IRON-BASED SUPERCONDUCTIVITY: A NEW GENERATION OF HIGH-T_c MATERIALS

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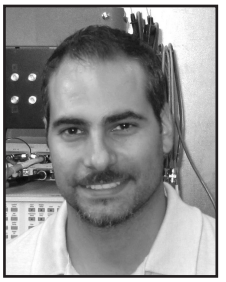
SUMMARY

The stunning discovery of superconductivity in iron-based materials has uncovered a new family of high-temperature superconductors with properties that are both similar to and different than those of the copper-oxide family of superconductors. With transition temperatures approaching the boiling point of liquid nitrogen, these materials promise to provide a rich playground in which to study the fundamentals of superconductivity, while advancing the prospects for widespread technological applications.

Since the discovery of superconductivity by H. Kamerlingh Onnes in 1911, fundamental research has strived to understand the physics behind this fascinating phenomenon, while technology has capitalized on the unique properties of superconductors to enable critical applications to be developed. It is thus fitting to celebrate the centennial anniversary by reporting on recent developments in a new family of superconductors that has reinvigorated interest and motivated a renewed effort to understand and optimize high-temperature superconductivity.

It is without a doubt that iron is one of the most famous, and most useful, materials on earth. But for superconductivity, it was recognized early on that iron, and for that matter all magnetic elements, do not play well with superconductivity due to the spin-singlet nature of the Cooper-paired quasiparticles that make up a superconducting condensate. Thus it seemed surprising when superconductivity was first reported to occur below 2 K in elemental iron near 20 GPa of applied pressure [1], except for the fact that iron transforms to a non-magnetic state under these extreme pressures. In 2006, iron once again surprised us as a superconductivity promoter when bonded with phosphorus in the compound LaFePO, which exhibits superconductivity below a transition temperature $T_c = 4$ K [2].

But the real excitement arose in early 2008 when the same researchers reported a new iron-based material with $T_c = 26$ K in $LaFeAsO_{1-x}F_x$ [3], jump-starting a new field of research that continues in full force today. Being cited close to 2000 times within three years of appearing in print, this seminal work has lead to an explosion of effort aimed at hunting down materials with even higher transition temperatures. The application of external pressure was the first method shown to raise T_c to an astonishing 43 K in the same material [4], but chemical manipulation soon followed using rare earth elemental substitution in the same compound to reach the current record-holding transition temperature of 55 K in $SmFeAsO_{1-x}F_x$ [5] and in $Sr_{1-x}Sm_xFeAsF$ [6] and $Ca_{1-x}Nd_xFeAsF$ [7].



This family of materials has since grown to include well over 50 different compounds identified to show superconducting transition temperatures approaching 60 K. To date, five unique crystallographic structures with tetragonal symmetry at room temperature have been shown to support high-T_c superconductivity — including the simplest α-PbO-type binary element structure, the intermetallic $ThCr_2Si_2$ structure shown in Figure 1, and more complicated quinternary structures composed of elements that span the entire periodic table. The essential component for 20+ K superconductivity in all of these structures is a square lattice of iron atoms with bonds to either phosphorus, arsenic, selenium or tellurium anions that are staggered above and below the iron lattice, resulting in a quasi-two-dimensional tetrahedral-

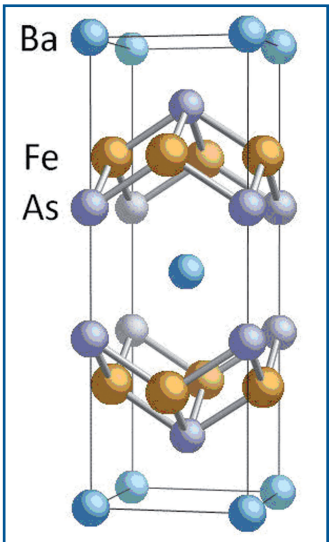


Fig. 1 Atomic arrangement of the iron-based superconducting compounds with $ThCr_2Si_2$-type structure, shown for the intermetallic material $BaFe_2As_2$. The FeAs-type tetrahedrally coordinated layers are the key structural ingredient in all iron-based superconducting materials known to date.

