Superconductivity gets an iron boost

Igor I. Mazin¹

Superconductivity, the resistance-free flow of electrical charges, is one of the most exotic phenomena in solid-state physics. Even though it was discovered almost a century ago, many questions remain unanswered, in particular those concerning the physics of high-temperature superconductivity. The recent discovery of iron-based superconductors was arguably the most important breakthrough in this field for more than two decades and may provide new avenues for understanding this high-temperature phenomenon. Here I present my view of the recent developments in this field that have led to the current understanding of this important new class of superconductor.

A once popular joke asked how a physicist would interpret experimental data on odd numbers. As the first experiments reveal that 1, 3, 5 and 7 are all prime numbers, the physicist becomes convinced that all odd numbers are prime and that a correct theory of 'primeness' should be able to explain this experimental fact. Further studies, however, show that 9 is not a prime number. The community initially disregards this as an experimental error; however, after more experiments, the researchers are forced to admit that 9 is indeed not prime, making it a unique case. This view is reinforced when further experiments show that the next odd numbers in the series, 11 and 13, are both prime. Only after it is found that, in violation of 'conventional wisdom', 15 is not a prime number, does the idea that there are infinitely many odd numbers, but not prime numbers, take root in researchers' minds.

This joke can be seen as an allegory of the modern history of superconductivity. During the 1960s and 1970s, the recorded transition temperature, T_{c} , for superconductors very slowly inched its way up, culminating in the 1976 finding of $T_c = 23.2$ K in Nb₃Ge, largely thanks to the efforts of Berndt Matthias. At about that time, according to physicists' folklore, Matthias formulated his famous six rules for a successful search for new superconductors¹. One, a high symmetry is good; cubic symmetry is the best. Two, a high density of electronic states is good. Three, stay away from oxygen. Four, stay away from magnetism. Five, stay away from insulators. Six, stay away from theorists. All of these rules, with the possible exception of rule six (I'll leave that to the judgement of my experimental colleagues), not only have been proved incorrect but also their exact opposite seems to be true.

Following this stagnation in the search for superconductors with a higher T_c than 23–24 K, between 1976 and 1986 an increasingly large number of physicists became convinced, and openly sounded their conviction (a notable exception being Vitaly Ginzburg²), that a quantitative theory of superconductivity ultimately would provide proof that T_c has a fundamental limit of about 25-30 K. It is ironic that in the chemical cabinets of many of these distinguished scientists was magnesium diboride (MgB_2) , which, as has been known since 2001, has a T_c of 40 K.

This conviction was radically challenged when copper-oxide-based superconductors with a high T_c were discovered in 1986. The rapid climb of the maximum known T_c up to 140 K created the first paradigm shift; it became clear that high-T_c superconductivity (with critical temperatures larger than the anticipated 25-30 K) was possible, even though the underlying mechanism remained unknown. The following two decades, however, brought little progress towards a further increase of T_c . No new high- T_c materials were found, although some superconductors that broke the old record of 23.2 K (but not by much) were discovered, for example (Ba,K)BiO₃, doped fullerenes and MgB₂. Inevitably, a growing number of physicists started to look for the unique combination of physical properties that makes copper oxides such a spectacular exception in the materials universe.

The new, iron-based, superconductors (initially called iron-pnictide superconductors, before another, chalcogen-based subfamily was found) were discovered in 2008 (ref. 3). Their epistemological value is that they did not fit the same mould as copper oxides. Their discovery demonstrated that unconventional (that is, not phonon-mediated) high- T_c superconductivity, such as that found in copper oxides, is not unique and is probably just as ubiquitous as the conventional, 'low- T_c ,' kind, if researchers would look in the right places. What is special about iron-based superconductors is that the more they are studied, the less they look like copper oxides, suggesting that high- T_c superconductivity is not limited to copper oxides and might not even be limited to any particular class of materials. (This

Table 1 Properties of different classes of superconductor				
Property	Conventional superconductors	Copper oxides	MgB ₂	Iron-based superconductors
T _c (maximum)	<30 K	134 K	39 K	56 K
Correlation effects	None (nearly-free electrons)	Strong local electronic interaction	None (nearly-free electrons)	Long-range (non-local) magnetic correlations
Relationship to magnetism	No magnetism	Parent compounds are magnetic insulators	No magnetism	Parent compounds are magnetic metals
Order parameter	One band, same-sign s wave	One band, sign-changing <i>d</i> wave	Two band, same-sign s wave	Two band, presumably sign- changing s wave
Pairing interaction	Electron-phonon	Probably magnetic (no consensus)	Electron-phonon	Presumably magnetic
Dimensionality	Three dimensional	Two dimensional	Three dimensional	Variable

¹Naval Research Laboratory, code 6390, 4555 Overlook Avenue Southwest, Washington DC 20375, USA.

may not be entirely true; as discussed below, there might be some common conditions for high- T_c superconductivity, such as proximity to magnetism. But if these conditions exist, they are of a general character.)

