HIGH-TEMPERATURE SUPERCONDUCTIVITY

The great quantum conundrum

Twenty-five years on from its discovery, high-temperature superconductivity remains without a satisfactory explanation. The latest studies on the electronic phase diagram of copper oxide compounds reveal why this is so. SEE LETTER P.73

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Some years ago, I lectured at a National Science Foundation summer workshop for high-school physics teachers. My subject was superconductivity. One of my co-instructors was Robert Laughlin. Scrawled across the top of Bob's first projector slide was the phrase, 'The Theory of Everything', and I thought, "Oh, boy, here we go, the standard model of particle physics — again". But underneath the title, he had written instead the many-body Schrödinger equation, summed over all the interactions between electrons and nuclei, and thus containing, once electron spin is included, the complete chemistry and physics of ordinary, terrestrial matter.

Of course, the devil is always in the details, in this case the enormous summation over particle coordinates that is required to achieve a scale of, say, Avogadro's number. From this summation emerge life, the climate, smartphones … and high-temperature (high-T_C) superconductivity. And it is on this last that Jin *et al.*[1] (page 73 of this issue) and He *et al.*[2] (in an earlier study published in *Science*) make the latest effort to illuminate qualitatively the microscopic origins. They do this by attempting to unravel the enigmas of the electronic phase diagram of materials known as copper oxide perovskites. Within this phase diagram (Fig. 1) reside several quantum states, characterized by one or more 'quantum critical points', in rough analogy to the classical critical points characterizing the separation of the gas, liquid and solid states of macroscopic matter. How the various phases in the electronic phase diagram compete or cooperate in generating the emergent superconducting state constitutes what I term the great quantum conundrum.

The physics of the '3*d*-transition-metal' monoxides, such as copper monoxide, is fascinating. By conventional energy-band theory, these compounds should all be metals. But they are not: they are a form of non-conductor called an antiferromagnetic Mott insulator, in which neighbouring cations (metal atoms) contain one or more opposite spins. This was the great quantum conundrum of my generation, which was formally cleared up by John Hubbard[3].

Things get even more interesting when we consider what happens if charge from some external 'dopant' source is added to (with electrons) or subtracted from (with holes) the material's copper–oxygen energy bands. Researchers had tried this approach with other transition-metal oxide compounds, but found nothing much. Then Georg Bednorz and Alex Müller ran across barium-doped, layered lanthanum copper oxide and discovered high-T_C superconductivity. The presence of barium introduced holes into the copper oxide bands, destroying long-range antiferromagnetic order and creating — depending on the temperature and charge-carrier concentration — either normal conductivity or superconductivity. Similar behaviour was also later found when electron-donating cations were employed. As Phil Anderson cogently pointed out in 1986, once the Bednorz–Müller findings had received wide notice, it was "unlikely an accident that the original host material for high

temperature superconductivity was an antiferromagnetic insulator".

The explosion of high-T_C superconductors wrought by modern materials science has meanwhile produced a plethora of phase diagrams of temperature versus local charge density (induced by doping and/or pressure), typified by Figure 1. One common feature of these diagrams is a $T = 0$ line, plotted as a function of local charge density, which begins at low values describing a doped antiferromagnetic insulator and eventually reaches a quantum critical point, beyond which conductivity emerges.

The latest efforts at improving these qualitative descriptions are reported by Jin *et al.*[1] and by He *et al.*[2]. Jin and colleagues focused on the electron-doped copper oxides, whereas He *et al.* addressed their hole-doped counterparts. However, the two groups approach their subject from different directions and arrive at somewhat different points of view.

It has long been speculated that some remnant of magnetic order remains behind when the nascent copper oxides are doped into a conducting or a superconducting state — I like to term this the fond memories of antiferromagnetism. In principle, such memories can be detected experimentally and may be linked to a phenomenon known as the pseudogap. The pseudogap, whose existence is revealed by anomalies in photoemission experiments, has been observed by a number of groups, especially in the hole-doped copper oxides. It is characterized by a transition temperature beyond which a metallic-like state emerges, and lies on top of the dome-shaped superconducting region of the phase diagram (Fig. 1). A central issue, however, is whether the pseudogap has a competitive or collaborative role in engendering high-T_C superconductivity. He *et al.*[2] claim the latter, pointing out that the energy of the pseudogap approaches that of the superconducting gap, as both converge in temperature towards the summit of the superconducting dome.

For electron-doped copper oxides, the case for the demarcation of a pseudogap phase is less clear than for hole-doped materials. Therefore, Jin *et al.*[1] focused on a common feature seen in both systems — that the resistance of the normal conducting state shows a subquadratic or quasi-linear dependence on temperature that is observed in broad regions of local charge density above the superconducting dome. I recall hearing Phil Anderson remark that the linear dependence of the normal conducting-state resistance on temperature was as unusual as the appearance of superconductivity. This temperature dependence in ordinary metals at low temperature goes as T^2.