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ly coordinated Fe-As slab that is separated by "filler" ions (*e.g.*, Ba in $BaFe_2As_2$) in some cases and is simply stacked together (*e.g.*, FeSe) in others.

Iron appears to play the key role. While there are indeed superconducting materials based on other transition metals such as Ni [8], iron is the only element that appears to support transition temperatures above a few degrees kelvin. What is it about this ubiquitous element that has once again made it famous? Recent theoretical and experimental efforts have tried to answer this question using a variety of techniques. In particular, the internal chemical structure and nature of bonding in these materials is thought to play a significant role in determining the magnetic and superconducting properties. For instance, long range magnetic order shares a similar pattern in all of the FeAs-based superconducting systems [9], where the iron sublattice undergoes magnetic ordering with an arrangement consisting of ferromagnetically arranged spins along one chain of nearest neighbours within the iron lattice plane, and antiferromagnetically arranged along the other direction. This occurs after these systems undergo an orthorhombic distortion, where the distance between iron atoms with ferromagnetically aligned nearest neighbor spins shortens by ~1%. The origin of this magnetic ordering is a topic of current debate [10], but oscillates between the possibilities of itinerant electron magnetism, involving a spin-density wave order and an electronic structure derived mainly from iron *d*-orbitals, and more localized-type order stemming from magnetic exchange interactions on the iron sublattice.

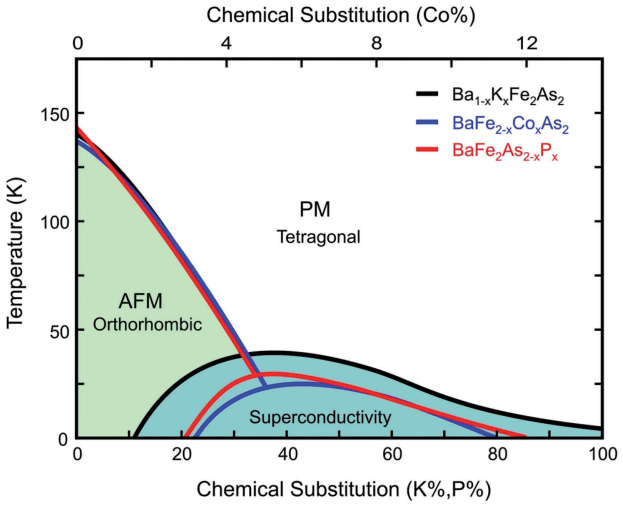

Fig. 2 Phase diagram of iron-based superconducting systems derived from the $BaFe_2As_2$ parent compound, including potassium- (black) [13], cobalt- (blue) [14] and phosphorus-substituted (red) [15] series as shown in the legend. In all cases, antiferromagnetism (AFM) is suppressed as a function of substitution (K, P - bottom scale; Co - top scale) and superconductivity appears over a wide range of substitutions.

Either way, it is clear that this magnetic state must be "destabilized" for superconductivity to take hold. As shown in Figure 2, the generic phase diagram of the iron pnictide materials involves an antiferromagnet/orthorhombic ordered phase that is suppressed in temperature by a tuning parameter involving either the amount of chemical substitution (*i.e.*, x in $Ba_{1-x}K_xFe_2As_2$) or the change in lattice density (*i.e.*, pressure). Before reaching a quantum critical point at absolute zero temperature, this phase transition is interrupted by a superconducting phase that is typically spread over a range of tuning to encompass both magnetic and non-magnetic regions of the phase diagram. The resultant phase diagram, as shown in Figure 2, is strikingly similar to other systems, including the cuprates [11] and several other heavy-electron metals [12].