In this Perspective article, I discuss the commonalities and differences between the two previously known classes of high- T_c superconductors, copper oxides and MgB₂, and what can be learned from this comparison. I then take a look at how far the understanding of iron-based superconductors has advanced and what the remaining challenges and prospects are in this field.

True siblings or lookalikes

Eighteen months after the discovery of superconductivity in copper oxides, there was almost no understanding of the underlying physics. Eighteen months after superconductivity was found in MgB₂, there was almost a complete theory for it⁴. Some twenty months into the 'iron age', and the physics community's understanding lies between these limits: much is known, and there is a plausible theoretical hypothesis that the majority of researchers in the field seem to agree on (curiously, proposed within days of the original discovery^{5,6}). However, there is not a complete theory, and there are several facts that are difficult to explain and to reconcile with one another⁷.

In many respects, iron-based superconductors sit between copper oxides and MgB₂ (Table 1). Undoped ('parent') copper oxides are strong magnets and insulators. This is because two electrons located on the same copper ion are subject to strong Coulomb repulsion, leading to strong correlations and hence electron localization⁸. The undoped compounds have exactly one valence electron for each copper atom, which makes them strong magnets - each electron has a spin of 1/2 and therefore a magnetic moment. When extra charge carriers are introduced by way of doping, these carriers are free to move about and screen the Coulomb repulsion. Given enough doping, the static magnetism disappears, and the electron states form a single band, as is the case in simple metals. Crucially, there is a critical range of doping in which a superconducting phase appears within a characteristic 'superconducting dome' (Fig. 1b). Many, but not all, researchers think that the 'glue' that binds electrons into Cooper pairs, which give rise to superconductivity, is provided by the exchange of magnetic fluctuations. Another important characteristic of copper oxides is that the wavefunction of the Cooper pairs — also known as the superconducting order parameter - has *d*-wave symmetry (Fig. 2b). This means that the paired electrons orbit each other with a particular angular momentum, avoiding close contact with each other, and thereby reducing the effect of their mutual Coulomb repulsion. Many think that such 'Coulomb avoidance' is an important component of high- T_c superconductivity⁸.

In contrast to copper oxides, MgB₂ has no trace of magnetism, has delocalized electrons (which are not subject to strong on-site correlations), and has a complex electronic structure, featuring two distinctively different groups of electrons. These two groups form two kinds of electronic band (hence the term two-band superconductors), which give rise to two separate sets of Fermi surfaces⁴.

Iron-based superconductors, on the one hand, resemble copper oxides in that they are strong magnets in parts of their phase diagram (Fig. 1c) and in that superconductivity develops when magnetism is destroyed by doping. On the other hand, unlike copper oxides, the parent (magnetic) iron-based compounds are metallic, so the increase in the charge carrier concentration as a result of doping is not a decisive factor in the development of superconductivity. Indeed, magnetism can be suppressed and superconductivity induced in these materials without charge doping. This can be achieved by applying pressure, by partially substituting arsenic with phosphorus, or by simply diluting the iron layer with a nonmagnetic species, such as ruthenium. With few exceptions, one of the main characteristic features of iron-based superconductivity emerges⁹.

Another property that sets iron-based superconductors apart from copper oxides is the strength of the Coulomb correlations. The latest calculations, as well as estimates from spectroscopic experiments, seem to be in agreement that the correlation strength is weak to moderate^{10,11}, although not as weak as in MgB₂, in which Coulomb correlations are almost absent. Another important property, which iron-based superconductors have in common with MgB₂, is that electrons form a multi-sheet Fermi surface that can be separated into two distinct sets of surfaces (Fig. 3). But, as discussed below, there seem to be significant differences between these two classes of materials regarding the nature of the superconducting states.

