CO_2 removed from surface waters at elevated CO_2 was not balanced by increases in particulate organic carbon (POC) in the surface layer. Furthermore, the loss of nitrate from the surface waters was the same in all three CO_2 treatments, indicating that the ratio of carbon to nitrogen uptake increased at higher CO_2 concentrations whereas the cellular carbon/nitrogen ratio of the phytoplankton remained unchanged.

This result suggests that, although higher ambient CO_2 concentrations increased CO_2 uptake by phytoplankton, the additional carbon incorporated into cells was rapidly lost as dissolved organic carbon (DOC). However, although DOC concentrations in the mesocosms increased, these were insufficient to balance the measured CO_2 deficits. In nature, organic molecules excreted from phytoplankton (for example, as DOC), or otherwise lost as these organisms die or are grazed, can coalesce to form semi-solid structures called transparent exopolymer particles (TEPs). These structures are sticky and facilitate the aggregation and increased sinking speeds of other particulate matter. In the mesocosms, TEP concentrations increased fourfold during the experiment (the carbon content of these TEPs is not presented by Riebesell *et al.*).

The authors propose that accumulations of TEPs in the elevated-CO_2 treatments facilitated aggregate formation, increasing the flux of particulate matter from the mesocosm surface. Coupled with higher DOC production, this may explain why POC did not increase in the elevated CO_2 treatments. Thus, it seems that increased CO_2 uptake fuelled by higher CO_2 concentrations was rapidly converted to DOC and TEPs, and any additional carbon incorporated into POC was lost from the surface of the mesocosm owing to increased particle aggregation and sinking (Fig. 1). Assuming that their results are representative of the larger ocean, increased atmospheric CO_2 may lead indirectly to increased particle fluxes from the surface ocean to depth, providing a negative feedback to increasing atmospheric CO_2 concentrations. Unfortunately, the authors did not measure POC sinking fluxes in their mesocosms to confirm this link.

Nevertheless, there are some notable conclusions to be drawn from this study. First, although CO_2 uptake by phytoplankton may be stimulated in a high-CO_2 world, this negative feedback will only partly offset expected increases in atmospheric CO_2. In fact, Riebesell *et al.* perform some clever calculations to show that the CO_2-enhancement effect they identified has probably reduced the rise in atmospheric CO_2 by only 11 μatm (about 10%) since the dawn of the industrial revolution.

More importantly, their study provides a vivid example of the fact that ocean biology is not in steady-state and that fundamental biological and biogeochemical processes are likely to respond to climate change, resulting in either positive or negative feedbacks that are difficult to predict. One positive feedback between biology and climate has already been identified, whereby future increases in stratification of the Southern Ocean could favour types of phytoplankton that have a reduced capacity to take up CO_2 (ref. 4). Conversely, increased CO_2 has been shown to enhance fixation of free nitrogen, thereby relaxing nutrient limitation by nitrogen availability and increasing CO_2 uptake[5]. Riebesell and colleagues document another negative feedback whereby CO_2 use by the dominant bloom-forming groups of phytoplankton could increase as atmospheric levels of CO_2 rise. Neither these, nor other possible non-steady-state biological feedbacks, are currently accounted for in models of global climate — a potentially serious omission, given that the biological pump is responsible for much of the vertical CO_2 gradient in the ocean. ■

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HIGH-TEMPERATURE SUPERCONDUCTIVITY

Schizophrenic electrons

Christian Pfleiderer and Rudi Hackl

The split personality of the conduction electrons in one high-temperature superconductor might indicate that periodic modulations of their spin and charge density are a general feature of these mystifying materials.

In simple metals, conduction electrons undergo well-understood phase transitions: they can become superconducting or ferromagnetic, or acquire periodic modulations of their spin and charge density. But just over 20 years ago, high-temperature superconductors were discovered, a class of materials in which the conduction electrons behave almost entirely outside these traditional models of order. Or do they? On page 533 of this issue, LeBoeuf *et al.*[1] report measurements of a classic high-temperature superconductor, yttrium barium copper oxide (YBCO), that hint at the presence of order in the form of a periodic density wave of conduction electrons. Together with similar sightings in other materials[2,3], this finding might indicate that this form of order is shared by all high-temperature superconductors.

