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Journal
The Philosophical Magazine A Journal of Theoretical Experimental and Applied Physics, 89(22-24)

ISSN
1478-6435

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Publication Date
2009-08-01

DOI
10.1080/14786430902724962

Philosophical Magazine
Vol. 89, Nos. 22–24, 1–21 August 2009, 2111–2115

Superconducting materials: What the record tells us†

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(*Received in final version 5 January 2009*)

We argue that the materials which appear to maximize the superconducting transition temperature can be regarded as living at the interface between chemistry and physics.

Although the phenomenon of superconductivity in common metals mainly affects the system of itinerant charge carriers in an electrically conducting solid, it is not completely independent of the atomic arrangement in the crystal lattice of the corresponding material. While the latter is dictated by minimizing chemical energies of the order of 1 eV or more, the electronic instability that provides the transition to the superconducting state involves much smaller energy gains. This difference is most obvious in the observation that at the superconducting transition, the thermal expansion coefficient and the compressibility of the solid, both mainly dictated by the bonding of the atoms in the crystal lattice, undergo some, but rather insignificant, changes compared to the resistivity and the magnetic susceptibility, for instance. Likewise, the influence of external pressure on the critical temperature T_c is usually, with typical values of $\partial T_c/\partial p$ in the order of 10^{-2} K/kbar, rather modest. This is due to the fact that the degenerate Fermi gas of the conduction electrons is intrinsically under very high pressure and the lattice excitation spectrum usually does not change much with varying external pressure.

Apart from superconductivity, other electronic instabilities, such as charge- or spin density wave-states have been identified. Some of them seem to be favored by special symmetries of the crystal lattice; in particular, if the atomic arrangements exhibit trends to lower dimensional features, such as stacking of weakly interacting planes or chains. These obviously result from aspects of chemical bonding and, hence, the instabilities are dictated by chemistry as much as by physics. In some of the more recent developments of superconducting materials, it has been recognized that, here also, aspects of solid-state chemistry play an increasingly important role and that the instabilities mentioned above are much more closely related.

A striking aspect of superconductivity materials is the remarkable phase space they inhabit. From the alkali metals to the halides, some 50+ elements are

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†In honour of James L. Smith's 65th birthday.

ISSN 1478–6435 print/ISSN 1478–6443 online

DOI: 10.1080/14786430902724962
http://www.informaworld.com

superconducting but, for more than half of these, the transition is observed only under external pressure. For some of them, e.g. gallium, the so-called high-pressure phases exhibit considerably higher T_c values than the ambient pressure variety. Here, external pressure induces changes in the crystal structure, i.e. the atomic arrangement. Intermetallics, B-doped diamond, rare-earth antiferromagnetic compounds, alkali metal C_{60} fullerides, organics, a variety of oxides and, recently, Fe and Fe–pnictides all exhibit superconductivity. Superconductivity is everywhere but, nevertheless, sparse. For all the ternary intermetallics examined *inter alia*, it is surprising how few are superconductors. So the central question in superconductivity and the search for new superconducting materials is whether there is anything common to the known superconductors?

Fröhlich's, in retrospect, inadequate theory of electron–phonon-mediated superconductivity [1] immediately provoked the objection that the lattice would be unstable against the electron–phonon coupling strength needed[1]. This consideration persisted as a limit to achievable T_c values, i.e., avoiding intervening lattice instabilities in the later, successful Baedeen–Cooper–Schrieffer (BCS) theory [2]. In fact, among the materials with the highest known T_c values at the time, the cubic A15 compounds, such instabilities were known. They appeared as the so-called martensitic transformations at T_m, just above the T_c observed in V_3Si and Nb_3Sn [3], with T_c values in the range of 17 K. In V_3Si and Nb_3Sn, T_c and T_m have an opposite sign variation with pressure; in the former they approach each other at positive pressure; in the latter at negative pressure. Our viewpoint here is that we have a phase diagram for these superconductors where T_c appears to be approaching a maximum in the T–P phase diagram at the terminal point of another phase transition line, in this case T_m. For V_3Si, T_m exceeds T_c by a few degrees Kelvin. The growing lattice distortion with decreasing temperature below T_m is abruptly terminated at the onset of superconductivity at T_c [4].

For heavy Fermion materials, it is a generally held belief that all the superconductors are found in the vicinity of a magnetic quantum critical point where an antiferromagnetic ordering temperature has been driven to $T = 0$ K (Figure 1).

The observation, in general, is very close to this, as shown, for example, in Figure 2 [5]. What we see is the antiferromagnetic line of phase transitions intersecting near the maximum observed T_c in the phase diagram. Note the similarity to the previously discussed electron–phonon phase diagram.

The generic features of high T_c cuprates are often discussed on the basis of the phase diagram shown in Figure 3. Here, the so-called pseudogap line intersects the boundary to superconductivity at maximum T_c; but some claim that the pseudogap is also seen in tunnelling beyond T_c^{max}. While most experiments give no indication that the pseudogap line represents a true phase transition, polar Kerr rotation experiments suggest it might [6]. Nevertheless, it is a temperature below which a distinct and measurable change in the electronic properties develops. Again, the similarity to the previously discussed phase diagrams is apparent, with the pseudogap temperature intersecting a maximum in the T_c versus doping phase diagram.

