

Iron-based superconductors

Charles Day

For 22 years ceramic oxides of copper seemed to offer the only way to reach high-temperature superconductivity. Now, a new and unexpected route is being charted: through semimetal compounds of iron.

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Iron, the archetypal ferromagnet, is not supposed to be compatible with superconductivity. Iron's locally polarized spins, all pointing in the same direction, create a magnetic field that would wring apart any Cooper pairs that tried to form. It therefore came as a surprise when, in February of last year, Hideo Hosono of the Tokyo Institute of Technology published the discovery of a superconductor that contains iron:¹ fluorine-doped LaFeAsO (see PHYSICS TODAY, May 2008, page 11).

From the outset, differences and similarities were apparent between the new superconductor and the established exemplars of high- T_c superconductivity, the cuprates. LaFeAsO and the parent compounds of other subsequently discovered Fe-based superconductors all belong to the class of poor conductors known as semimetals; the cuprates' parents are insulators. And although the symmetry of order parameter in the Fe-based superconductors has not been pinned down, the leading contender is an s -wave variant, not a d -wave as in the cuprates. On the other hand, both types of superconductor are layered materials. Antiferromagnetism—or, rather, the weakening of antiferromagnetic order—appears to play a key role in their superconductivity, which is mediated by electron–electron interactions, most likely spin fluctuations.

The new superconductors are captivating theorists and experimenters alike. Since Hosono's discovery, preprints

about them have appeared on the arXiv server at a near-steady rate of 2.5 a day. Those papers document a remarkable explosion of knowledge. Within just two months, physicists, mostly in China, had substituted other rare-earth elements for lanthanum, found optimal electron and hole dopants, and doubled T_c to 55 K. Within six months, LaFeAsO was joined by three other families of Fe-based superconductors that share the first family's iron-containing layers but with different, or no, interlayers.

Meanwhile, physicists around the world have subjected the compounds to the tests they had developed for the cuprates, heavy-fermion, and other types of superconductor: nuclear magnetic resonance (NMR), muon spin relaxation (μ SR), quantum oscillations, angle-resolved photoemission spectroscopy (ARPES), and so on.

For some measurements, the samples' quality, size, or both remain insufficient to discriminate among the theoretical ideas that have sprouted. In the case of the cuprates, it took almost a decade for samples to become good enough to yield a definitive determination of the superconducting order parameter. Nevertheless, after 18 months of near-worldwide investigation, we know a lot about Fe-based superconductors.

