SUPERCONDUCTORS

Clathrates join the covalent club

Covalent metals, such as MgB_2 and the alkali-doped fullerenes, form an unusual class of superconductors. The mechanism of superconductivity in a new member of this family — the silicon clathrates — has now been determined.

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For each new class of superconductors that is discovered, a handful of critical experiments must be performed to pin down the mechanism of superconductivity. One such measurement is of the 'isotope effect', the change in T_c (the transition temperature to the superconducting state) as the mass M of the atomic constituents is changed. Katsumi Tanigaki and co-workers[1] have now succeeded in measuring the superconducting isotope effect and thus determining the mechanism of superconductivity in a barium-doped silicon clathrate superconductor, Ba_8Si_{46}. This superconductor is unusual in that the structure is dominated by strong covalent bonds between silicon atoms, rather than the metallic bonding that is more typical of traditional superconductors. As such, the silicon clathrates are members of an exclusive club of covalent metals, whose other members include the well-known high-temperature copper oxide superconductors[2], MgB_2 (ref. 3), and the alkali-doped fullerenes[4,5]. The measurements conducted by Tanigaki and colleagues reveal that superconductivity in Ba_8Si_{46} is of the classic kind, arising from the so-called electron–phonon interaction. Superconductors with strong covalent bonding are unusual, so the insights gained here are a valuable addition to our knowledge of covalent metals.

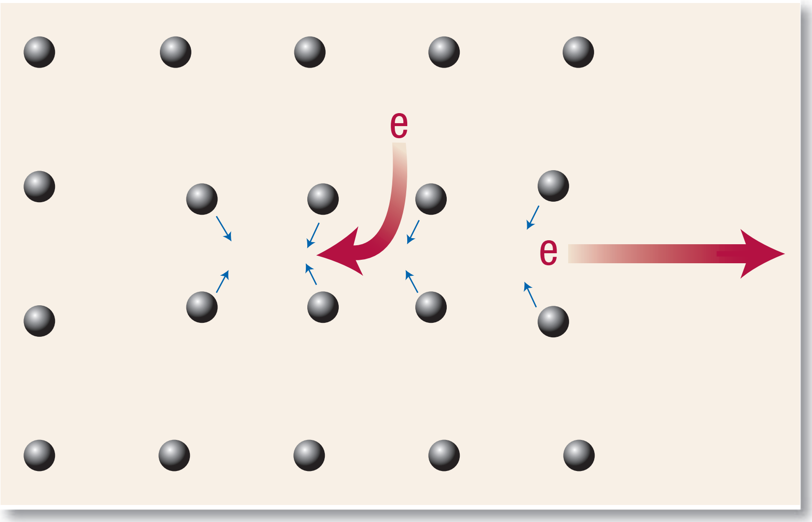

Figure 1 Electron organization in superconductivity. The leftward moving electron is attracted to the transient accumulation of positive charge that remains in the wake of the rightward moving electron, yielding a net attraction between electrons.

The physical origin of electron–phonon-mediated superconductivity is subtle, but we can approach it by means of an analogy between interacting electrons and human relations. First, consider a woman hiking through a large open field; there may be other hikers around, but they do not affect her motion. The hiker represents the free-electron model, which treats every conduction electron in a metal as unaffected by the surrounding electrons. Now consider the same person trying to jostle her way through a crowded room. The harried walker in the crowded room better represents an electron in a real metal. When all of the random jostles from neighbouring electrons are added up, the net result is simply that the electron moves with an effective mass that is different from the free-electron mass. This way of modelling the interactions as an effective mass works best when the electrons are disorganized, so that the jostles can be averaged together. The situation would be quite different if the crowd was better organized.

As the temperature of a metal drops, the free-energy advantage of disorder is reduced, so the electrons can organize into a collective wavefunction that has a higher degree of order than does our milling crowd. Superconductivity is a form of electron organization that is induced by an attractive interaction between electrons. Although electrons, being of like charge, tend to repel each other, the sea of positive ions in which they move can create a net attractive interaction between them. As an electron moves through the lattice, it attracts the slow and heavy positive ions towards it. However, the fast and fleeting electron soon moves on, leaving the slow ions still moving towards where the electron once was. This transient accumulation of positive charge, caused by a vibration of the lattice (or 'phonon'), can attract a second electron to the wake of the first. The positively charged lattice of ions thereby mediates an effective attraction between electrons (Fig. 1).

If this phonon-mediated attraction is strong enough, the electrons in the metal will organize themselves, at a sufficiently low temperature, into a sea of electron pairs. On a dance floor, every human pair feels the air of romance, while every dancer in a pair has eyes only for his or her mate. Each pair can glide through the room seemingly oblivious to their surroundings. Similarly, the electron pairs in a superconductor can glide through the metal without impediment. The collective superconducting electron wavefunction is stabilized by the electron–phonon interaction — the air of romance.

