



Why MgFeGe is not a superconductor

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The recently synthesized MgFeGe compound is isostructural and isoelectronic with superconducting LiFeAs. Both materials are paramagnetic metals at room temperature. Inspection of their electronic structures without spin polarization reveals hardly any difference between the two. This fact was interpreted as evidence against popular theories relating superconductivity in Fe-based materials with spin fluctuations. We show that in the magnetic domain the two compounds are dramatically different, and the fact that MgFeGe does not superconduct, is, on the contrary, a strong argument in favor of theories based on spin fluctuations.

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Soon after the discovery of iron-based superconductors,¹ spin fluctuations have been proposed as the pairing glue.² So far, many experiments are compatible with or even supportive of a spin-fluctuation-mediated mechanism.^{3,4} In the weak coupling approach to this pairing scenario, the nesting properties of the Fermi surface are important. Therefore, two materials with virtually identical Fermi surfaces and electron count, where one of the materials superconducts and the other does not, would at first glance cast a doubt on the validity of such an approach to superconducting pairing.

The recently discovered MgFeGe compound⁵ [Fig. 1(a)] is isostructural and isoelectronic to the so-called 111 iron pnictides, LiFeAs and NaFeAs. In particular, the former is a good superconductor with $T_c = 18$ K,⁶ and, like MgFeGe, is a paramagnetic metal in its normal state. Moreover, the electronic structures of both compounds, including their Fermi surfaces, calculated without any account of magnetism (which seems logical, in view of the experimental situation), are nearly identical,^{5,7} and so are the calculated noninteracting susceptibilities. By implication, the spin-fluctuation spectra in both compounds must be also very close, which seems, at first glance, to invalidate theories ascribing superconductivity in iron pnictides to spin fluctuations.

In this Rapid Communication we show that this is not the case. In fact, spin fluctuations in the two materials are qualitatively different. The popular weak coupling scenario,^{2,4,8} attempts to describe these materials as nonmagnetic (not paramagnetic), in terms of the linear response of the nonmagnetic Fermi surface. However, according to the result obtained by Rhee and Pickett,⁷ the weak coupling approach appears to be inadequate for MgFeGe.

The main problem with the density functional description of the paramagnetic phases of Fe pnictides is that standard density functional calculations cannot handle paramagnetism as disordered local moments. The standard approach⁹ when calculations are performed without allowing for a nonzero spin density simply forces each ion into a completely nonmagnetic state. As discussed in numerous papers,^{10–13} in all Fe pnictides, with a notable exception of the collapsed tetragonal phase in CaFe₂As₂, not only the local moments of the order of $2\mu_B$ remain, but they are apparently correlated in the standard stripe manner. This is evidenced, for instance, by the fact that the lattice dynamics and equilibrium structure of formally

nonmagnetic pnictides only agree with the experiment in spin-unrestricted calculations with the full density functional theory (DFT) magnetic moment of $\sim 2\mu_B$.^{11–13} Also, de Haas–van Alphen experiments on BaFe₂As₂ are much better described by DFT calculations with the full self-consistent magnetization, rather than with the much smaller experimentally reported magnetic moment.¹⁴ Computationally, the hallmark of local moments is the possibility to converge calculations to different magnetically ordered states, with the energy difference between them considerably smaller than between any of them and the nonmagnetic state.¹⁵

With this in mind, we have deliberately stepped out of the weak coupling domain and searched for magnetic solutions. Note that DFT *per se* is a mean-field theory, but not a weak coupling theory. The investigation of different magnetic configurations gives us a clue as to what kind of local correlations one can expect and what the structure of the spin susceptibility, as opposed to weak coupling, should be.

In most iron pnictides these two approaches (strong and weak coupling) give the same result: Spin fluctuations are peaked at (π, π) in the folded Brillouin zone. In iron selenides this is not exactly the case. In the pure FeTe compound, the ground state (experimental and calculated) is a so-called double stripe, corresponding, in the same notation, to the $(\pi/2, 0)$ ordering vector. However, the more familiar stripe state is very close in energy, and when magnetism is suppressed by alloying with Se, not only is the long-range order suppressed, but also, to the same degree, the local moments. As a result, spin fluctuations corresponding to stripelike local correlations reappear and gradually overcome the $(\pi/2, 0)$ fluctuations. The former are pairing in the s_{\pm} scenario, and, in agreement with the concept, superconductivity appears.