Iron pnictides, iron chalcogenides

Although most of the Fe-based superconductors contain ar-

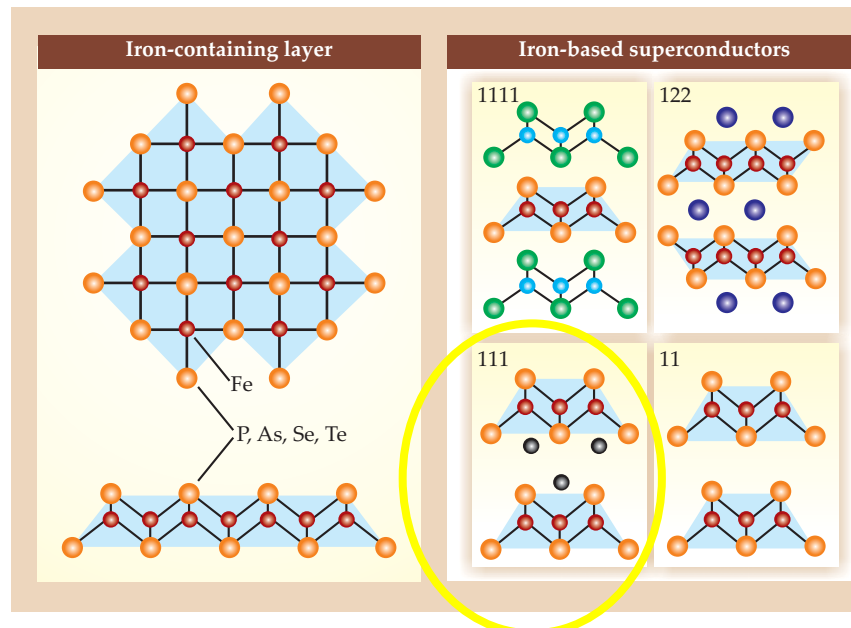


Figure 1. Superconductivity in the new Fe-based materials takes place in a corrugated layer made up of Fe and one of two pnictogens (phosphorus, arsenic) or one of two chalcogens (selenium, tellurium). Four structural families, depicted schematically on the right, incorporate the layer with a characteristically different interlayer. In the 1111 family, the interlayer consists of a rare earth (blue) and oxygen (green); in the 122 family, an alkaline earth (violet); and in the 111 family, an alkali (gray). There's no interlayer in the 11 family; to preserve the layer's charge balance, the pnictogen is replaced by a chalcogen. (Adapted from K. Ishida, Y. Nakai, H. Hosono, *J. Phys. Soc. Jpn.* **78**, 062001, 2009.)

Discovering new superconductors in old materials

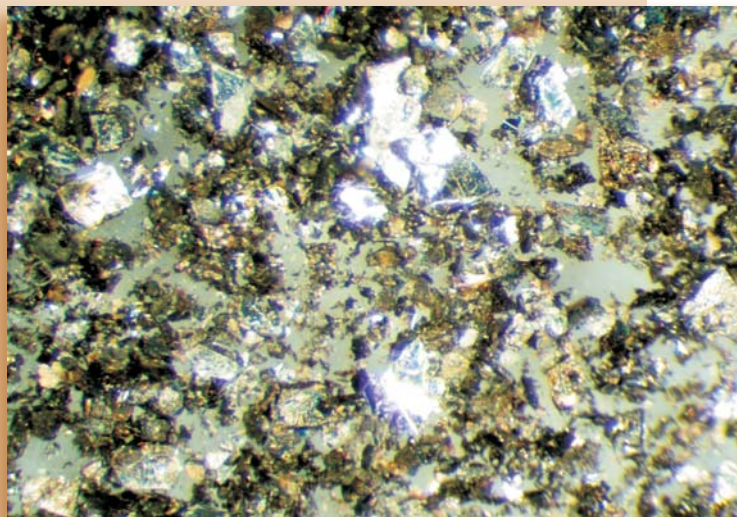
Finding new superconductors was not Hideo Hosono's primary goal when he synthesized LaFeAsO in 2007. He and his group from the Tokyo Institute of Technology were trying to find transparent semiconductors for use in computer screens and other display devices. That search turned up a promising family of materials based on LaOCuCh, where Ch represents a chalcogen (sulfur, selenium, or tellurium).

Discovering a transparent semiconductor with magnetic properties was Hosono's next goal. Replacing Cu with Fe or another open *d*-shell transition metal could provide the magnetism, but at the cost of lowering the lattice's net valence and destabilizing its structure. To restore the valence, he replaced a divalent chalcogen with a trivalent pnictogen (phosphorus, arsenic, or antimony). The Tokyo Tech team found that LaFePO superconducts at 4 K and fluorine-doped LaFeAsO superconducts at 26 K. A new front in the struggle to understand high- T_c superconductivity had opened up.

Dirk Johrendt of Ludwig-Maximilians University in Germany suspected in the mid-1990s that SrRh₂P₂ and SrCo₂P₂ might be superconductors, based on their proximity to an electronic instability. Johrendt was put off pursuing those and other 122 compounds by their ferromagnetism, which is generally hostile to superconductivity. When he heard of Hosono's discovery, he recalled a 1980 paper that reported the structure and basic properties of BaFe₂As₂ and other ternary arsenides. The resemblance of BaFe₂As₂ to LaFeAsO encouraged Johrendt and his students to look for superconductivity. Their first attempt,¹³ doping with 40% potassium, yielded a superconductor with a T_c of 38 K. The photo shows crystals of BaFe₂As₂ from Johrendt's lab.

