

Figure 2 | **Chordates and vertebrates.** The chordates contain invertebrate groups (amphioxus and tunicates) and vertebrate groups (the jawless vertebrates, such as the lamprey, and the jawed vertebrates or gnathostomes). Amphioxus is the most 'basal' of chordates, a conclusion¹¹ confirmed by the draft genome sequence of *Branchiostoma floridae*¹. The closest non-chordate invertebrate relatives of amphioxus are the hemichordates (acorn worms and their allies) and echinoderms (sea urchins and allies).

'synteny' with vertebrate genomes, including the human genome. This shared possession of similar blocks of genes (even though the genes within each block might have been shuffled substantially) is notable, given that the last common ancestor of the amphioxus and vertebrates lived more than 550 million years ago. More remarkable still is the presence of modest amounts of sequence homology between stretches of non-protein-coding DNA in humans and the amphioxus. This information suggests that whatever the common ancestor of all chordates looked like, its genome was similar to that of a modern amphioxus. Such findings also illustrate the degree of morphological and genomic divergence of tunicates from the chordate lineage. Although sequence homology shows tunicates to be more closely related to vertebrates than is the amphioxus¹¹, their unique pattern of development has been accompanied by dramatic genomic rearrangements and losses of both coding and non-coding stretches of DNA.

This extensive synteny has allowed substantive insight into a suspected episode in the early history of vertebrates when the genome underwent tetraploidization (that is, became quadrupled). Work on the amphioxus shows that this episode - or two closely linked episodes of diploidization, one following hard on the heels of the other — occurred at around the time that the lineage of jawless vertebrates, now represented by forms such as the lamprey (Petromyzon), emerged. The extent to which this genomic storm was manifested in the origin of morphological novelty is not known. Yet it is not unreasonable to suggest that it was connected with the origin of gnathostomes -vertebrates with jaws and paired limbs. This is a subject that is little explored as yet, but is likely to be the subject of revelations in coming years, both from genomics and from the discovery of fossil forms.

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Prospecting for an iron age

Paul M. Grant

Different material options for high-temperature superconductivity — conduction of electricity with little or no resistance at 'practical' temperatures — have arrived. Iron compounds are the latest thing.

High-temperature superconductivity is back in the public eye, and with a bang. But as ever with this topic, we must first journey back to 1986 and 1987, and to Georg Bednorz and Alex Müller¹, and Paul Chu and his colleagues². To start with, there was the headline news¹ of the onset of superconductivity in a previously unexplored class of compounds, the copper oxide perovskites, or layered cuprates, at the then record-setting temperature of 35 kelvins. Shortly afterwards², this transition temperature (T_c) was pushed up to 90 K — beyond the temperature of liquid nitrogen.

The initial announcement prompted practically every superconductivity centre on the planet, including my own home lab at IBM Almaden, to ransack the periodic table hoping to strike pay dirt again. So frantic became the search that Tom Lehrer's 1950s classic *The Elements* was chosen as the theme song for a 1988 BBC Horizon documentary, *Superconductor* — *Race for the Prize*. Special attention was paid to oxides of the first-row transition metals, running from scandium to zinc, with iron compounds among them, in the hope that a companion to copper would emerge. Alas, although the ensuing years saw the transition temperatures climb to 135 K by 1993 (165 K under pressure), that hope remained unfulfilled. The central cation remained copper, complexed in a plane of nearest-neighbour oxygen anions. And the dream of superconductivity at anything close to room temperature, around 300 K, has remained just that.

It now seems we should have looked not only at the transition-metal oxides but also at the transition-metal pnictides - compounds that contain elements from group V (now group 15) of the periodic table, such as nitrogen, phosphorus and arsenic. In mid-May of 2006, a Japanese collaboration³ reported superconductivity with $T_c \sim 5 \text{ K}$ in a compound of stoichiometry originally $La(O_{1-x}F_x)FeP$, consisting of alternating layers of lanthanum-series oxyfluorides and tetrahedrally coordinated ferrous pnictide (Fig. 1). By January 2008 the same group⁴ had lifted T_c to 26 K on substituting arsenic for phosphorus, and in April that was raised⁵ to 43 K, albeit under an applied pressure of 4 gigapascals. In the meantime, the appearance of papers on the preprint server arXiv posted by a collaboration in China sparked rumours of a T_c of 54 K in $Sm(O_{1-x}F_x)$ FeAs. Late last month, that group published a paper⁶ describing a T_c of 53.5 K in a pnictide with gadolinium in the lanthanum position.

