( f \) level position is set slightly below the lower band edge to obtain moderate valence fluctuations, \( \epsilon_f = -2.3 \text{ eV} \).

The properties of the local-moment antiferromagnetic phase are determined by the exchange couplings \( x J_1 \) and \( x J_2 \). For a stable AFM ground state with wavevector \((\pi, 0)\), we choose the ratio \( J_2^0/J_1^0 = 1.5 \). We employ two parameter sets: \( x = 0.3, J_1^0 = 200 \text{ meV} \), \( J_2^0 = 300 \text{ meV} \) and \( x = 0.4, J_1^0 = 150 \text{ meV} \), \( J_2^0 = 225 \text{ meV} \). The resulting \( x J_1^0 \) and \( x J_2^0 \) coincide with the theoretical values for BaFe\(_2\)As\(_2\) from [54]. For CaFe\(_2\)As\(_2\), experimental and theoretical values have been determined in the orthorhombic phase in [29]. For our model with \( S = 1/2 \), those results yield \( J_1 \approx (J_{1x} + J_{1y})/2 \approx 40 \text{ meV} \) and \( J_2 \approx 50 \text{ meV} \).

The electronic phase diagram, obtained for fixed \( \epsilon_{x,y,z} = 0 \) as function of temperature \( T \) and hybridization \( V_0 \), is shown in figure 1, for decoupling parameters \( x = 0.3 \) and 0.4. We find magnetism and superconductivity to be mutually exclusive and separated by a first-order transition: at this transition, both \( m_s \) and \( r_0 \) jump, i.e. the system switches from a local-moment dominated AFM to a fully itinerant SC. At low \( T \), spinon pairing co-exists with local-moment antiferromagnetism on the small-\( V \) side of the phase diagram. The thermal magnetic transition is very weakly first order within our accuracy, but we cannot exclude it to be continuous. The superconductivity is of \( d_{xy} \) character, i.e. driven by the exchange interaction \( J_2 \) (A small \( 1d_{x^2-y^2} \) admixture develops at low temperatures for \( x = 0.3 \)). The finite-temperature transition between the decoupled regime and the FL will be smeared into a crossover by fluctuations beyond mean field; the other transitions are accompanied by physical symmetry breaking and survive.

A variation of the decoupling parameter \( x \) within the range \( x \in (0.25, 0.45) \) (keeping \( x J_{1,2}^0 \) fixed) mainly influences the stability of the superconducting phase, figure 1. Increasing \( x \) disfavors pairing and further stabilizes antiferromagnetism. For small \( x < 0.25 \) a paramagnetic
Figure 1. Electronic mean-field phase diagram in the temperature–hybridization plane, for fixed lattice parameters $\epsilon_{x,y,z} = 0$. Left: mean-field decoupling parameter $x = 0.3$. Right: $x = 0.4$. Thick (thin) lines denote first-order (continuous) phase transitions. For small hybridization, the $f$ electrons are localized and magnetism dominates at low $T$, whereas large hybridization leads to itinerant $f$ electrons and superconductivity. For details and parameters see text.

$\text{FL}^*$ phase is realized at small hybridization $V_0$, whereas for large $x > 0.45$ superconductivity disappears. For $x \geq 0.5$, antiferromagnetism appears even in the large-FS FL regime. (A related mean-field theory with spinon hopping (instead of pairing) generically displays an itinerant antiferromagnetic phase [35].) In general and beyond simple mean-field approximations, the superconducting $T_c$ will sensitively depend on band structure details and nesting conditions; a variation of $x$ in our calculations mimics such changes.

3.5. Phase diagram with electron–lattice coupling

The central result of our mean-field study is the phase diagram in figure 2, which accounts for lattice distortions and external pressure. It has been obtained from minimizing the free enthalpy $G_{\text{el}} + G_{\text{lat}}$, where $G_{\text{lat}}$ is in equation (2) and $G_{\text{el}}$ is the electronic contribution according to the Hamiltonian $\mathcal{H}$ (1), with the lattice dependence of all parameters as in section 3.2 and the mean-field approximation as in section 3.3. As experimental data for the elastic constants of the 122 materials were not available to us, we choose elastic constants of $c_1 = 441$ kBar, $c_3 = 198$ kBar, and $c_{12} = c_{13} = 66$ kBar. The employed electron–lattice couplings are $\gamma^+ = 3.1$, $\gamma^- = -5.2$, $\gamma_1^+ = 35$, $\gamma_1^- = 1.0$, $\gamma_2^+ = 8.0$ and $\gamma_2^- = 5.0$, see section 3.2. The values for $c_i$, $c_{ij}$, $\gamma^+$ and $\gamma^-$ were adjusted to reproduce the experimentally observed lattice distortions. The couplings $\gamma_1^+$, $\gamma_2^+$ and $\gamma_2^-$ had little influence on the lattice distortions. They were adjusted to reproduce the experimentally observed phase boundary of the superconducting phase.