Ironing out the last wrinkles

So what is known about these materials, and how has this information been uncovered? It is known that iron-based superconductors comprise a broad variety of materials⁹ and that they all have similar phase diagrams (Fig. 1c) and presumably have the same mechanism of superconductivity. All iron-based superconductors have the same



Figure 1 | **Iron-based superconductors and copper-oxide-based superconductors. a**, Generic crystal structure of iron-based superconductors. Fe atoms are shown in red, and pnictogens (As or P) or chalcogens (Se or Te) are indicated in blue. The filler layer, shown without atomic detail, can contain any of the following constituents (for each two iron atoms): one alkaline earth atom; two alkali atoms; two rare-earth atoms and two oxygen atoms; or more complex layers with various atoms. It is also possible for there to be no filler layer. **b**, Schematic phase diagram of copper-oxide-based superconductors. Note how both electron doping and hole doping suppress the magnetism of the parent compounds and

induce superconductivity under the characteristic superconducting dome. The green lines between the paramagnetic and pseuodogap phases (green shading) represent crossover transitions, black lines between paramagnetic and antiferromagnetic phases are well-defined transitions. **c**, Schematic phase diagram for the 122 family of iron-based superconductors. An example is $BaFe_2As_2$, in which Ba atoms can be substituted with K atoms, thereby doping the parent compound with holes; Fe atoms can be substituted with Co atoms, doping the parent compound with electrons; or Fe atoms can be substituted with Ru atoms (or As atoms by P atoms), to suppress magnetism without changing the carrier concentration.



Figure 2 | **Superconducting order parameter.** A schematic representation of the superconducting order parameter in different cases: a conventional, uniform, *s* wave, such as in an 'old-fashioned' superconductor (for example aluminium) (**a**); a *d* wave, as is the case in copper oxides (**b**); a two-band *s* wave with the same sign, as in MgB₂(**c**); an s_{\pm} wave, as is thought to be the case in iron-based superconductors (**d**). In **a** and **b**, the two-dimensional Fermi surface is approximated by one circle. In **c** and **d**, the Fermi surface is approximated by a small circle in the centre (the first band) surrounded by four larger circles (to comply with the tetragonal symmetry; the second band). In all cases, the height of the 'rubber sheet' is proportional to the magnitude of the order parameter (including its sign).

crystallographic motif (Fig. 1a), with the main component being a square lattice of iron atoms sandwiched between two square lattices of pnictogen (arsenic or phosphorus) — hence the initial name — or chalcogen (selenium or tellurium) atoms. Between these crucial trilayers, various 'filler slabs' can be placed (although this is not essential): for example, a single crystallographic layer of sodium, barium, strontium or calcium; a trilayer consisting of a layer of oxygen between layers of a rare-earth element (the highest T_c so far, 56 K, has been observed in this family); or an even more complex filler slab.

Superconductivity can be induced in all materials by chemical doping or pressure, or a combination of both, as long as this results in the suppression of magnetism. In contrast to copper oxides, which have very low electrical conductivity along the direction perpendicular to the copper-oxide layers, none of these systems is truly two dimensional. This is beneficial in terms of practical applications, because in polycrystalline two-dimensional materials superconductivity can be destroyed by a relatively small current.

What can be inferred from the large number of iron-based superconductors and the known properties of these materials? So far, no simple correlation has been noticed between anisotropy, the distance between planes in the crystal lattice, the temperature at which antiferromagnetic ordering occurs in the parent phase (or even the pattern of the magnetic order of this phase) and the superconducting T_c . Initially, it seemed as though T_c is optimized when the four anions around an iron ion form an ideal tetrahedron¹². However, after more iron-based superconductors had been uncovered, this finding seemed not to be universal¹³.

By contrast, phase diagrams of essentially all iron-based superconductors have both superconducting phases and a strongly antiferromagnetic phase (see Fig. 1, which is a schematic view of the generic features of the phase diagram). All iron-based superconductors contain iron in a valence state that is close or equal to Fe^{2+} . All materials that have been studied so far show a peak in inelastic neutron-scattering spectra that corresponds to magnetic excitations at a particular wavevector, Q_m (even though for at least one family, $FeTe_xSe_{1-x}$, the static magnetic order occurs at a different wavevector). In cases in which the Fermi surface has been mapped by angle-resolved photoemission spectroscopy (ARPES), two sets of Fermi surfaces, roughly separated by the same wavevector, Q_m , have been revealed (Fig. 3).

It is tempting to assume (and in fact almost the entire community has succumbed to this temptation) that the features that such disparate ironbased superconductors have in common reflect a common origin for the observed superconductivity. Adopting this path, it can be concluded that proximity to a magnetic quantum critical point (as is seen in the phase diagram) signals that magnetic (spin) fluctuations play an important role. The fact that neutron-scattering measurements always uncover magnetic excitations with a particular wavevector, $Q_{\rm m}$, also suggests that these excitations are instrumental for mediating the pairing of electrons. Note that the two electrons in a singlet Cooper pair have the same charge but opposite spins. A corollary of this is that magnetic excitations lead to pairing only if the corresponding wavevector spans parts of the Fermi surface with order parameters (that is, the pair wavefunction) of opposite sign (see ref. 14 for further explanation). Now, noting that there are two sets of Fermi surfaces that are roughly separated by the same wavevector $Q_{\rm m}$ (Fig. 3), the so-called s_{+} superconductivity is derived, in which the sign of the order parameter is switched between the two sets of Fermi surfaces (Fig. 2).

