

Effect of doping and pressure on magnetism and lattice structure of Fe-based superconductors

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Using first principles calculations, we analyze structural and magnetic trends as a function of charge doping and pressure in BaFe_2As_2 , and compare to experimentally established facts. We find that density functional theory, while accurately reproducing the structural and magnetic ordering at ambient pressure, fails to reproduce some structural trends as pressure is increased. Most notably, the Fe-As bondlength which is a gauge of the magnitude of the magnetic moment, μ , is rigid in experiment, but soft in calculation, indicating residual local Coulomb interactions. By calculating the magnitude of the magnetic ordering energy, we show that the disruption of magnetic order as a function of pressure or doping can be qualitatively reproduced, but that in calculation, it is achieved through diminishment of $|\mu|$, and therefore likely does not reflect the same physics as detected in experiment. We also find that the strength of the stripe order as a function of doping is strongly site-dependent: magnetism decreases monotonically with the number of electrons doped at the Fe site, but increases monotonically with the number of electrons doped at the Ba site. Intra-planar magnetic ordering energy (the difference between checkerboard and stripe orderings) and interplanar coupling both follow a similar trend. We also investigate the evolution of the orthorhombic distortion, $e = (a - b)/(a + b)$, as a function of μ , and find that in the regime where experiment finds a linear relationship, our calculations are impossible to converge, indicating that in density functional theory, the transition is first order, signalling anomalously large higher order terms in the Landau functional.

I. INTRODUCTION

The magnetic properties of the Fe-based superconductors are believed to be the key to understanding their normal and superconducting properties¹. Yet a consensus about the microscopic physics of magnetism in these materials is still lacking. There are several widely held ideas that are arguably supported by most researchers in the field. First, the magnetism is intimately related to the crystal structure, both in terms of the Fe-As bond length, which is reduced when the local magnetic moment on Fe disappears (a simple reflection of the magnetostrictive nature of Fe), and in terms of an orthorhombic distortion in the magnetically ordered state (it is nearly universally believed that the distortion is driven by magnetism and not the other way around). The orthorhombicity of up to 1% is comparable with, say, the rhombohedral distortion of 1.2% in FeO upon the antiferromagnetic ordering.

Second, although initial opinions about the origin of the magnetic ordering in Fe pnictides stretched from a spin-Peierls philosophy^{2,3} to Mott physics⁴, it has now been recognized that while the local magnetic moments on Fe are formed independently of the fermiology, their mutual interaction is largely controlled by the itinerant electrons' response and by the Fermi surface geometry^{5,6}. A corollary of this fact is that when the long-range order is destroyed (whereupon superconductivity usually emerges), the system should be described as *paramagnetic*, a collection of disordered magnetic moments, rather than *nonmagnetic*, with the magnetic moment uniformly suppressed, as in non-spin-polarized density functional calculations. Particularly questionable are attempts to describe the evolution of magnetic

(and therefore crystallographic) properties when magnetism is suppressed (for instance, by pressure). It has been established⁷⁻¹⁰ that density functional theory within the generalized gradient approximation (DFT-GGA) describes the crystal structure (as well as the phonon spectra) of the parent compounds very accurately at ambient pressure, as long as full magnetization is allowed. It is not clear, however, whether DFT-GGA will work as well under pressure (the argument above suggests it may not). One purpose of this paper is to address this question.

Another unresolved and important question is the underlying mechanism by which the AFM order is destroyed by external means. Experimentally, one can proceed in three different ways. Chronologically the first method used was formally similar to that used in superconducting cuprates: charge doping. Naturally, it was implicitly assumed that, as in cuprates, charge doping increases the number of carriers, improves the metallic screening and renders the system less strongly interacting, and thus, less magnetic. In accordance with this concept, it was discovered¹¹ that Ni (which donates two electrons) is about twice more efficient in destroying the long-range magnetism as Co (which donates only one), and that electron doping (substituting O by F, or Fe by Co and Ni) has qualitatively the same effect as hole doping (substituting Ba by K). However, later it was found that pressure and/or strain can lead to essentially the same effect^{12,13}, suggesting that the carrier concentration is not the only, and maybe not even the most important change brought about by the chemical doping. This view was further reinforced by the fact that partial substitution of As by P (which exerts chemical pressure on Fe) has again the same effect¹⁴. Finally, it was also shown

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that diluting the Fe plane by nonmagnetic atoms, such as Ru, again destroys the magnetic order and triggers superconductivity^{15,16}.