The superconducting isotope effect is described with a parameter α, defined by $T_c \sim M^{-\alpha}$. For superconductivity mediated by the electron–phonon interaction, T_c is set by two things: the character of the overall interaction between the electrons and the average frequency of vibration of the crystal lattice. The specific formulae that predict T_c always have the form of a vibrational frequency multiplied by some function of the interaction. As atoms in a crystal vibrate like masses on springs, the vibrational frequency is proportional to $M^{-1/2}$. In an idealized case, where the interaction is independent of M, T_c would be proportional to $M^{-1/2}$ and $\alpha = 1/2$. In actual electron–phonon-mediated superconductors, the Coulomb repulsion between electrons reduces the sensitivity of T_c to M, so that α is generally between 0.1 and 0.4. For an exotic superconductor whose mechanism does not rely on lattice vibrations at all, one would expect $\alpha = 0$. By measuring the change in T_c between $Ba_8{}^{28}Si_{46}$ (containing naturally abundant Si) and $Ba_8{}^{30}Si_{46}$ (the isotopic composition), and also measuring the shift in the phonon modes in the Raman spectra of the two compositions, Tanigaki and colleagues were able to determine that $\alpha = 0.12$–0.23 for the silicon clathrate Ba_8Si_{46}.

Therefore, we can now welcome the unusual covalent metal Ba_8Si_{46} into the fold of classical electron–phonon-mediated superconductors. With a bit of further data analysis, Tanigaki and co-workers also extract an estimate for the strength of the electron–phonon coupling, measured by a dimensionless parameter λ. The result is $\lambda \sim 1$, comparable to the coupling strength in the higher-T_c materials magnesium diboride ($T_c \sim 40$ K) or alkali-doped fullerenes ($T_c \sim 30$ K). These boron- and carbon-based systems have higher transition temperatures, mainly because C and B are lighter than Si and thus have higher-frequency lattice vibrations. Using the new insights gained here, it may be possible to create new metallic alloys from the light main-group covalent elements — perhaps through non-equilibrium processes — to obtain even higher T_cs in new covalent metals.

References

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MATERIAL WITNESS

Portentous polymers

'Mylar' does not appear in my Webster's dictionary, which is nevertheless content to include 'myristic acid' and 'myxomycete'. My Oxford English dictionary acknowledges it ("a form of polyester resin used to make heat-resistant plastic films and sheets"), but I submit that it is not exactly a household word.

Which makes it curious that American novelist Don DeLillo sees fit to refer repeatedly to Mylar in his 1985 book *White Noise*. The neighbourhood of protagonist Jack Gladney becomes haunted by men in Mylar suits testing for toxic fallout from a chemical accident.

He didn't have to specify the Mylar. Indeed, arguably DeLillo would have made himself clearer to many readers by calling the protective clothing simply that. There is no indication of why the properties of Mylar dispose it to such a use, or even any explicit mention that it is protective.

But 'Mylar' is precisely the right choice. It gives readers the frisson of being surrounded with materials the names of which they barely know and the provenance of which they cannot guess. And the capitalization tells us that this is not merely some new word, but a trade name devised, trademarked and marketed by some big corporation. It fits with the novel's themes of alienation and disorientation in contemporary US society.

DeLillo is one of a small, influential group of American writers who insist that chemical and materials technology is one of the pervasive aspects of twentieth century life. Theirs is not the prosaic assertion that 'materials are all around us' (which of course has always been true) but that the textures, the sights and smells of modern life have typically been designed, synthesized and patented. Styrofoam, Kevlar, neoprene. If these writers are not always exactly friendly to the new substances — which often appear in ominous contexts — they do recognize and in some sense embrace them.

Thomas Pynchon's *Gravity's Rainbow* (1973) is the most remarkable fable of materials chemistry in the English language, laced with the tale of a sinister and sensual polymer called Imipolex G: "the first plastic that is actually *erectile*". Having studied engineering at Cornell before working at Boeing, Pynchon knows what he is talking about when he mentions "aromatic polyamides, polycarbonates, polyethers."

But crucially, he does not much care whether his readers know what he means by "giant heterocyclic rings" and so on: these words and phrases are talismans, half-glimpsed clues to a world of power, commerce and arcane knowledge. DeLillo too is interested not in dispelling this bewilderment but in exploring it.

A more recent initiate into this group is Richard Powers, whose 1998 novel *Gain* recounts the development of a Boston chemicals company. Again, the uncompromising details: page 171 has no text but a diagram showing the synthesis and uses of Glauber's salt.

We should be heartened by this. Patiently demystifying materials technology is one way to disseminate it. But for writers like DeLillo, Pynchon and Powers, it is already here, seamlessly embedded in our cultural experience, and we had better get used to it.

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