In the previous paragraph, I describe how the s_{\pm} superconductivity model could have been arrived at, by using data from ARPES and neutron-scattering experiments that became available roughly one year after the initial discovery. It is gratifying that theorists were able to come up with this model within a few weeks of the initial discovery, solely on the basis of electronic structure calculations and theoretical models^{5,6}.

Farther down the road

It is still not clear beyond a reasonable doubt that the superconducting symmetry realized in iron-based superconductors is s_{\pm} symmetry and that pairing is due to spin fluctuations. The jury is still out. This is a jury that is deeply convinced by the prosecution but is reluctant to base its verdict solely on circumstantial evidence. However, circumstantial evidence is plenty in this case, and physicists might be *en route* to uncovering a direct proof.

It is known (from nuclear-magnetic-resonance spectroscopy data) that the Cooper pairs in iron-based superconductors are spin singlets (formed by electrons with antiparallel spins). In this class, three possible symmetries of the order parameter are compatible with the tetragonal



Figure 3 | A typical calculated Fermi surface of an iron-pnictide

superconductor. The Fermi surface (projected onto the k_x - k_y plane, where k is electron momentum) shown is calculated for 10% electron-doped LaFeAsO. Experimentally observed Fermi surfaces show similar geometries. The momentum connecting the two sets of Fermi surfaces, Q_m , is shown by the arrow. Spin fluctuations with this moment were predicted theoretically and found experimentally, and they are now thought to be instrumental for creating high- T_c superconductivity in iron-based superconductors.

symmetry of iron-based superconductor crystals: a *d*-wave symmetry; an *s*-wave symmetry without sign change; or the s_{\pm} -symmetry model, which combines *s*-wave symmetry with a sign change of the order parameter. All of these models are illustrated in Fig. 2.

As can be seen in Fig. 2, an *s*-wave order parameter (of either flavour) and a *d*-wave order parameter differ by their rotational symmetry: the s wave does not change under a 90° rotation, whereas the d wave changes sign. This difference allows the design of 'phase-sensitive' experiments¹⁵ that can distinguish between the two. The preliminary indications are strongly against iron-based superconductors having *d*-wave symmetry. However, arguably the most convincing evidence against the *d*-wave model (or any finite angular momentum model) is that such a state, according to its symmetry, has nodes in the order parameter, which implies that there is a zero minimal excitation gap in the superconducting state. In other words, excitations with arbitrarily small energy exist. Because this is mandated by the symmetry, such zero minimal excitation gaps should be present in all iron-based superconductors, but numerous experiments have established that some iron-pnictide superconductors have a finite minimal gap. By contrast, an *s* state (whether *s* or s_+) may or may not have nodes (depending on the particular combination of material-dependent parameters). Indeed, some of iron-pnictide superconductors (KFe₂As₂, LaFePO and BaFe₂As_{2-x}P_x) show clear indications of nodes, whereas others are fully gapped.

Taken together, the above considerations lead to the idea that the overall symmetry of the superconducting state in iron-based superconductors is *s*-wave symmetry. It still remains to be experimentally established whether this is a conventional *s*-wave state (such as is in MgB₂), which in some cases becomes disrupted (by magnetic or Coulomb interactions) and develops nodes, or an s_{\pm} state, which also may exist with or without nodes, depending on the material. At present, the preponderance of experimental evidence^{7.9} favours an s_{\pm} state, which is also favoured theoretically⁷.

Reproducibly confirming the proposed s_{\pm} symmetry remains the main experimental challenge. Phase-sensitive experiments¹⁵ have provided such confirmation for the superconductivity in copper oxides, which has a *d*-wave symmetry. Given that the *s* and the s_{\pm} state belong to the same rotational symmetry group, it is far more challenging to devise a phase-sensitive experiment to distinguish between them. But, having excluded *d*-wave symmetry, researchers need to prove only that the order parameter in iron-based superconductors changes sign (while not becoming zero anywhere on the Fermi surface). Several experimental designs along these lines have been proposed, and several groups are working to implement these. Within a year or two, the final experimental answer is likely to have been revealed.