Because superconductivity appears to be optimal (*i.e.*, reaches the highest value of T_c) near the putative quantum critical point, it is widely thought that the pairing mechanism is intimately related to the fluctuations of the magnetic order parameter. Also recognized as the likely pairing mechanism in other nearly-magnetic superconductors such as the cuprates and heavy-fermion systems, these magnetic fluctuations can indeed provide the spin-1 boson that mediates the interaction between electrons, analogous to how phonons do the same in conventional superconductors. Alternatively, superconductivity may arise from another mechanism and simply benefit from the suppression of long range magnetic order, which is indeed a competing ground state [16]. However, the suppression of superconductivity upon further tuning suggests that magnetism, or at least fluctuations of magnetic order, play a key role in pairing electrons into a coherent superconducting condensate.

In any case, whatever provides the "glue" that binds Cooper pairs together leaves a signature of its symmetry imprinted on the superconducting wave function, or order parameter, giving an experimentally observable property that provides a window into the mechanism itself. Just as electronic clouds surround an atomic nucleus with different symmetries (*i.e.*, *s*-, *p*-, *d*- and *f*-orbitals), paired electrons in a superconducting condensate also take on different symmetries that must respect the parity of their wave function, which is comprised of orbital and spin components. Through nuclear magnetic resonance experiments that are sensitive to local spin properties, the spin component in the iron-pnictides has been established as a singlet state, constraining the orbital component to even symmetry (*i.e.*, *s*-wave, *d*-wave, etc.; see [10] for details).

Unconventional superconductors, defined as those superconductors that break an additional symmetry (beyond the usual gauge symmetry that is broken in every superconducting phase), tend to pair with a lower symmetry than *s*-wave, and can favor certain symmetries that map onto a "directional" type of pairing mechanism, such as in the case of magnetic spin fluctuations that tend to be peaked along a certain momentum direction that favors a *d*-wave superconducting order parameter [17]. The most famous superconductors with *d*-wave orbital symmetry are the

cuprates, but several other superconductors with tendencies toward magnetism also likely harbor a *d*-wave order parameter symmetry driven by magnetic fluctuations [12]. With the simplest *s*-wave gap symmetry unable to explain all of the observed properties of the iron pnictides, a more complicated scenario is required. In particular, circumstantial evidence supports a picture where a change in the sign of the order parameter must occur either directly at the Fermi wavevector (*i.e.*, *d*-wave) or away from it, lying somewhere between plus and minus regions of the order parameter phase (so-called *s*±). In addition, a modulation of the order parameter amplitude can occur such that, even in the *s*-wave case, so-called "accidental" nodes are present on at least some Fermi surfaces. This, in combination with the multi-band nature of the electronic structure, makes for a complicated case to solve in determining the underlying order parameter symmetry.

Thermal conductivity is a powerful tool that can be used to indirectly probe the symmetry of the SC order parameter [18]. Because condensed Cooper pairs share the same quantum mechanical state, and therefore cannot carry entropy, a measurement of thermal conductivity in a superconductor can probe the "leftover" remnants of uncondensed quasiparticle excitations which do transport heat, thus indirectly sensing the influence of the superconducting energy gap. To date, thermal conductivity experiments on iron-based superconductors have produced an interesting diversity of results. In these experiments, both temperature and magnetic field are important parameters with which to probe the remnant quasiparticle excitations: probing the lowest temperatures provides a true measure of the electronic component, while increasing magnetic field allows for a continuous suppression of the superconducting gap. In addition, the directional nature of thermal transport provides an added sensitivity to the momentum dependence of the gap.

Figure 3 exhibits a sample of experiments done on several iron-pnictide superconductors with the 122 structure, with electronic thermal conductivity plotted as a function of reduced magnetic field and normalized to normal state values. As shown, even in this limited set of data for superconductors with the same crystal structure, a widely varying set of characteristics emerges. In particular, the thermal conductivity in the zero-temperature, zero-field limit (*i.e.*, y-axis intercept of Figure 3) has been observed to be both negligible, as expected in a fully-gapped s-wave superconductor, and finite, consistent with the existence of low-lying quasiparticle excitations. These low-energy excitations can emerge from the existence of either a strongly anisotropic gap function, with local minima, or a gap function with zeros, or nodes, where the phase of the order parameter changes sign as a function of momentum. As shown, both types of behaviors are present for materials with similar superconducting properties, providing a clue for determining the underlying order parameter symmetry.