Three groups on three continents discovered the next family more or less simultaneously, but by pursuing different search strategies. Paul C. W. Chu of the University of Houston and his colleagues had been working on the alkali-doped 122 compounds. Would 100% doping raise T_c , they wondered? It doesn't. Although the 122 structure survives the heavy doping, T_c plummets to 3.5 K. A different structure with 111 stoichiometry is also stable; LiFeAs and NaFeAs turned out to be superconductors.¹⁴ Simon Clarke of Oxford University in England sought new Fe-based superconductors by combing through the Inorganic Crystal Structure Database for compounds that contain iron arsenide

layers. The search turned up LiFeAs.¹⁵ Robert Juza had synthesized the compound 40 years ago, but its superconductivity had been overlooked. Meanwhile, at the Institute of Physics in Beijing, Changqing Jin wanted to find an Fe-based superconductor



that his colleagues were not already working on. Drawing on his experience with cuprates, he reasoned that the simplest way to balance the valence of the Fe–As layers would be to interleave them with Li or Na.¹⁶

Safety regulations were responsible in part for the discovery of the simplest 11 family. Maw-Kuen Wu was barred from working with arsenic by his home institution, the Academia Sinica's Institute of Physics in Taipei, Taiwan. In essence, he and his collaborators took Jin's approach one step further. They balanced the valence of the Fe–As layer by removing monovalent Li and replacing trivalent As with divalent—and less toxic—selenium.¹⁷ The iron selenide superconductor has a formula of Fe_{1.01}Se, reflecting the structure's slight Fe excess.

Very recently, IoP's Haihu Wen and his collaborators synthesized the first member of what could become a new family.¹⁸ Its chemical formula is Sr₂VO₃FeAs and its T_c is 37.2 K.

senic, some contain phosphorus, which comes from the same pnictogen (or nitrogen) group of the periodic table. Others contain selenium or tellurium from the chalcogen (or oxygen) group. Experiments and theory agree that the superconducting electrons in all the Fe-based superconductors flow in the planes that contain Fe. Despite the compositional variety, the planes have the same structure from material to material.

Figure 1 shows the plane's structure along with the structures of the four families found so far that exhibit superconductivity. Those families are named after the stoichiometries of their parental prototypes: 1111 (LaFeAsO), 122 (BaFe₂As₂), 111 (LiFeAs), and 11 (FeSe). Their respective discoveries are recounted in the box above.

The iron-containing plane is not flat; pnictogen (*Pn*) or chalcogen (*Ch*) atoms protrude above and below the plane. Because the *Pn* and *Ch* atoms are much larger than Fe atoms, they pack themselves in edge-sharing tetrahedra. By contrast, the smaller size difference between the copper and oxygen atoms in a cuprate superconductor leads to corner-sharing octahedral packing. That structural difference is crucial. Thanks to their tetrahedral configuration, the Fe atoms in an

Fe-based superconductor are closer to each other than the Cu atoms are in a cuprate superconductor. Both Fe and Cu occupy the same row of the periodic table. Their valence electrons occupy 3*d* orbitals. But because of the Fe atoms' closer packing, all five Fe 3*d* orbitals contribute charge carriers. In the cuprates, only one Cu 3*d* orbital contributes.

The *Pn* and *Ch* atoms also play a role. Their *p* orbitals hybridize with the five Fe 3*d* orbitals, leading, as figure 2 shows, to a complicated electronic band structure and a characteristic, multicomponent Fermi surface. Like graphite, boron nitride, and other semimetals, the Fe-based superconductors have electron and hole bands. In momentum space, electrons at the Fermi level occupy two tubes centered on the M point (the center of an edge in the Brillouin zone), while the holes occupy two or more tubes at the Γ point (the origin of the Brillouin zone).

Tubes in momentum space correspond to planes in real space. Superconductivity in the Fe-based superconductors is largely two-dimensional, although less so than in the cuprates. The admixture of three-dimensionality, which arises from interlayer coupling, makes the materials