Therefore, in order to properly compare LiFeAs and MgFeGe and to understand the character of the spin fluctuations, we need to perform a spin-unrestricted mean-field DFT calculation for both, and only if the results will be reasonably close we can claim a failure of the spin-fluctuation model.

In Table I, we compare the energies of various calculated^{16–18} magnetic structures for LiFeAs and MgFeGe.^{19,20} It has been pointed out previously that, compared to 1111 and 122 structures, in LiFeAs the ferromagnetic state is relatively stable, even though still definitely energetically above the antiferromagnetic stripe phase.^{21,22}

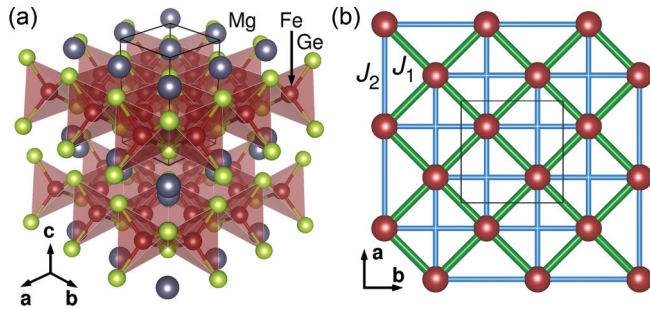


FIG. 1. (Color online) (a) Structure of MgFeGe. (b) Exchange coupling paths J_1 and J_2 in the Fe plane.

In MgFeGe this tendency is much stronger than in LiFeAs and leads to an unexpected result: The calculated ground state is actually ferromagnetic. Moreover, one can quantify the effect by extracting the nearest- and the next-nearest-neighbor effective exchange constants.²³ For LiFeAs we find, as expected, two antiferromagnetic exchange constants, $J_1 = 52$ meV and $J_2 = 102$ meV, corresponding to the Fe-Fe interaction paths shown in Fig. 1. The fact that $J_2 > J_1/2$ reflects the stripe phase being the ground state. For MgFeGe we obtain $J_1 = -71$ meV and $J_2 = 32$ meV. Note that now the nearest-neighbor interaction is ferromagnetic. These exchange constants are consistent²⁴ with the tendency towards ferromagnetism we find for MgFeGe (compare Table I).

The origin of this phenomenon can be understood by comparing the density of states (DOS) of the two compounds in ferromagnetic and stripe-type antiferromagnetic configurations (see Fig. 2). We observe that in LiFeAs the DOS in the stripe phase is drastically reduced with respect to the DOS in the ferromagnetic phase and a pseudogap forms around the Fermi energy with a substantial gain of the one-electron energy. In MgFeGe, on the other hand, ferromagnetic and stripe order lead to similar DOS at the Fermi energy and ferromagnetism wins by a small energy amount (see Table I). Also, an analysis of the Fermi surfaces of the two compounds in the antiferromagnetic stripe configuration support these results (see Fig. 3). Indeed, while in the nonmagnetic phase, as shown in Ref. 7, the Fermi surfaces of the two compounds are nearly identical, in the stripe phase of LiFeAs, just as in all other Fe pnictides, the Fermi surface is mostly gapped. In MgFeGe, on the other hand, the gapping is much smaller, and so is the corresponding energy gain.

One can also ask another question: Is this difference due to different crystallographic parameters or different ionic properties? To answer this question, we have performed calculations for a hypothetical compound with the composition of MgFeGe, but crystallographic parameters as in LiFeAs. Interestingly, we found that the energy difference between the