We can also bring into this discussion the recently discovered Fe–pnictide superconductors [7]. In this set of materials, we have two high-temperature

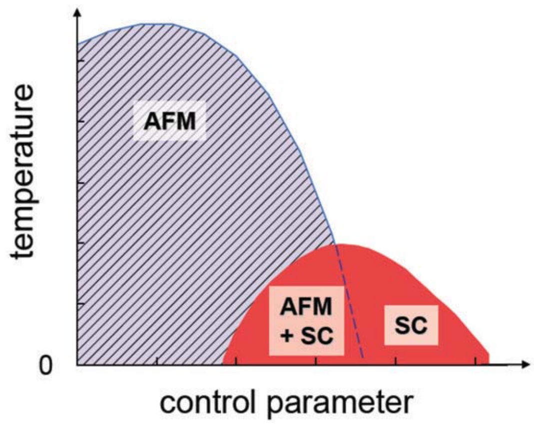

Figure 1. (Color online). Schematic phase diagram for occurrence of superconductivity in heavy Fermion systems.

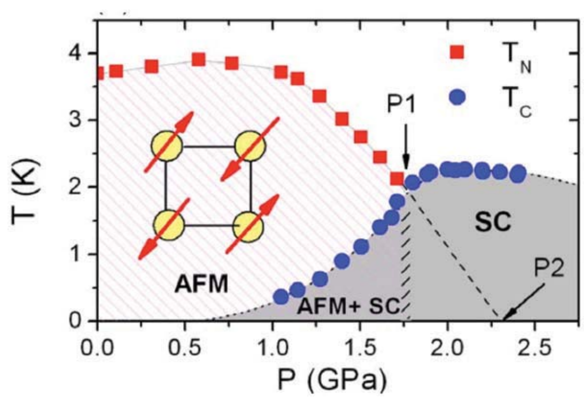

Figure 2. (Color online). Pressure–temperature phase diagram of $CeRhIn_5$.

transitions in the phase diagram – a structural and a spin-density wave transition. These appear to occur close to each other in temperature, sometimes coinciding and sometimes not exactly at the same temperature. Pressure is found to strongly suppress the transition temperature for both these phases, and superconductivity does not appear to coexist with the spin-density wave. At present, data do not allow one to make the claim that, in the ideal case, the spin-density wave transition will intersect a maximum in the T_c versus pressure curve for these materials, but the data are suggestive of this. Also note the organics in which phase diagrams, similar to those under discussion, are found.

The simplest way to think about the phase-diagram similarity discussed above is that we have, in all interesting cases where we are trying to maximize T_c, a competing second phase, with superconductivity winning out when the ordering temperature of the competing phase is brought down to the T_c of the superconducting phase. Nevertheless, this does not explain why this happens in the vicinity of the maximum observed for the superconducting T_c. It is an old idea that a sufficient increase in the

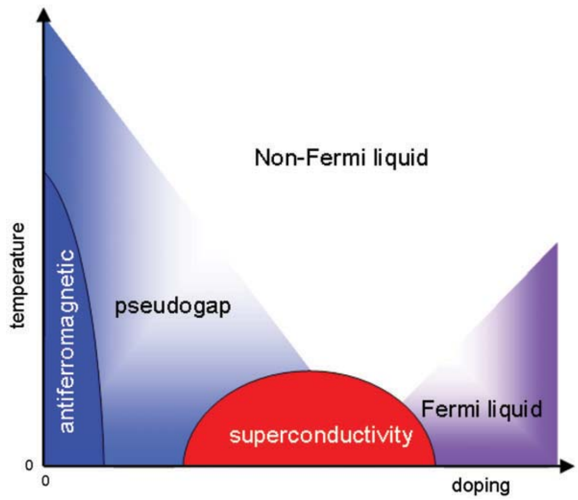

Figure 3. (Color online). Generic phase diagram of high T_c cuprates as a function of doping.

superconducting pairing interaction will lead to some instability limiting T_c. In the electron–phonon case for instance, it is a lattice distortion which relieves, so to speak, the tension arising from the large coupling. However, the coincidence noted above suggests that it is more useful to think in different terms, namely that the fundamental instability is that of the Fermi surface and that this instability is perhaps related to the mechanism behind the nearby phase whose boundary intersects the maximum T_c. Experiments have often suggested that superconductivity is competing for Fermi surface with another phase. However, our viewpoint is that this competition results from a more fundamental instability, which indicates that the material is balanced between conflicting tendencies corresponding to quite different ground states. This 'pairing' of phases is reminiscent of dualities used in discussions of other condensed matter phenomena, such as localized/delocalized, magnetic/non-magnetic or bonding/non-bonding. Another way to think about the dichotomy is in terms of real space versus momentum space condensation, similar to the differing chemical and physical viewpoints of bonds versus bands. Cohen and Anderson [2], in their early BCS-based discussion of maximum T_c, observed that the limit of large electron–phonon coupling is equivalent to something like a covalent bond. The point to note is the possibility that some type of localization may be limiting T_c. Thus, superconductivity is a phenomenon, when pushed to its limit, underlying some type of complementarity principle at the intersect of chemistry and physics.

Acknowledgements

ZF thanks V. Zlatic and R. B. Laughlin for discussions on this topic and NSF-DMR-0710492 for support. Work at Los Alamos was performed under the auspices of the US DOE/Office of Science.

Note

1. According to Zürich folklore, it was Pauli who claimed that if the coupling to the lattice played a decisive role in superconductivity, a T_c above 30 K was unlikely owing to the stability of the lattice. Unfortunately, there is no evidence in the literature which could be cited. At the same time, in the early 1950s, he suggested pressure experiments to test Fröhlich's scheme.

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