DFT calculations can account for the last two effects, at least on the qualitative level: both physical (volume reduction) or chemical (reducing the iron-pnictogen height) pressure in calculations reduces the tendency to magnetism. However, it is not immediately clear what effect charge doping should have on magnetism inside DFT. In particular, if the mechanism of suppression is not the same as in cuprates, why would both hole and electron doping have the same, negative effect on magnetism? Answering this question is the second goal of this paper. We find that DFT does show the same qualitative behavior, doping electrons at the Fe site in BaFe_2As_2 depresses the magnetism, as does doping holes at the Ba site, while, intriguingly, doping holes on the Fe site and electrons on the Ba site enhances it.

Last but not least, there have been experimental indications of a *linear* as opposed to quadratic relation between the orthorhombic order parameter, $e = (a-b)/(a+b)$, and the measured magnetic moment. Such a relationship is formally prohibited by symmetry in the Landau theory, being only possible if the neutron measured magnetic moment is not the actual order parameter, or if the Landau functional includes anomalously large higher order terms and thus the quadratic regime extends only over very small magnetization. This anomalous behavior has been observed both as a function of temperature¹⁷ and as a function of doping¹⁸. While there is no guarantee (as discussed above) that DFT is capable of describing this magnetic phase transition correctly, it is still of interest to see whether the Landau functional *as calculated in DFT* does have anomalously large high-order terms. This is the third issue we address in this publication.

II. METHODS

All calculations as a function of pressure were carried out using the Vienna ab-initio simulation package (VASP)¹⁹, a projector augmented wave (PAW) based pseudopotential formalism. We employed the generalized gradient approximation (GGA) to the exchange potential of Perdew-Burke-Ernzerhof (PBE)²¹. We fully relaxed a series of structures (both lattice and internal coordinates) at a variety of volumes and extracted the pressure by fitting to an equation of state. All calculations as a function of doping were carried out using Wien2k²², which employs an APW+lo (augmented plane wave plus local orbitals) basis set, again using PBE-GGA. The lattice coordinates used were $a = 5.576$, $b = 5.616$, $c = 12.950$ Å, and $z_{\text{As}} = 0.8972$ (as a fraction of c), corresponding to the fully relaxed structure at zero pressure described previously. To simulate charge doping without using a supercell, we employed the virtual crystal approximation (vca). This technique involves replacing each atom of a certain type in the unit cell with a fictitious element

with a non-integer atomic number. For electron doping at the Fe site, we replace $Z = 26$ with $Z = 26 + x$ (toward Co) and for hole doping at the Ba site we use an element with $Z = 56 - x$ (toward Cs), using the same crystal structure. The number of electrons in the systems is increased commensurately, so that overall charge balance is maintained (alternate hole/electron doping at the Co/Ba site is achieved by simply subtracting/adding to Z). For calculations of intra- and interplanar coupling, we used two separate symmetries, Cmmm (space group 66) for the observed antiferromagnetically stacked stripe ordering, Cmma (space group 67) for the ferromagnetically stacked stripe order, and $\bar{1}4m2$ (space group 119) for the checkerboard ordering.

III. STRUCTURE AS A FUNCTION OF PRESSURE

In Ref. 13, Kimber *et al.* found that both doping and pressure cause the lattice parameters to decrease linearly. The Fe-As bond is found to be extremely rigid, in good agreement with a previous experimental study³³, while the As-Fe-As angle shrinks substantially with increasing pressure. Additionally, they find no indication of a structural anomaly or even change in structural trends occurring around the critical pressure or critical doping. Our DFT calculations of a , the parameter connecting FM-aligned spins, and b , the parameter connecting AFM-aligned spins, show very good agreement with the single in-plane lattice parameter measured by experiment (note that, due to overestimation of the static magnetic moment, DFT maintains the magnetically induced orthorhombic distortion up to ~ 12 GPa, whereas no long range ordering is experimentally detected after 1.3 GPa). The agreement extends, both in absolute value (not shown) and in trend with pressure (Fig. 1), throughout the measured range of pressures (1-6 GPa). The c -axis parameter agrees well with experiment at zero pressure, but is stiffer in our calculations than in experiment.