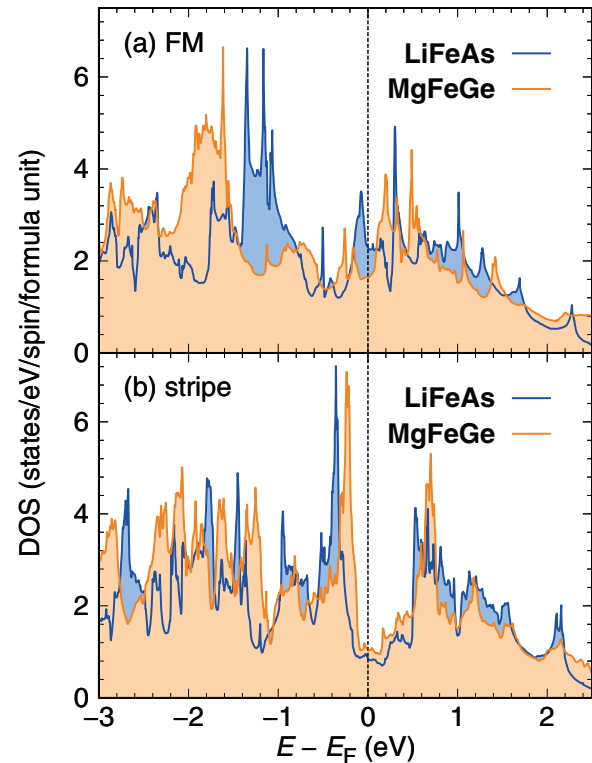


FIG. 2. (Color online) Comparison of densities of states for LiFeAs and MgFeGe in different magnetic configurations. Total DOS in (a) ferromagnetic order, and in (b) stripe-type antiferromagnetic order.

stripe and the ferromagnetic states was strongly reduced (by about a factor of 7), but the sign was still the same, favoring the ferromagnetic order. This indicates that both chemistry and crystallography contribute to the difference in magnetic properties between the two compounds.

To summarize, by investigating the magnetic behavior of MgFeGe versus LiFeAs we found that MgFeGe is most stable in a ferromagnetic configuration in contrast to LiFeAs that stabilizes in the more familiar antiferromagnetic stripelike pattern. This has important consequences for the actual behavior of MgFeGe: The short-range correlations, and, by implication, fluctuations in the paramagnetic state, are stronger at $q = 0$ than at $\mathbf{q} = (\pi, \pi)$. Thus, they actually destroy, rather than support, the s_{\pm} pairing. The fact that MgFeGe is not superconducting therefore supports the spin-fluctuation-induced pairing model and the s_{\pm} pairing state. Another, probably more critical, message is that, although many useful results have been obtained using the weak coupling linear response methodology, this path is slippery. Neglecting the fact that DFT calculations, as well as certain experiments, for iron-based superconductors point toward strong coupling and large local moments, may be dangerous.

The last note concerns the role of correlations in MgFeGe. Inclusion of correlation effects beyond DFT in LiFeAs (Refs. 25–27) yields a better description of its Fermi surface, in agreement with experimental observations. MgFeGe is probably more strongly correlated than LiFeAs, since it has

TABLE I. Energies of various spin configurations with respect to the nonmagnetic solution for MgFeGe and LiFeAs, in meV/Fe.

	Néel	Double stripe	Stripe	Ferromagnetic
MgFeGe	-113	-175	-179	-183
LiFeAs	-56	-94	-133	-37

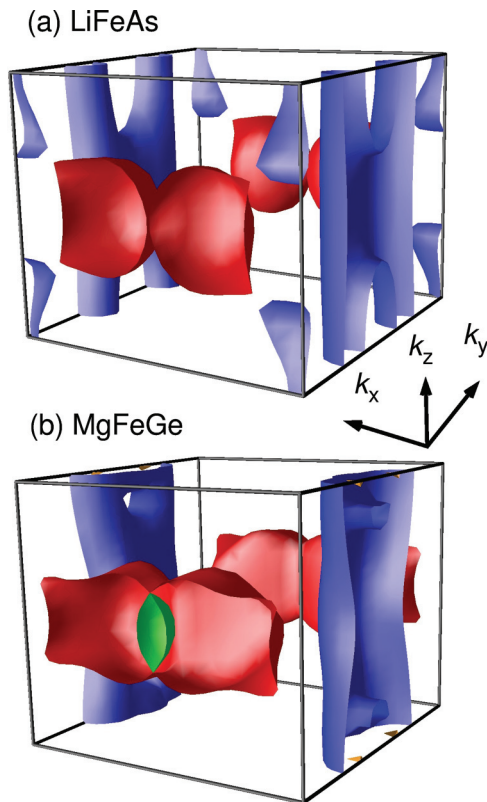


FIG. 3. (Color online) Fermi surfaces in the antiferromagnetic (AF) stripe configuration for (a) LiFeAs and (b) MgFeGe. The corners of the reciprocal lattice unit cell are at the Γ points, and x and y are the ferro- and antiferromagnetic directions, respectively.

