

SUPERCONDUCTORS

Electrons living apart together

The non-superconducting state of a high-temperature superconductor is in many ways more anomalous than the superconducting state. Unlike a standard metal, the ‘normal’ state shows possible signs that adding or removing one electron affects all the others.

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The oxide $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ and similar oxides containing two-dimensional copper oxygen planes are superconductors with the highest transition temperatures (T_c) ever observed in a solid, the record being 134 K at ambient pressure. The superconductivity in these materials, discovered in 1986 by George Bednorz and Alex Müller¹, who shared the Nobel Prize a year later, is a macroscopic quantum phenomenon: electrons form pairs that all condense into the same quantum mechanical ground state. The high- T_c superconductors have this aspect in common with all known superconductors, including aluminium and lead. But in the copper oxides, the two electrons forming a condensed pair systematically avoid getting close to each other, where ‘close’ means the distance between two neighbouring atoms. This mutual avoidance is in fact imposed by the presence of zeros (or nodes) in the wavefunction describing the relative motion of the paired electrons.

In the ‘normal’ state of the high- T_c superconductors, unlike in normal metals, the electrons also tend to stay apart. The samples are therefore insulating when the conduction band is half-filled — that is, when the number of holes corresponds to 0.5 per copper site and per spin². According to the textbooks a half-filled band corresponds to a highly conducting metal. However, the conduction electrons are confined primarily to the copper atoms from which two electrons have been stripped, although tunnelling enables them to move from one copper site to the next. Among the transition-metal elements, ionized copper has the smallest size with a radius of only 100 pm. Consequently the repulsive Coulomb energy U between two electrons occupying a copper ion is huge: $U = 8$ eV (ref. 3). This repulsive interaction keeps two electrons of opposite spin from entering the same site. The carrier concentration of one electron per unit cell implies that every site is occupied by precisely one electron, and any flow of charge is inhibited by the repulsion: this condition

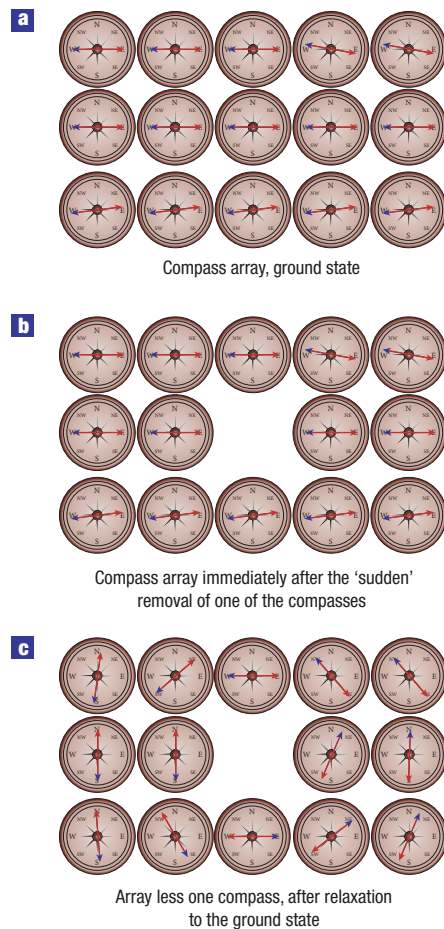


Figure 1 Correlated compasses. **a**, A ‘lattice’ of N compasses at equilibrium. **b**, If one compass is suddenly removed, the rest will still be in their original configuration — now considered an excited state for $(N - 1)$ compasses — until they finally relax into a new equilibrium minimum-energy state (**c**).

is the Mott–Hubbard insulating state. On page 626 of this issue, P. W. Anderson⁴ considers the limit of infinite U , with the aim of getting to grips with the essentials of the tunnelling spectra and the optical conductivity. Infinite U suppresses superconductivity in the normal state.

The actors in the theatre of high-temperature superconductivity — elementary charge, pairs, stripes and so on — are colourful and manifold in their appearance; they are dressed with phonons, and spin and charge fluctuations, and each is

cheered noisily by separate parts of the audience. The play itself contains elements of drama, comedy and, at times, truth. Aiming to capture the essence of the plot, the actors in ref. 4 are electrons and holes, with U as the only interaction between them. According to Anderson⁴, the ground state in the limit of infinite U is the 'projected Fermi liquid', $P\Phi$. Here Φ describes the filling of the momentum eigenstates with $(1-x)$ electrons per unit cell, whereas the effect of P (the 'Gutzwiller projection') is to suppress double occupancy completely. In the spirit of Occam's razor, the 'projected Fermi liquid' represents the minimal model for the normal state. It also provides the stage on which the play of high- T_c superconductivity is performed.