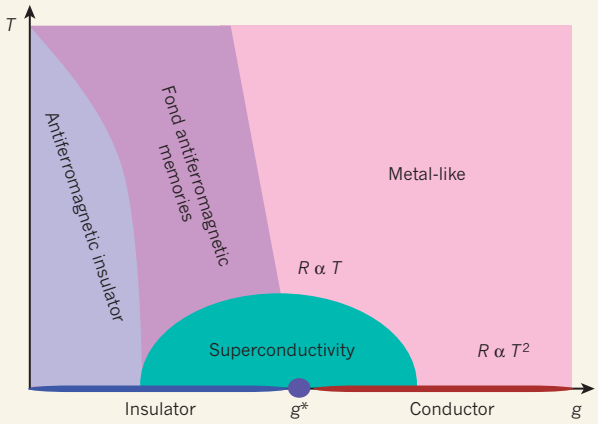

Figure 1 | Generic electronic phase diagram of the copper oxide superconductors. The diagram shows the major observed phases as a function of temperature (T) and local charge density (g), which is introduced by either doping or pressure: from left to right, an antiferromagnetic insulator, a state in which carriers start to move but 'fondly remember' their antiferromagnetic origins (this is where the pseudogap phenomenon is located), and a metal-like phase whose resistance (R) varies linearly to quadratically with temperature as g increases. These phases sit above a 'superconducting dome' whose boundary remains a subject of intense debate and which is vital to understanding the origin of high-temperature superconductivity. At zero temperature, as g increases and reaches a 'quantum critical point' (g^*), the copper oxides cease to be insulators and become conductors. The studies by Jin *et al.*[1] and by He *et al.*[2] attempt to provide insights towards a better understanding of this phase diagram.

Jin *et al.* attribute this linear temperature dependence to 'spin-fluctuation' scattering of carriers, and speculate that this scattering is also responsible for the carrier-pairing mechanism underlying superconductivity in the layered copper oxides. They point to an analogous behaviour in the layered organic Bechgaard salts, compounds in which the local charge density can be varied by applying hydrostatic pressure, rather than by direct doping. This results in a superconducting state at around 10 kilobar up to a T_C of about 1.2 kelvin, and a subquadratic temperature dependence in the normal conducting-state resistance at higher temperatures.

So, there is certainly circumstantial evidence that high-T_C is mediated by spin fluctuations, but is it compelling? Or, put another way, there does seem to be a 'smoking gun' here, but what was it that pulled the trigger? What exactly is a spin fluctuation? One might think that there should even be a model at the microscopic scale from which one could calculate the coefficient of proportionality in the linear-temperature formula outlined by Jin *et al.*[1]. However, a search of the reference list in the papers by He *et al.* and Jin *et al.* revealed no source for such a model, nor did perusal of several recent texts on the theory of unconventional superconductors. What the theoretical framework of superconductivity in the layered copper oxides presently lacks is an equivalent to the Eliashberg–McMillan tool[4,5], which can be used to 'post-dict' the transition temperature of simple low-T_C superconductors using an electron–lattice vibration (phonon) interaction. This can be calculated directly for, say, aluminium or niobium using a computational method known as density functional theory, but same methodology could, in principle, be used to treat spin-fluctuation scattering.

Having mentioned electron–phonon coupling, I should point out that most, if not all, of the layered copper oxides display an isotope effect. This occurs when one of the elements is exchanged for a lighter or a heavier one, which has a different number of neutrons in its nucleus. The substitution changes the 'strength' of the electron–phonon interaction, and causes a shift in T_C. In addition, in those instances when it has been measured, the neutron diffraction pattern shows anomalies near T_C. Both of these effects strongly suggest that phonons are somehow involved in whatever carrier-pairing physics applies to high-T_C superconductors.

Let us return to the 3*d*-transition-metal monoxides. Most of the heavier ones (manganese, iron, cobalt, nickel, copper, zinc) can be found in 'everything Laughlin' in cubic rock-salt form. The one exception is copper monoxide, which emerges as the mineral tenorite, and which has a highly distorted crystal structure. I have applied[6] density functional theory to investigate the stability of 'cubic rock-salt' copper monoxide, and found it to be extremely unstable, easily undergoing uniaxial deformation. Such instability results from the highly degenerate copper–oxygen bond, in effect reflecting an unusually strong electron–phonon interaction, much greater than is found in the other transition-metal monoxides. It is just this kind of interaction, originally postulated by Alex Müller, that he concluded might lead to unusually high-temperature superconductivity in the copper oxides. Was he right, after all?

So, does high-T_C superconductivity emerge from 'everything Laughlin' because of 'lattice shakes' or 'bouncing spins'? And do these effects compete or cooperate? I suspect the latter. At the end of the day, one should try to look beyond the current fashions of jargon and arguments-by-analogy, and move towards a formalism for high-T_C carrier pairing that can be used to compute T_C on a more-or-less first-principles basis, much as now can be done for low-T_C superconductors. A newly published paper by Le Tacon and colleagues[7], which

attempts a model calculation of spin-fluctuation-mediated pairing, provides an encouraging start. In this context, it may be pertinent to quote the response to David Mermin's observation[8], when questioning the physics faculty while a graduate student at Harvard, about the weirdness of that first quantum conundrum — entanglement. He was advised to simply "shut up and calculate". ■

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