a larger magnetic moment (compare in Fig. 4 the up and down DOS). By the same argument, it is probably less correlated than FeSe, and thus correlation effects are unlikely to be responsible for the absence of superconductivity, as opposed to proximity

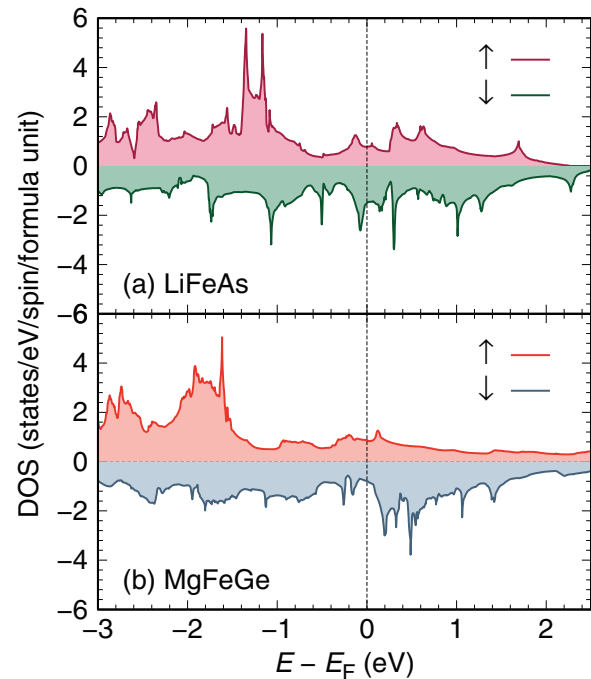


FIG. 4. (Color online) Densities of states in the ferromagnetic (FM) configuration for (a) LiFeAs and (b) MgFeGe.

to the ferromagnetic instability, which does not appear in any superconducting Fe pnictide or chalcogenide.

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¹⁵Note that a trivial, but often overlooked, fact is that local magnetic moments do not necessarily imply localized electrons; for instance, metallic iron has itinerant electrons and local moments.

¹⁶We used two full potential all electron codes and report energy differences for which both methods are in very good agreement. We report numbers from the full potential local orbitals (FPLO) code (Ref. 17) using a generalized gradient approximation (GGA) functional (Ref. 28) and a $16 \times 16 \times 16$ k mesh. We verified the energy differences with those obtained from the linear augmented plane wave method (LAPW) (Ref. 18) with the same settings as in Ref. 2, including a gradient correction to the exchange-correlation

functional. We have not optimized the crystal structure, but use the experimental one reported in Ref. 5.

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¹⁹In Ref. 5 structural optimization was performed for several different magnetic configurations by means of the pseudopotential plane wave code VASP (Ref. 20), and it was found that the *optimized* FM structure is higher in energy than the optimized stripe structure. We have used instead the experimental structure, for the following three reasons: (i) The spin fluctuations that we want to describe occur in a crystal with no long-range order, no orthorhombic distortion, etc. (ii) All-electron calculations are generally more reliable than pseudopotential calculations. While we were able to confirm the Liu *et al.* result that full structural optimization in VASP renders the stripe structure to be lower in energy, in our calculations the Fe magnetic moment in the FM state was substantially larger than in Ref. 5, and the energy difference between the two magnetic patterns in their respective VASP-optimized structures was very small. (iii) The FM-optimized structure is rather close to the experimentally measured one (atomic displacements less than 0.01 Å), while the stripe-optimized structure is considerably different from the experiment (displacements on the order of 0.05 Å). On the

other hand, this unusual sensitivity to computational details again emphasizes that MgFeGe is magnetically very different from Fe pnictides and chalcogenides.

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²³Note that the estimation of the nearest- and next-nearest-neighbor exchange constants does not mean that we endorse using the short-range Heisenberg model as a physically meaningful description of these itinerant systems; it is well known that proper mapping of the DFT energy differences requires not only going beyond the second coordination shell, but even beyond the Heisenberg model.

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