The main disagreement occurs in the Fe-As bond length and As-Fe-As angle (Figure 2). The former shrinks linearly with pressure in DFT calculations, instead of maintaining the observed constant value. The As-Fe-As angle, on the other hand, is rather constant over the pressure range, whereas in experiment it decreases. Both discrepancies are due to a single factor: the perpendicular height of the As atom above the Fe plane (the in-plane component of the Fe-As bond length is determined by a and b which both match well with experiment). This height scales linearly with the magnetic moment of the Fe atom, μ . The physical meaning of this is clear: as discussed, the Fe ion is characterized by a large magnetostrictive effect; compressing the ion results in a loss of the local magnetic moment. The Fe-As bond length controls the chemical pressure on Fe and thus is strongly correlated with the moment. The constant bond length in experiment reveals that the

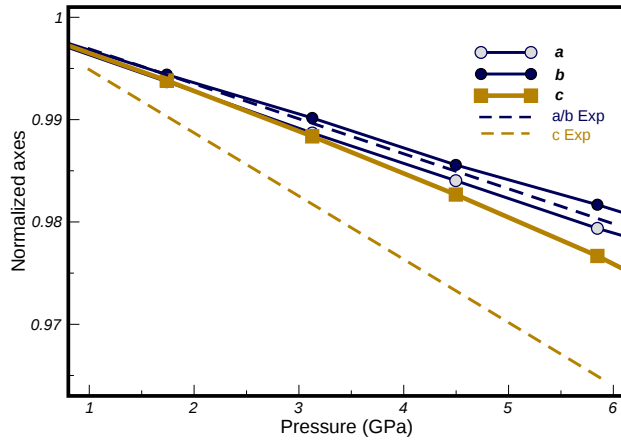


FIG. 1: A comparison of the lattice parameters a (short in-plane axis), b (long in-plane axis) and c (out-of-plane axis) to experiment. All parameters are normalized to the zero pressure value; the experimental lines are taken from Ref. ¹³.

magnitude of the magnetic moment does *not* change under pressure, indicating that the suppression of magnetic ordering occurs through increased spin fluctuations and orientational disorder rather than through an actual decrease in the absolute magnitude of the moment. DFT does not capture this effect, compensating instead by decreasing the overall moment. The calculated As-Fe-As angle suffers similarly from a decrease in As height that offsets the decrease in a, b , leaving a relatively constant value.

In view of the fact that the calculated equilibrium moment is larger than the experimentally measured one, one might assume that it would be *more* rigid than in experiment. The fact that the opposite relationship takes place tells us that while DFT overestimates the ordered moment, it underestimates the local moment. In retrospect, this is not that surprising because there exist residual Coulomb correlations in the system (DMFT calculations in the 1111 systems²³ indicate about 70% mass renormalization due to local Coulomb correlation, a small but not negligible number, which enhances the tendency toward local magnetism²⁴.

IV. MAGNETISM AS A FUNCTION OF PRESSURE

Outside the pressure range explored by Ref. ¹³, we find that the a and b lattice parameters decrease in a non-linear fashion. The short Fe-Fe (FM) bond does not decrease monotonically, while the long (AFM) bond does. This causes the ratio of the two to reach a definite minimum and is the origin of the minimum in $e = (a - b)/(a + b)$ around 6 GPa, corresponding to 1.55

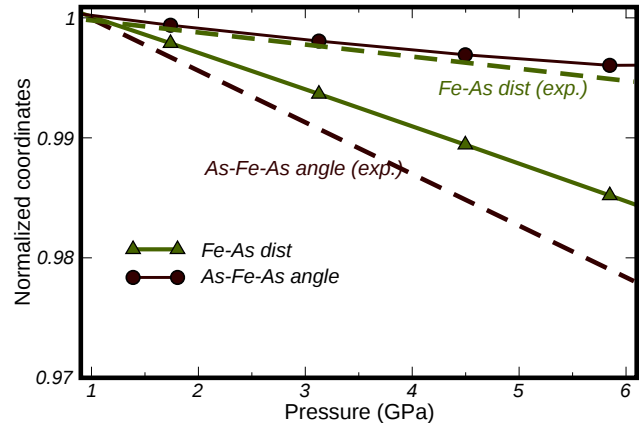


FIG. 2: The Fe-As bondlength and As-Fe-As angle normalized to their values at 1 GPa (solid lines) in comparison to similarly normalized experimental values from Ref. ¹³ (dashed lines). In experiment, the Fe-As distance is nearly constant, while the As-Fe-As angle changes, whereas in DFT calculations, the opposite is true.