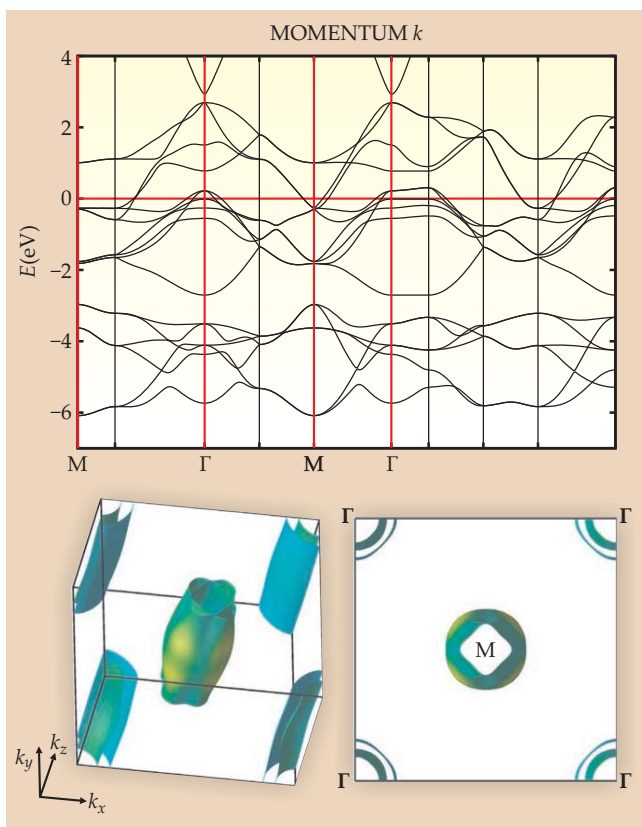


Figure 2. The band structure of iron selenide (top) is complex and typical of the other Fe-based superconductors. All five of Fe's 3d orbitals make contributions (black lines) to the Fermi level ($E = 0$). The Fermi surface of FeSe (bottom) is also typical. Holes occupy two more-or-less cylindrical surfaces around the Γ point; electrons occupy two more-or-less cylindrical surfaces around the M point. The Fermi surfaces of the cuprates are simpler: just a single electron or hole cylinder. (Adapted from A. Subedi, L. Zhang, D. J. Singh, M. H. Du, *Phys. Rev. B* **78**, 134514, 2008.)

potentially more useful in devices and other applications.

The Fe-based superconductors and cuprates are different in another respect: chemical substitution. In the 1111 family, for example, dopants can be inserted at any of the four ionic positions, even into the iron layer. By contrast, chemical manipulation of the copper layer in the cuprates proved severely detrimental to their superconductivity.

Out of the normal

Superconductors often require chemical doping or external pressure either to become superconducting in the first place or to raise T_c . Condensed-matter physicists therefore talk of superconductivity as emerging at T_c from the so-called normal state of the undoped parent. Studying the normal state not only provides clues about what causes the superconductivity, it's also easier. Doping complicates sample preparation; pressurization complicates experiments.

One of the key normal-state properties of the Fe-based superconductors was described in Hosono's original discovery paper. As undoped LaFeAsO is cooled, its resistivity ρ more or less retains the room-temperature value of 8 m Ω cm until the temperature reaches 150 K. At that point, ρ abruptly drops, as if the material undergoes a phase transition. BaFe₂As₂ and the other parents have a similar anomaly.

Neutron-scattering experiments probed the structural and magnetic changes that accompany the transition.² At 155 K and below, LaFeAsO gives up its tetragonal space group in favor of the less symmetrical orthorhombic space group. At 137 K, electrons organize themselves into a spin density wave. The spins align parallel to the Fe-As plane in stripes of alternating head-to-head, tail-to-tail pairs. The SDW shows up in the undoped parents of the other Fe-based superconductors and was predicted by theory. Although the structural transition precedes the SDW, various theoretical approaches point to magnetism as the structural transition's instigator.

The presence of a magnetic transition is consistent with the widespread view that superconductivity occurs close to an instability of some kind. In an undoped parent, lowering the temperature causes antiferromagnetism or some other ordered electronic state to form. The ordered state is stable and becomes more so as the temperature nears absolute zero. Doping the parent destabilizes the ordered state, turning a stable, rigid configuration into an unstable, flexible configuration that supports fluctuations. At optimal doping, the fluctuations acquire the properties needed to mediate electron pairing and give rise to superconductivity at the material's highest T_c . Overdoping, like loosening a guitar string until it's slack, makes the state floppy and the fluctuations too weak to mediate pairing. To many physicists, it looks as though the SDW is the state whose induced instability leads to superconductivity in the Fe-based materials.