With this parameter choice, the main effect of increasing pressure is an increasing hybridization, while the magnetic exchange couplings decrease somewhat. Consequently, the topology of the phase diagram is similar to that of figure 1, however, with a few crucial differences. (i) The orbital-selective Mott transition becomes strongly first order, at both low and high temperatures. (ii) The antiferromagnetic phase is accompanied by an orthorhombic lattice distortion and the thermal phase transition is of first order. (iii) Pressure drives a volume collapse transition, which is tetragonal $\leftrightarrow$ tetragonal at elevated $T$ and orthorhombic $\leftrightarrow$ tetragonal at...
The present mean-field approach is not able to distinguish the nematic transition from the magnetic transition, which are separated in experiment, but coincide in figure 2. This deficiency could be in principle repaired by including an additional nematic order parameter in the mean-field treatment, but would not change the other features of the phase diagram.
Figure 3. Pressure dependence of several microscopic parameters for low \( T = 0.5 \) meV and decoupling parameter \( x = 0.3 \). (a) Lattice parameters \( \epsilon_{x,y,z} \). Below temperatures of 30 meV, the \( \epsilon \) depend only weakly on temperature, therefore this plot is representative for most parts of the phase diagram. (b) Magnetic exchange constants \( J_{1,2} \). (c) Hybridization \( V \). (d) Pairing fields \( \Delta \). Note that \( \Delta \) reflects superconductivity only in the FL regime at large pressure, whereas it only describes spinon pairing in the orbital-selective Mott phase at small pressure.

elastic energy connected with the volume collapse. The pairing fields undergo several changes as a function of pressure, see figure 3(d) for \( x = 0.3 \), which depend sensitively on the pressure dependence of the exchange couplings and other microscopic parameters. The dominant pairing is of \( d_{x,y} \) symmetry as above, both for the spinon pairing of localized \( f \) electrons in the magnetic small-pressure phase as well as for the superconductivity of itinerant \( f \) electrons at high pressure (again with a small \( id_{x^2-y^2} \) admixture at low temperatures, which disappears for \( x = 0.4 \)). Slight changes of \( J_2/J_1 \) stabilize saddle points with other pairing symmetries, but leave the non-superconducting part of the phase diagram essentially unchanged. Finally, the \( f \) occupation jumps from 1 to \( \approx 0.80 \) across the transition for all temperatures below 60 meV (not shown).

4. Discussion

In this paper, we have proposed a theoretical scenario to rationalize the pressure-induced phase transitions in \( \text{CaFe}_2\text{As}_2 \). Underlying the scenario is the physics of the Anderson lattice,
used for heavy-fermion metals: strongly localized electrons hybridize with more itinerant electrons. Microscopically, both may be primarily of Fe 3d character, as discussed in [22] (although this is not required within our phenomenological approach). At ambient pressure, the localized electrons order antiferromagnetically in a collinear arrangement at low temperatures, accompanied by an orthorhombic lattice distortion. The system is weakly metallic, due to the presence of the itinerant carriers with a 'small' Fermi volume. Increasing pressure drives a transition towards a paramagnetic FL, where the previously localized electrons become itinerant and non-magnetic. The coupling to the lattice degrees of freedom in CaFe$_2$As$_2$ renders this transition strongly first order—this is akin to a Kondo volume collapse (although the system is not in the Kondo regime, and valence fluctuations are sizeable). The first-order nature of the transition, already in the purely electronic theory, implies a tendency towards phase separation, which appears to be present experimentally [55].

This set of ideas holds plausible explanations for (i) the coincidence of volume collapse and magnetic–non-magnetic transition (which is also borne out by first-principles approaches [14, 16, 20], (ii) the bad metallic behavior and (iii) the reduced magnetic moment of the magnetic phase. Note that (ii) and (iii) are not described by the mean-field theory, but arise from residual scattering between itinerant and localized electrons in the orbital-selective Mott regime as small pressure. Moreover, the abrupt disappearance of strong magnetism in the high-pressure phase is a natural part of the story. Theoretically, superconductivity mediated by residual spin fluctuations emerges at high pressure and low temperatures. The conflicting experimental reports [14, 15, 17] on superconductivity in CaFe$_2$As$_2$ may be consistent with the strong sensitivity of $T_c$ to microscopic parameters expected from theory and to sample inhomogeneities as proposed in [17].

The strong first-order volume collapse has only been observed in CaFe$_2$As$_2$—so what is special about this compound? While we cannot give a definite answer at this point, the current status of both theory and experiment suggests that CaFe$_2$As$_2$ (i) is a particularly soft material with a small c-axis lattice constant, (ii) displays a large electron–phonon coupling and (iii) is located in close proximity to a magnetic–non-magnetic transition. Indeed, first-principles calculations [56] have reported a giant magneto-elastic coupling. In particular, the magnitude of the Fe moment has been found to be coupled to the c-axis lattice constant, with this effect being strongest in CaFe$_2$As$_2$ as compared to other 122 and also to 1111 compounds. Moreover, a soft lattice is known to be a crucial ingredient in a first-order volume-collapse scenario [37], [40]–[43]. Note that, in our calculations, a small volume jump remains even for hard lattices due to the first-order nature of the purely electronic transition.

Our conceptual ideas are not in conflict with itinerant spin-density-wave descriptions of the FeAs magnetism, but constitute a more strong-coupling-inspired view of the same physics. We speculate that an orbital-selective Mott scenario, likely with a continuous instead of a first-order transition, could apply to doping-driven transitions in iron arsenides as well, as a specific filling of the conduction band is not required.

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*New Journal of Physics* 11 (2009) 055064 (http://www.njp.org/)
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