μ_B in Fig. ³. (The qualitative behavior of a and b as a function of pressure matches very well with a previous DFT study²⁵ of the 1111 compound, LaFeAsO). The calculated minimum in e is a consequence of moving from a magnetic state to a non-magnetic state via full suppression of the magnetic moment. As discussed previously, the magnetic moment is rigid in experiment, so the calculated behavior is not expected to manifest in real systems. The original intent of performing this calculation was to examine e in the range where it increases linearly with μ , as seen in experiment^{17,18}, *i.e.* as μ grows away from zero. Unfortunately, we find that calculations in this region are essentially impossible to converge, suggesting a Landau functional with anomalously large high-power terms. In other words, the AFM phase transition induced by pressure or chemical pressure in the calculations seems to be first order, at least at the level of DFT-GGA.

We also investigated the interplanar coupling (the total energy difference between stripe layers stacked antiferromagnetically and ferromagnetically) as a function of pressure. If the coupling were a result of superexchange between Fe layers (whether directly through As-As hopping or through Ba atoms), one would expect it to increase as the layers are pushed closer together. As can be seen in Fig. ⁴, there is a very slight increase in $J_\perp$, defined as $\Delta E = J_\perp \mu^2$, as the pressure increases, but it is offset by a decrease in the magnetic moment, leaving the net coupling parameter essentially constant (even *decreasing* very slightly) across the pressure range of 0-6 GPa. In conjunction with the fact that we find that energy difference between the checkerboard and stripe in-plane magnetic configurations decreases with pressure

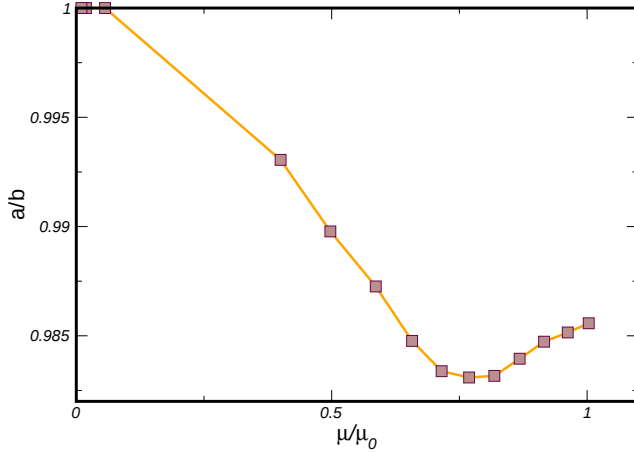


FIG. 3: The ratio of the a (short) to b (long) lattice parameters as a function of the relative magnetic moment μ/μ_0 , where μ_0 is the magnetic moment at zero pressure. No calculations could be converged between $\mu=0$ and $\mu=0.4$, indicating a first order transition.

(not shown), these results are again consistent with a picture in which increased spin fluctuations destroy the long range order. However, as pointed out earlier, the decrease in the magnitude of μ as calculated by DFT may not accurately represent reality. It seems more likely that $|\mu|$ is constant, but increasingly fluctuates with pressure. In this case, the interplanar coupling would indeed increase with pressure and the observed suppression of magnetic long-range order must have a different origin, perhaps stemming from in-plane fluctuations.

V. MAGNETISM AS A FUNCTION OF DOPING

One way to gauge the strength of the tendency toward magnetism is to evaluate the energy difference between a magnetic and a nonmagnetic (no local moments) solution. We have calculated this energy difference (Fig. 5) by using the virtual crystal approximation imitating the Co doping on the Fe site and the K doping on the Ba site (see Methods section for details) using the relaxed structure at ambient pressure, *i.e.* the effects of charge doping on the structure were not accounted for. We have further verified (Fig. 5) that supercell calculations for $\text{Ba}_2\text{Fe}_3\text{CoAs}_2$ are quantitatively consistent with the VCA, and for $\text{BaKFe}_4\text{As}_4$ semi-quantitatively consistent.

Our results show that, in agreement with the experiment, both types of doping weaken the magnetism (reduce the magnetization energy). But, we also found that extending our VCA calculations onto the opposite sides of the phase diagrams, that is, introducing holes on Fe sites or electrons on Ba sites, the trend simply continues, so that in these two cases the magnetism is *enhanced*.