For the copper oxides, $P\Phi$ plays a role similar to that of the Fermi gas in, for example, aluminium. In a Fermi gas, electrons can be added or removed without seriously affecting the other electrons inside the material. The density of states function (or spectral function) of such a process takes the form of a sharp peak centred at the binding energy of the removed electron. The tunnelling spectrum probes the momentum-averaged spectral function. The projected Fermi liquid differs from a Fermi gas in a fundamental way. Technically $P\Phi$ is a superposition of a huge number of Slater determinants, which grows exponentially with the number of doped charges. Removing an electron causes a rearrangement of the coordinates of the $(N-1)$ remaining electrons in the sample. Imagine that we suddenly remove an electron without allowing the remaining ones to relax to the ground state. The resulting $(N-1)$ electron state is not an eigenstate of the interacting system, and its projection on each of the eigenstates becomes vanishingly small in the thermodynamic limit.

This situation can be visualized with a simple home experiment that requires just a bunch of compasses (Fig. 1). When placed in a two-dimensional array, the needles will influence each other's directions through their magnetic fields, resulting in an equilibrium orientational pattern when the system has come to rest. Let us now remove one of the compasses, rather suddenly in order to prevent the needles from moving perceptibly during the process. The remaining compass needles will be in a highly excited state, and will start rotating and eventually come to rest in their new equilibrium pattern.

Let's come back to the projected Fermi liquid⁴. In a tunnelling experiment, electrons are either added or removed depending on the voltage bias V , leaving the projected Fermi liquid in a highly excited state similar to the compass experiment. The resulting electron addition spectrum turns out to be $dI/dV = V^p$, or $dI/dV = V^{2p}$ in the case of electron removal, where $p = (1-x)^2/8$, and $(1-x)$ is the number of electrons per unit cell of the sample. Moreover, the tunnelling spectrum must be asymmetric about the Fermi energy E_F as observed experimentally⁵. The optical conductivity σ involves the simultaneous creation of an electron and a hole, resulting in a power law of the form $\sigma(\omega) \propto 1/(i\omega)^{1-3p}$, where ω is the frequency of the

probing light. The doping dependence of the power itself is quite weak: $(1-3p) = 0.625$ for the undoped Mott insulator, increasing to $(1-3p) = 0.82$ for $x = 0.3$. The experimental values are roughly equal to $2/3$ and have a weak doping dependence⁶⁻⁸.

In reality U is not infinite, so that double occupancy is not completely excluded. This fact permits the occurrence of 'super-exchange' processes in which electrons on neighbouring atoms can lower their kinetic energy if their spins are oppositely aligned. Under favourable conditions, these processes lead, among other things, to antiferromagnetic order. The finiteness of U also introduces a lower energy bound below which the power-law behaviour terminates⁴; the cusp in the tunnelling spectrum does not reach all the way to zero at $V = 0$, and the power law of the optical conductivity is truncated either through thermal smearing, or by the opening of a gap. The former will change the power decay into a simple $e^{-t/\tau}$, with a Drude-Lorentzian shape determined by the time constant τ . At optimal doping the resistivity is a linear function of temperature, implying that $1/\tau = k_B T$, a property sometimes associated with quantum criticality. Then the optical conductivity must have the scaling form $T\sigma(\omega, T) = f(\omega/T)$ for $\omega/T \ll 1$, in agreement with experimental data and apparently unrelated to the aforementioned power law at higher frequencies⁹.

The tunnelling asymmetry arises from the difference between removing and adding an electron to a doped Mott insulator. As the model of a projected Fermi liquid itself conserves electron-hole symmetry, the tunnelling spectrum of a sample with $(1+x)$ electrons ('electron-doped') should be the mirror image of a sample with $(1-x)$ electrons. Using different arguments, Marsiglio and Hirsch¹⁰ concluded that the tunnelling asymmetry should always have the same sign. If the asymmetry is due to a maximum in the density of states corresponding to a van Hove singularity (a point in momentum space where the energy reaches an extremal value) just below the Fermi energy¹¹, this asymmetry will change sign when E_F is shifted below the van Hove singularity by hole-doping (roughly for $x > 0.25$). Hence (1) the projected Fermi liquid model⁴ gives the opposite sign of the tunnelling asymmetry for electron- and hole-doped samples, in contrast to the other two models^{10,11}, and (2) if the (hole-) doping is increased, a sign-change of the tunnelling asymmetry will occur according to the van Hove picture¹¹, but not according to the work in refs 4 and 10. Useful theories provide experimentally testable conjectures, and Anderson's work is exemplary in this respect.

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