The increase of T_c in the ferrous pnictides from 2006 and its acceleration since January 2008 is reminiscent of the 'hockey stick' graph seen two decades earlier for increasing T_c in the layered cuprates. Over the past four months, the pnictides have spawned unprecedented numbers of submissions to the condensed-matter part of the arXiv site, sometimes three a day. Most of these contributions are theoretical in nature (theory being a much safer pursuit than experiment, at least physically, especially when a synthesis involving arsenic compounds is concerned), bringing to mind a comment by the late Pierre de Gennes. At a conference that followed the discovery of high T_c , de Gennes admitted that all theoreticians have a "clothes closet" of favourite "models, or suits ... used, unused and over-under-sized", and that when some new superconductor is found they will pull one out, try it on, and "see if it fits".

Where do we go from here? Well, to start with we can see several striking similarities between the ferrous pnictides and the layered copper oxide perovskites. First, both are layered systems. Second, the Ln–O–F layers provide 'charge reservoirs' for doping; they also sterically reduce the overall symmetry with respect to the intervening ferrous pnictide transport planes, quite possibly driving 'Jahn–Teller-like' phonon-driven instabilities. Third, both systems are, to varying degrees, spin-correlated,

NEWS & VIEWS

quasi-two-dimensional, Mott–Hubbard charge transfer antiferromagnetic insulators in their undoped ground state. These last three properties are believed to be key to high-temperature superconductivity, and are about the only criteria on which you can find (almost) universal agreement among those trying to choose between the bespoke fashions hanging in the high- T_c theoretical closet.

However, observe in Figure 1 that the Fe ions, although nominally Fe²⁺, analogous to Cu²⁺, are tetrahedrally coordinated relative to the pnictide anions, as opposed to the square-planar symmetry of the copper oxide compounds. In the first-row transition metals — scandium to zinc — there are ten *d*-electron states (five described by orbital momentum), each of which can hold two electrons with one spin up and another down. We can play with these states to build various cationic configurations. A simple vardstick, called Hund's rule, helps build possible combinations in isolated atoms and ions. It says we have to start filling from the bottom, first occupying each orbital with an up-spin and then starting over again with spin-down, until all available *d*-electrons are consumed. Thus Fe^{2+} , with six electrons at large, will result in a ground state one electron in excess of a half-filled Hund's occupation distribution, and Cu²⁺, with nine electrons to spend, will yield one electron fewer (a 'hole' or effective positive charge) than a filled *d*-orbital shell. Therefore, in a very crude sense, the new FeAs superconductors can be thought of as the electron analogues of the hole-transporting CuO complexes, and both measurements and theoretical studies bear this out.

The real situation is far more complex than just stated, and simple Hund's rule arguments are confounded by symmetry, position and overlap of neighbouring anions $(O^{2-}, As^{-(3-x)})$, and by Coulomb repulsion that tends to separate spins in otherwise 'Pauli-allowed' cation states from the next nearest cation neighbour. The trade jargon for these effects is 'crystal field splitting', 'hybridization' and 'Hubbard U', respectively. You can be assured each of these is currently undergoing intense exploration. All this notwithstanding, the simple Hund's rule picture that the ferrous pnictides and copper oxides are electron-hole 'duals' may not be simply fortuitous. It may be the reason that, after years of intense searching, nickel and cobalt complexes have not yielded high-temperature superconductors (at least not yet).