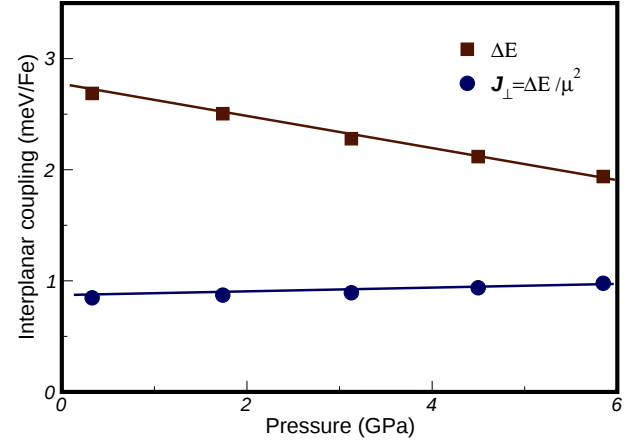


FIG. 4: Interplanar coupling, calculated as the difference in total energies between a system in which the in-plane stripe order is anti-aligned in successive planes and a system in which in-plane stripe orders are aligned in successive planes.

This same trend was found for a DFT study of the Sr-based 122 compound^{26,27}. Neither of the regimes precisely corresponding to our calculations has been accessible so far experimentally. Hole doping on the Fe site formally corresponds to Mn or Cr substitution. These indeed strengthen the magnetism (in agreement with our prediction)^{26,27}, but these dopants are likely themselves to have large local magnetic moments as impurities, and it is fairly possible that this is the reason for the experimental behavior, and not charge doping *per se*. Substituting Ba (or even better, Sr) by a rare earth like La or Yb seems to be chemically natural (*cf.* superconducting cuprates or colossal magnetoresistance manganites), yet so far there has been no success in achieving it. The DFT prediction is that such doping will enhance or at least not suppress the magnetism. It should be noted that the increase/decrease in magnetic energy occurs in conjunction with, and obviously partially due to, an increase/decrease in $|\mu|$.

Apart from local magnetism, the actual long range order depends on exchange interactions. These fall into two categories, the in-plane interactions (which, in these systems, appear to be long range^{28,29} and non-Heisenberg^{28,30}), and the interplanar coupling.

In particular, it has been suggested that the increase in spin fluctuations is due to an increased two-dimensionality brought about by a decrease in interplanar coupling³¹. We have calculated this coupling for both hole and electron doping, again using the virtual crystal approximation. The interplanar coupling does vaguely decrease in both directions (see Fig.6) with the conventional doping sites (holes on Ba, electrons on Fe), although within the error bars, set by total energy convergence in our calculation, the trend can be consid-

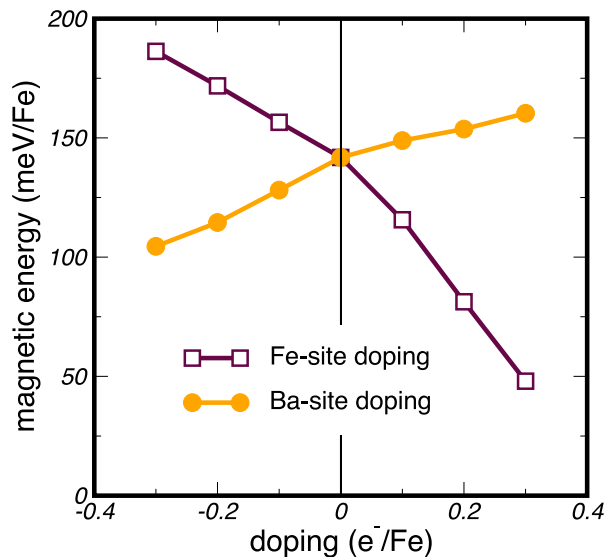


FIG. 5: The magnetic energy, defined as the total energy of the system in the magnetic stripe phase minus the total energy of the nonmagnetic system, as a function of hole and electron doping. Doping at the Fe site and on the Ba site for are shown for the virtual crystal approximation. Filled symbols show supercell calculations.

ered as entirely flat. The trends show the same site-dependence as the previously calculated magnetic energies. This is consistent with, albeit not proof of, the contention that magnetism is affected by the degree of two-dimensionality.

As mentioned, the intraplane interactions are long-range and non-Heisenberg, therefore instead of mapping them onto simplified models like Heisenberg or Ising, we look directly at the magnetic ordering energy (energy difference between magnetic and non-magnetic) states. We find that the intraplane coupling strongly decreases as a function of doping in the conventional scheme and yet again shows a strong site dependence. At zero doping, the scale of the intra-planar coupling is an order of magnitude greater than the interplanar coupling, but by $x \approx 1.5$ (where x is the number of electrons per Fe), the energy advantage of the stripe order over checkerboard has disappeared entirely. Collectively, the doping calculations point to a picture in which the primary influence of adding or subtracting charge (as with pressure) is to increase spin fluctuations.

