

the superconducting critical temperature,  $T_c$ , reaches its maximum value, which is suggestive of an intimate connection between the two types of order. (Similar behaviour is also observed in the systematic doping study of another iron pnictide,  $\text{LaFeAsO}_{1-x}\text{F}_x$  (ref. 3), hinting that this behaviour may be generic in iron pnictides.) A similar structural phase diagram is seen in at least some materials in the cuprate family (for example  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ ). The most interesting comparison, which was not made by Zhao *et al.*, is to measurements on the underdoped cuprate superconductor YBCO, which imply the existence of an electronic nematic phase<sup>4</sup> with a critical temperature that vanishes, seemingly at a quantum critical point, somewhere under the superconducting dome, as illustrated by the green line in Fig. 1b. (A nematic phase, like the phase below  $T_0$  in the iron pnictides, is one that spontaneously breaks the square symmetry of the underlying ideal crystal, resulting in a rectangular (or related) symmetry in which the  $a$  and  $b$  axes are inequivalent.)

The correspondence between the roles of the structurally distorted phase in  $\text{CeAsFeO}_{1-x}\text{F}_x$  and the nematic phase

in YBCO is one of the potentially most important aspects<sup>5,6</sup> of the Zhao *et al.* paper. However, partly because various cuprates have different crystal structures to begin with, and partly because there have been so many studies of these materials, the number of transition and crossover lines that have been identified in the phase diagram of the cuprates is enormous, as is illustrated in Fig. 1b. If one looks hard enough, one can find in the cuprates something that is reminiscent of almost any interesting phenomenon in solid state physics.

The work of Zhao *et al.* offers no new information concerning the internal symmetries of the superconducting state. Some experiments, which find evidence of residual gapless ('nodal') quasiparticle excitations at low temperatures, indicate that it has  $d$ -wave symmetry (as does the superconducting state in the cuprates), and some indicate that it has a full gap, suggestive of a more conventional  $s$ -wave symmetry. Intriguingly, it has recently been suggested<sup>7-9</sup> on theoretical grounds that the superconducting order has an 'unconventional'  $s$ -wave symmetry, with an order parameter that changes sign in going from one Fermi surface pocket

to another. At the most basic level, the pairing symmetry may be less important than whether the order parameter changes sign as a function of momentum. Any unconventional order is plausibly related to strong local repulsions between electrons. In contrast, a conventional  $s$ -wave order most probably indicates that the pairing arises from induced attractions between electrons, as in conventional low-temperature superconductors. Clearly, the strength of the analogy between the two families of high-temperature superconductor will be much clearer when the symmetries of the superconducting state in the iron pnictides have been established.

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## MATERIAL WITNESS

### Juggling with liquids



Liquids aren't what they used to be. On the basis that all disorder must presumably lead to the same time-averaged structure, a liquid substance was assumed to be a unique state. But there is no fundamental reason why that should be so, for liquids are not after all structureless

over short ranges. There is now plenty of evidence that several substances possess more than one kind of liquid state, which can interconvert through phase transitions<sup>1</sup>.

Among the materials thought likely to display liquid–liquid phase transitions are silicon, silica, germanium, phosphorus and water. One indicator of this behaviour, evident for silicon and germanium, is the existence of distinct structures in the amorphous, glassy state, a property called polyamorphism. The notion is that the polyamorphs are 'arrested' forms of the liquid phases.

Water is one of the most compelling cases, not least because of its ubiquity and long-standing status as an 'anomalous' liquid. Water's unusual density maximum

at 4 °C and expansion on freezing have long been rationalized in terms of the directional nature of the hydrogen bonding between water molecules, which in turn seems to offer the possibility of a low-density, 'ice-like' liquid in which hydrogen bonding is preserved and a high-density liquid in which it is deformed or broken. Two-state models like this have a long history, but it's simplistic to imagine ordinary liquid water as being composed of an intimate mixture of such distinct regimes.

All the same, it's striking that many of the candidate systems for liquid–liquid transitions share with water either tetrahedral coordination or at least some degree of directionality in the associations between the component particles. Phosphorus is a curious case. A first-order liquid–liquid phase transition has been found experimentally<sup>2</sup>, but this seems to be an unusual transition between a molecular fluid and a polymeric liquid<sup>3</sup>.

Perhaps the first experimental claim for a liquid–liquid phase transition came from the seemingly exotic system of molten alumina–yttria ( $\text{Al}_2\text{O}_3$ – $\text{Y}_2\text{O}_3$ ) (ref. 4). Unlike several putative such transitions

that happen in metastable high-pressure or negative-pressure regimes, this one takes place at ambient pressure. All the same, the melt must be supercooled, so it is hard to study experimentally without triggering crystallization.

Neville Greaves of Aberystwyth University in Wales and colleagues have now found<sup>5</sup> a clever way to do that: by levitating a molten droplet in a stream of gas inside a furnace, eliminating all contact with a solid container. This has enabled them to verify that the transition is first-order — a point that has been contended for the analogous liquid–liquid transition of water. The researchers use X-ray scattering to identify the two states directly, clarifying how their atomic arrangements differ. The method, they say, might also be used to study other putative instabilities in deeply supercooled water.

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