Furthermore, the field evolution is also puzzling, with a wide range of results that span the expectations for slow-rising (*i.e.*, activated), fully-gapped behavior to unconventional, rapidly increasing conduction as a function of magnetic field. This remains as one of the more intriguing results: even within a controlled substitution series, such as in $BaFe_{2-x}Co_xAs_2$, there is a strong variation of the field enhancement of thermal carriers suggestive of a possible doping-dependent evolution of the gap structure. This is consistent with a similar enhancement that is dependent on heat current orientation, providing possible clues to the effects of band structure details on the exact gap structure [20].

Because the T_c values of all of the systems presented in Figure 3 are similar, it is intriguing that the presence or absence of low-energy quasiparticles does not seem to indicate a strong difference in the pairing strength. This is rather uncharacteristic of previous families of superconductors that tend to show either one set of behavior or the other. In the iron-based superconductors, this seems to suggest that the nodes, when present, are not enforced by symmetry constraints, such as found for the *d*-wave order parameter symmetry of the cuprates. However, the superconducting gap of the iron materials does appear to show strong momentum-dependent variations in many properties [10], reflecting a momentum-dependent interaction. All together, these observations point toward the likelihood of the multi-band *s*± state, which can indeed harbor "accidental" nodes that depend on details of the electronic structure, disorder and scattering behavior [23].

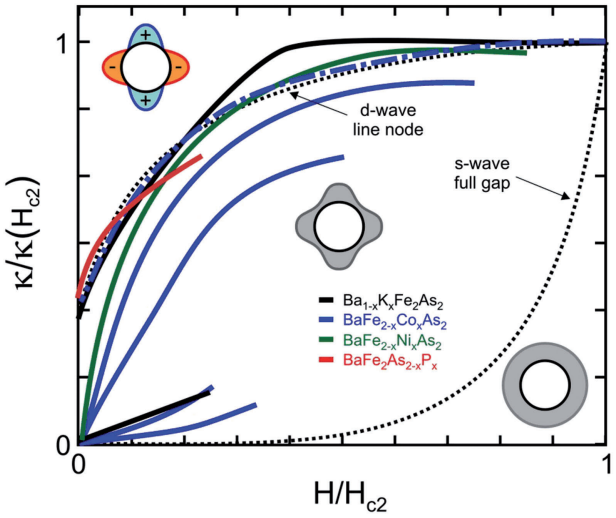

Fig. 3 Low-temperature thermal conductivity (κ) of several iron-based superconducting materials from the $BaFe_2As_2$ family, plotted as a function of magnetic field and normalized on both axes to the normal state values at the upper critical field H_{c2}. Different data sets include K- (black) [19], Co- (blue) [20] (dash-dotted line indicates *c*-axis transport), Ni- (green) [21], and P-substituted (red) [22] compounds. Dotted lines represent expectations for fully gapped and nodal order parameter symmetries, as depicted in the inset graphics for *d*-wave (top), anisotropic *s*-wave (middle) and fully gapped *s*-wave (bottom) symmetries.

Regardless of details, this new family of superconductors has provided a diverse array of materials useful for both the study of fundamental properties and the optimization of parameters relevant for applications. While the cuprates remain in the lead of the high-T_c race, practical applications utilizing cuprate superconductors have been hindered by the non-metallic nature of these oxide materials. However, the iron-based superconductors are bred from, of course, iron, which is a genuine metallic element, and they indeed possess metallic properties more amenable to applications such as wires, magnets and circuits. Although the highest-T_c iron-based superconductors are still composed of a combination of metallic elements and oxygen, researchers are now routinely synthesizing purely metallic 30+ K superconductors such as potassium-doped $BaFe_2As_2$, leaving arsenic as the remaining (toxic) hindrance to widespread application. The latest developments have revealed 30+ K superconductivity in FeSe-based intermetallic materials at ambient pressures [24], providing promise for cheap, workable materials that can be readily adapted to technologies beyond our research laboratories.

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