VI. CONCLUSIONS

To summarize, we have extended the familiar DFT-GGA calculations to address several issues not addressed previously. Our findings are as follows:

(1) Although spin-polarized DFT-GGA predicts the equilibrium crystal structure at zero pressure exceedingly well, it becomes increasingly worse with pressure. Specif-

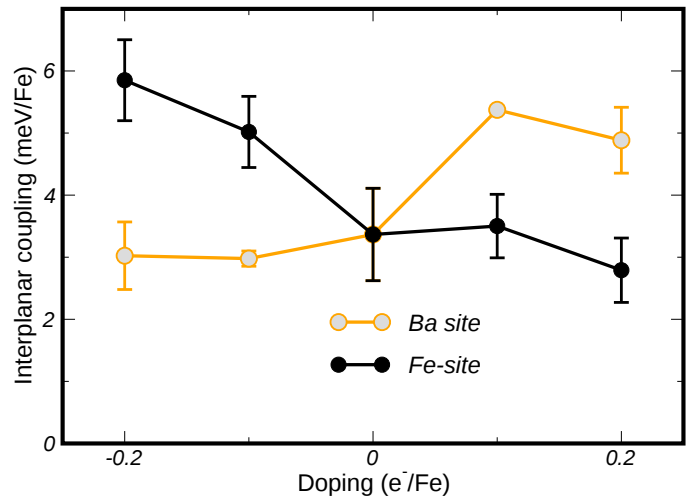


FIG. 6: Interplanar coupling, calculated as in Fig.4, but as a function of doping rather than pressure. The virtual crystal approximation is used, with hole doping taking place at the Ba site and electron doping taking place at the Fe site

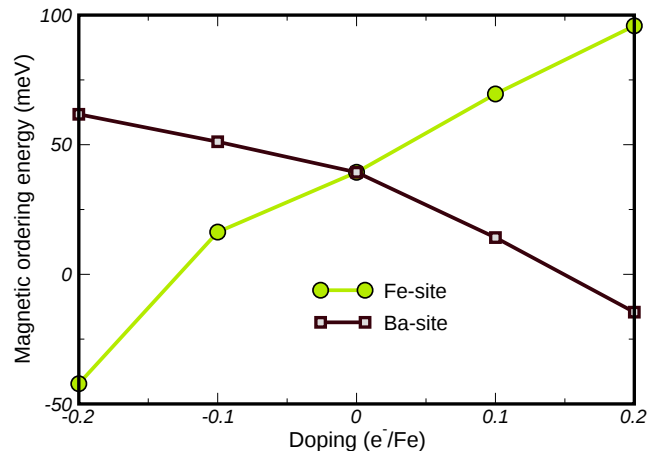


FIG. 7: The magnetic energy difference between in-plane stripe and in-plane checkerboard orderings as a function of doping in the virtual crystal approximation.

ically, the Fe-As bond is significantly softer in the calculations than in the experiment. We interpret this as evidence that the local magnetic moment (as opposed to the average ordered moment) is smaller in the calculations, not larger, than in the experiment, and ascribe this to residual local Coulomb correlations.

(2) The antiferromagnetic interlayer coupling is mainly constant as a function of pressure in DFT, which indicates that it is not of pure superexchange origin. We

interpret this as an indication of at least two competing interplanar interactions, one antiferromagnetic and one ferromagnetic (double exchange), whose pressure dependencies cancel one another.

(3) The small magnetic moment regime in BaFe_2As_2 is inaccessible to DFT-GGA calculations under hydrostatic pressure. This is likely an indication that within DFT-GGA the phase transition is first order, and that the Landau functional in the DFT-GGA has anomalously large high-order terms, consistent with the fact that experimentally the scalar orthorhombic order parameter follows the absolute value of the vector (magnetic) order parameter, and not the square of the latter.

(4) The effect of doping strongly depends on the location of the doped charge. Electronic doping in the Fe plane or hole doping in the Ba plane reduces the tendency to form local moments, while hole doping in the Fe plane or electron doping in the Ba plane enhances

it. Although we are unaware of any Ba-plane electron doping experiments to date, we predict that this effect should be verifiable via an increased magnetic ordering temperature and decreased superconductivity.

(5) The former two kinds of doping reduce the inter-layer coupling, while the latter two enhance it. The interplanar coupling is essentially insensitive to doping within conventional doping scheme (holes on the Ba site or electrons on the Fe site).

(6) Intralplanar interaction again shows strong site dependence, but decreases very strongly as a function of doping in either direction within the conventional doping scheme, further supporting the idea that the role of dopants in suppressing magnetism is to increase spin fluctuations.

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