Evidence for that point of view comes from NMR experiments. Freely precessing nuclear spins relax at a rate that depends in part on the electron spins that surround them. The more low-energy fluctuations the electrons support, the faster the nuclear spins will relax and the shorter will be the so-called spin-lattice relaxation time, τ_1 . The fluctuations typically become stronger as the temperature drops, but they disappear when antiferromagnetism sets in and freezes the spins.

Figure 3 shows how a proxy for the strength of spin fluctuations, $1/\tau_1 T$, depends on T for BaFe₂As₂ electron-doped to various values by replacing barium with cobalt. At zero doping, the spin fluctuations remain constant until the SDW appears at 135 K. Increasing the doping to 2% and then to 4% boosts the fluctuations, but they also succumb to the formation of the SDW, albeit at lower temperatures. The fluctuations weaken as the doping level approaches, attains, and then surpasses the optimal value of 8%. If the spin fluctuations are to mediate superconductivity, they must be just right: neither too strong nor too weak.

Gaps, nodes, and symmetries

Identifying the pairing mediators in the Fe-based superconductors is a necessary but far from sufficient step toward a full understanding of the materials' superconductivity. Electrons in crystals are confined to bands shaped by the lattice's constituent atoms and crystal structure. In the superconducting state, which is an intrinsically many-body state, the electrons must also obey Hund's and other quantum rules. Those restrictions on electrons' freedom of movement and association dictate perhaps the most eagerly sought characteristic of a new superconductor: its pairing symmetry.

The pairing symmetry consists of a phase and an amplitude, which is known as the superconducting energy gap. The wider the gap, the harder it is to break apart the Cooper pairs and destroy the superconducting state. Gaps are not necessarily uniform. They can vary in size around the Fermi surface and can even close at nodal points or lines.

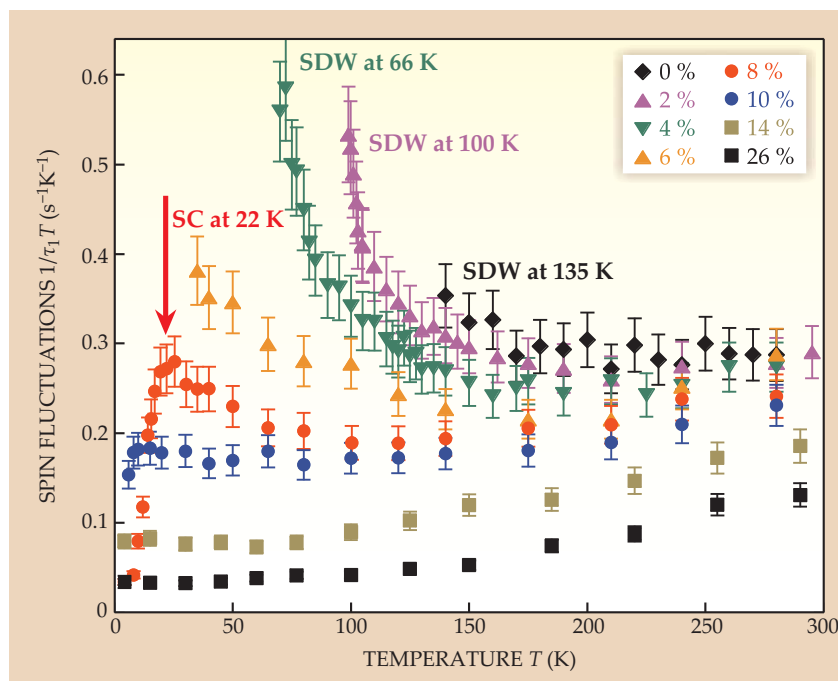


Figure 3. Nuclear magnetic resonance probes electron spin fluctuations, thanks to their influence on the rate, $1/\tau_1$, at which the nuclear spins relax. Ordinarily, the relaxation rate $1/\tau_1$ is proportional to temperature T . Dividing the rate by T emphasizes the presence or absence of coherent, many-body states such as antiferromagnetism or superconductivity. The plots shown here reveal how the fluctuations' strength varies with temperature and doping level in cobalt-doped BaFe_2As_2 . At zero or suboptimal doping, the fluctuations strengthen with decreasing temperature until a spin density wave (SDW) forms. The fluctuations also strengthen at optimal doping (8%), but then weaken sharply after the onset of superconductivity (SC). Overdoped samples show little change. (Adapted from F. Ning et al., *J. Phys. Soc. Jpn.* **78**, 013711, 2009.)