In fact, with T_c now at 55 K, are these ferrous pnictides truly 'high-temperature superconductors'? Simply answered, we don't know at present. But it is useful to remember that the expression 'high-temperature superconductivity' did not originate with Bednorz and Müller's paper¹ of 1986. Those who, like myself, are of mature years will recall that this description was coined as a result of studies^{7,8} in the 1960s that superconductivity mediated by electron–



Figure 1 | **The unit cell of LaOFeP.** In this generic example³ of the family of lanthanum-series oxyfluoride ferrous pnictides, the overall cell charge is neutral but the individual layers are not, implying electron doping of the FeP layer. Note also that the P coordination of Fe is tetrahedral, not square planar as is the case for the high- T_c copper oxide perovskites. (Reproduced from ref. 3.)

phonon pairing would top out at around 30 K, and compounds showing anything above this value would be referred to as 'high-temperature materials'. Although the mechanism of high T_c in the copper oxide perovskites remains in question, we do have evidence⁹ in MgB₂ that electron–phonon coupling can achieve a transition temperature of 40 K. Is 55 K really that much higher?

Although most of the theoretical tailoring for the various ferrous pnictides is styled after fashions for the cuprate superconductors, one experimental study harks back to much earlier designs. Chen et al.¹⁰ report direct measurement of the superconducting energy gap and its temperature dependence in polycrystalline samples of Sm(O_{0.85}F_{0.15})FeAs, with $T_c = 42$ K. The technique used is called Andreev spectroscopy. This is a variant of tunnelling spectroscopy whereby, at a contact between a normal metal and a superconductor, an electron from the metal injected into the superconductor at energies lower than the superconducting gap gives rise to a superconducting pair (Cooper pair of electrons of opposite spin), which are subsequently spin-charge compensated by a 'reflection' of positive polarity (a hole) back into the normal metal. The resulting current-voltage dependence is a direct measurement of the superconducting pairing energy.

Astonishingly, Chen *et al.*¹⁰ find that their results best fit the time-honoured Bardeen– Cooper–Schrieffer (BCS) theory¹¹, the breakthrough in the mid-twentieth century that solved the riddle of superconductivity in all materials available up to that time. Although originally formulated to accommodate the pairing of electrons mediated by lattice vibrations (phonons), in its broadest sense the BCS framework can encompass pairing

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of fermions in a boson field — perhaps even the 'flavours' found in neutron stars, quarks and gluons, giving rise to 'colour' superconductivity at the relatively low cosmological temperature of 10⁹ (the units don't matter). So Chen and colleagues' identification of classic BCS behaviour does not rule out the possibility that some more exotic bosonic glue than phonons might be behind superconductivity in these ferrous pnictides.

Whenever a new superconductor with a T_c higher than 30 K appears on the scene, I inevitably get asked if it will bring applications closer. The question is perhaps more pertinent when the material involves particularly noxious elements such as arsenic. My answer is always "Just follow the money." If the pot at the end of the rainbow has enough gold inside (and so far it does not for applied superconductivity), the environmental issues can be overcome. I give you semiconductor manufacture and processing, which uses some of the most toxic compounds (including arsenides) in creation, yet is tolerated and brought under control because its financial return is in the trillions. Again, the units don't matter.

Will T_c in the pnictides continue to go up, and perhaps double or triple as happened in 1987–88? I doubt it. We've now been on standby for several months, and to my mind the best hope is that the discovery of pnictide high-temperature superconductivity will help us understand better the physics of the cuprates. The iron age has yet to dawn. Paul M. Grant is at W2AGZ Technologies, 1147 Mockingbird Hill Lane, San Jose, California 95120, USA.

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Correction

The News & Views article "Genomics: Protein fossils live on as RNA", by Rajkumar Sasidharan and Mark Gerstein (*Nature* **453**, 729-731; 2008), contains the following incorrect statement: "..."reads' found using the Solexa sequencing technology^{1,4} can be intersected with some seven pseudogenes, for an average of roughly two reads each." In fact, these reads intersected with some 70 pseudogenes, for an average of roughly 12 reads each. Also, in the text of Box 1, 'nt' (nucleotide) was omitted from one passage, which should read "...to -27 nt Piwi-interacting RNAs (piRNAs)." These corrections have already been made to the online versions of this article.