So what comes next? Can we invent a new set of rules, Matthias's rules for the twenty-first century? It might be preposterous to think about a general strategy for finding new high- T_c superconductors, given that so far only two such families have been found. But this might be the time to start thinking about it. There are good reasons to believe that proximity to a magnetic transition is essential: magnetism is basically the only quantum coherence phenomenon that commonly occurs at room temperature. The magnetic exchange interaction is basically the only interaction that is strong (on the order of the Fermi energy) and yet does not conflict with electronic itineracy. Proximity to a magnetic quantum critical point ensures the abundance of spin fluctuations that may provide the necessary glue. It also seems important to have a Fermi surface topology that matches the structure of magnetic excitations.

A layered crystal structure may be another not-so-accidental component. One great advantage of a quasi-two-dimensional system is that the density of electronic states that are available for superconductivity depends very weakly on the carrier concentration. Although it is unclear why a low carrier concentration is beneficial, the possibility of changing this parameter provides additional flexibility that is not present in three-dimensional systems. In addition, low-dimensional systems generally fluctuate more, which may also be helpful for superconducting pairing.

The following is my attempt to concoct a set of rules that could replace Matthias's rules. One, layered structures are good. Two, the carrier density should not be too high (compared with, say, conventional metals). Three, transition metals of the fourth period (vanadium, chromium, manganese, iron, cobalt, nickel and copper) are good. Four, magnetism is essential. Five, proper Fermi surface geometry is essential (it must match the structure of the spin excitations). Six, enlist theorists, at least to compute the Fermi surfaces (I hope that theorists are more useful than this but do not dare insist). Note that there is one corollary to these rules. Materials of interest are likely to be complex chemical compounds — work closely with solid-state chemists.

- 1. Pickett, W. E. The other high-temperature superconductors. *Physica B* 296, 112-119 (2001).
- Mazin, I. I. Vitaly Ginzburg and high temperature superconductivity: personal reminiscences. *Physica C* 468, 105–110 (2008).
- Kamihara, Y., Watanabe, T., Hirano, M. & Hosono, H. Iron-based layered superconductor La[O_{1-x}F_x]FeAs (x = 0.05–0.12) with T_c = 26 K. J. Am. Chem. Soc. **130**, 3296–3297 (2008).
- Mazin, I. I. & Antropov, V. P. Electronic structure, electron-phonon coupling, and multiband effects in MgB₂. *Physica C* 385, 49–65 (2003).
- Mazin, I. I., Singh, D. J., Johannes, M. D. & Du, M. H. Unconventional sign-reversing superconductivity in LaFeAsO_{1-x}F_x. Phys. Rev. Lett. 101, 057003 (2008).
- Kuroki, K. et al. Unconventional superconductivity originating from disconnected Fermi surfaces in LaO_{1-x}F_xFeAs. Phys. Rev. Lett. 101, 087004 (2008).
- Mazin, I. I. & Schmalian, J. Pairing symmetry and pairing state in ferropnictides: theoretical overview. *Physica C* 469, 614–627 (2009).
- Lee, P. A., Nagaosa, N. & Wen, X. G. Doping a Mott insulator: physics of high-temperature superconductivity. *Rev. Mod. Phys.* 78, 17–85 (2006).
- Chu, P. C. W. et al. (eds) Superconductivity in iron-pnictides. *Physica C* 469 (special issue), 313–674 (2009).
- Anisimov, V. I., Kurmaev, E. Z., Moewes, A. & Izyumov, I. A. Strength of correlations in pnictides and its assessment by theoretical calculations and spectroscopy experiments. *Physica C* 469, 442–447 (2009).
- Yang, W. L. et al. Evidence for weak electronic correlations in iron pnictides. Phys. Rev. B 80, 014508 (2009).
- Lee, C.-H. et al. Effect of structural parameters on superconductivity in fluorine-free LnFeAsO_{1-v} (Ln = La, Nd). J. Phys. Soc. Jpn 77, 083704 (2008).
- Hosono, H., Matsuishi, S., Nomura, T. & Hiramatsu, H. Iron-based superconducting materials. Bull. Phys. Soc. Jpn 64, 807 (2009).
- Scalapino, D. J. Superconductivity and spin fluctuations. J. Low Temp. Phys. 117, 179–188 (1999).
- Van Harlingen, D. J. Phase-sensitive tests of the symmetry of the pairing state in the hightemperature superconductors — evidence for d_{x2-y2} symmetry. *Rev. Mod. Phys.* 67, 515–535 (1995).

Acknowledgements I dedicate this article to the memory of Vitaly Ginzburg, a relentless enthusiast of high-temperature superconductivity and my former teacher, who passed away while this article was being written.

Author Information Reprints and permissions information is available at www. nature.com/reprints. The author declares no competing financial interests. Correspondence should be addressed to the author (mazin@dave.nrl.navy.mil).