Theorists typically predict the pairing symmetry by starting with the band structure. Then they apply one of several approximations to handle the mutually interacting electrons and identify the fluctuations most likely to promote pairing. The final step is to select the pairing symmetry that is consistent with both the nature of the fluctuations and the shape of the Fermi surface.

The Fe-based superconductors do not yield easily to that approach. A calculation must handle not only five hybridized $3d$ orbitals but also a complication that arises from the semimetallic nature of the parent compounds: Do the pair-mediating fluctuations arise on local lattice sites, as they would in an insulator, or do they arise from freely roaming electrons, as they would in a metal? That question is one of the most contested among theorists. At least for one parent compound, CaFe_2As_2 , neutron-scattering studies reveal that both ranges of motion are present in a complicated mix.³

On the experimental front, the challenges are different. If the gap is open across the entire Fermi surface, then, as the temperature approaches absolute zero, electrons become harder to excite across the gap. A host of measurements, such as heat capacity and penetration depth, probe that excitation behavior, which manifests itself as an exponential dependence on temperature. But if the gap has nodal points or lines, some electrons will always make it across the gap, even at 0 K. A power law or other nonexponential temperature dependence results.

Those tests measure the momentum-averaged gap. Applying them to Fe-based superconductors is challenging because five bands cross the Fermi level, not one as in the cuprates. ARPES, by contrast, directly measures the momentum dependence by firing photons at the sample surface and measuring the momentum dependence of electrons kicked out of the sample. To work, ARPES requires single crystals whose surfaces represent the bulk.

Not all the measurements agree with each other, either within or among techniques, possibly because of differences in samples. Heat capacity and penetration depth measurements favor a nodeless gap. NMR relaxation rate measurements appear to favor nodes, but can be reconciled with

ARPES measurements, which favor a gap that is isotropic along any particular Fermi surface but varies significantly in size among different Fermi surfaces.⁴

Despite their respective limitations, experiment and theory appear to be coalescing around a single theoretical picture. None of the Fe-based superconductors has a nodeless, uniform gap like that of mercury, lead, or other materials whose phonon-mediated superconductivity is described by Bardeen-Cooper-Schrieffer theory. Some materials, like F-doped LaFeAsO and the 122s, have two nodeless gaps; other materials, like LaFePO appear to have nodes.

Phase-sensitive measurements based on the Josephson effect directly probe the parity of the order parameter—that is, whether the symmetry is singlet (s -wave or d -wave) or triplet (p -wave). They can also determine any phase changes that occur in the order parameter as a function of angle in momentum space. The two phase-sensitive experiments reported so far rule out triplet pairing and, like the phase-insensitive measurements, rule out a simple, BCS-style s -wave.^{5,6} They also rule out the particular flavor of d -wave, $d_{x^2-y^2}$, found in the cuprates.

What does that leave? Soon after F-doped LaFeAsO made its debut, Igor Mazin and Michelle Johannes of the Naval Research Laboratory in Washington, DC, and David Singh and Mao-Hua Du of Oak Ridge National Laboratory in Tennessee proposed⁷ what now appears to be the leading contender, a pairing symmetry known as s^\pm . Cooper pairs are often likened to dancing couples who circle each other, not face to face but separated by other couples dancing in the same way. In s^\pm pairing, two different sets of Fermi surfaces are involved. Each by itself is conventional, but with a phase difference of π , so the sign of their order parameters is opposite. In the dancing analogy, each member of each couple is on one of two separate dance floors. The s^\pm pairing isn't new. Mazin and others had proposed it in the context of cuprates, but, interestingly, the original dates from the early 1970s. Arkady Aronov and Edouard Sonin proposed it for superconductivity in semimetals.⁸

Certain d -wave symmetries are also consistent with both the experimental data and the calculated band structures. It's

possible that a particular Fe-based superconductor chooses s^{\pm} or one of the d -wave symmetries depending on the details of the material. Evidence, too, is building for an essential ingredient in s^{\pm} pairing: interband scattering. A neutron-scattering experiment on potassium-doped BaFe_2As_2 found a key resonance that appeared (in reciprocal space) not across the diagonal of the Brillouin zone, as in the cuprates, but along an edge, indicating scattering between adjacent Fermi-surface tubes.⁹ ARPES also reveals interband coupling. By driving the doping far above and below its optimal value, Hong Ding of the Institute of Physics in Beijing finds that the Fermi surfaces that participate in interband pairing in the superconducting state disappear along with the superconductivity.¹⁰

The highest T_c in the Fe-based superconductors, 55 K, is held by fluorine-doped SmFeAsO and was reported by IoP's Zhongxian Zhao and his collaborators in March 2008.¹¹ Since that milestone, T_c has not increased. An empirical correlation suggests that T_c depends on the Fe–As bond angle.¹⁰ Kazuhiko Kuroki of the University of Electrocommunications in Tokyo and his collaborators have recently analyzed the superconductivity of the 1111 compounds and found, consistent with observations, that both T_c and the presence or absence of nodes do indeed depend on Fe–As bond angle or, more specifically, on the height of the pnictogen or chalcogen above the Fe plane.¹² Their analysis also purports to explain why the gaps of some materials have nodes and others do not.

Unfortunately, for the 1111 family at least, the Fe–As bond angle seems to reach an optimum with the samarium member. That potential dead end has not deterred experiments from developing epitaxially grown thin films, which might prove useful in eventual applications. Standard growth methods are not effective. Still, by modifications, Hosono and his collaborators have succeeded¹³ in growing superconducting films of SrFe_2As_2 .

Whether or not the Fe-based superconductors prove technologically useful, they have certainly rejuvenated the field of high- T_c superconductivity. Funding agencies in Germany and Japan have inaugurated new streams of money for research into the new superconductors. The excitement may not be as high as when the cuprates made their debut in 1986, but progress has been faster.

References

1. Y. Kamihara, T. Watanabe, M. Hirano, H. Hosono, *J. Am. Chem. Soc.* **130**, 3296 (2008).
2. C. de la Cruz et al., *Nature* **453**, 899 (2008).
3. J. Zhao et al., *Nat. Phys.* (in press).
4. H. Ding et al., *Europhys. Lett.* **83**, 47001 (2008).
5. X. Zhang, Y. S. Oh, Y. Liu, L. Yan, K. H. Kim, R. L. Greene, I. Takeuchi, *Phys. Rev. Lett.* **102**, 147002 (2009).
6. C.-T. Chen, C. C. Tsuei, M. B. Ketchen, Z.-A. Ren, Z. X. Zhao, <http://arxiv.org/abs/0905.3571>.
7. I. I. Mazin, D. J. Singh, M. D. Johannes, M. H. Du, *Phys. Rev. Lett.* **101**, 057003 (2008).
8. A. G. Aronov, E. B. Sonin, *Sov. Phys. JETP* **36**, 556 (1973).
9. A. D. Christianson et al., *Nature* **456**, 930 (2008).
10. T. Sato et al., <http://arxiv.org/abs/0810.3047>.
11. Z. A. Ren et al., *Chin. Phys. Lett.* **25**, 2215 (2008).
12. K. Kuroki, H. Usui, S. Onari, R. Arita, H. Aoki, *Phys. Rev. B* **79**, 224511 (2009).
13. M. Rotter, M. Tegel, D. Johrendt, *Phys. Rev. Lett.* **101**, 107006 (2008).
14. J. H. Tapp, Z. Tang, B. Lv, K. Sasmal, B. Lorenz, P. C. W. Chu, A. M. Guloy, *Phys. Rev. B* **78**, 060505 (2008).
15. M. J. Pitcher et al., *Chem. Commun. (Cambridge)* 5918 (2008).
16. X. C. Wang, Q. Q. Liu, Y. X. Lv, W. B. Gao, L. X. Yang, R. C. Yu, F. Y. Li, C. Q. Jin, *Solid State Commun.* **148**, 538 (2008).
17. F.-C. Hsu et al., *Proc. Natl. Acad. Sci. USA* **105**, 14262 (2008).
18. X. Zhu et al., <http://arxiv.org/abs/0904.1732>. ■