High-temperature superconductivity — the conduction of electric current without resistance at temperatures of up to halfway between absolute zero and room temperature — presents a tremendous challenge to our understanding. All known high-temperature superconductors are copper-oxide (cuprate) materials. The highest superconducting transition temperature (the temperature above which superconducting behaviour is lost) occurs in a regime where the concentration of charge carriers in the material is somewhere between that of its magnetically ordered insulator state and that of its non-magnetic metallic state.

The charge-carrier concentration in YBCO and many other cuprates is controlled by 'doping' through the addition or subtraction of a small number of oxygen atoms. One might expect not just the number but also the placing of these atoms (and the crystal structure in general) to influence the transition temperature. But oddly, the superconductivity seems fairly insensitive to the precise crystallographic arrangement. What is worse, the energy scales of all other phenomena that might cause the superconducting behaviour — the frequency of vibrations in the material's crystal structure, the speed of movement of conduction electrons, the rate at which islands of magnetization and modulations of charge density form and decay in the material — are similar, making it difficult to single out any particular one as the culprit. Any reasonable suggestion of primary forms of electronic order underlying the superconductivity would therefore be gratefully received.

In pursuit of such order, LeBoeuf *et al.*[1] set out to study the nature of charge carriers in YBCO superconductors. In solids such as YBCO, electrons reside in energy bands that form when the atomic orbitals of participating atoms overlap, establishing a relationship between an electron's energy and its momentum. The highest energy up to which bands are filled determines a surface, the Fermi surface, in a three-dimensional momentum space. As long as a band is occupied by just a few electrons, these behave as if they are essentially free, and can contribute to a flow of electric current. As soon as a band is completely occupied, this contribution ceases. But a strange thing happens if just a few electrons are missing from an otherwise fully occupied band. In this case, it is as if the missing electrons are free to

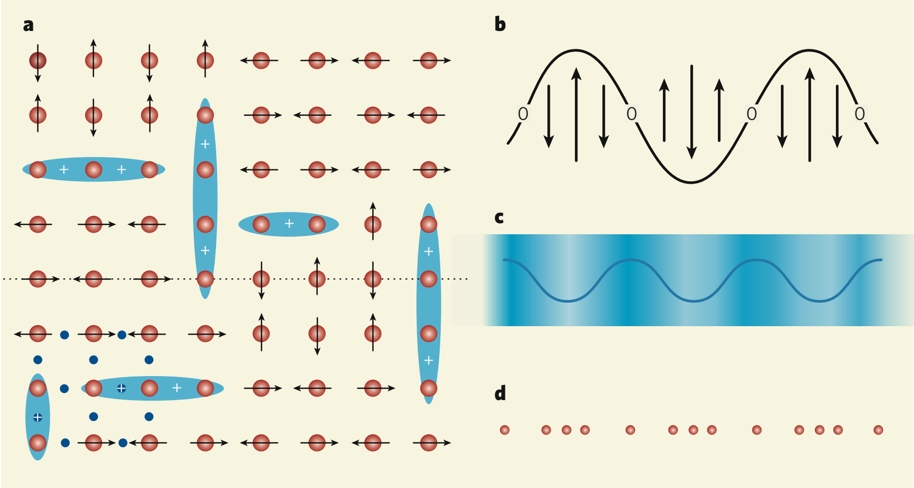

Figure 1 | Density wave in YBCO. a, In the copper–oxygen plane of the high-temperature superconductor yttrium barium copper oxide (YBCO; copper atoms are shown in red; for clarity, oxygen atoms (blue) are shown only in the lower left corner), positively charged holes introduced by doping (+) organize in stripe-like regions that break up long-range magnetic order. (In YBCO's insulating state at low doping, spins are arranged with antiferromagnetic order, with adjacent spins pointing in opposite directions.) Under doping and at higher temperatures, this pattern is not rigid, but fluctuates ever more rapidly. **b, c,** A snapshot of the modulation of the spin (**b**) and charge (**c**) densities along a cut indicated by the dashed line in (**a**). The charge modulation has twice the periodicity of the spin modulation. **d,** If the charge density modulation varies slowly enough, the copper and oxygen atoms may follow, exhibiting a new periodicity. A possible explanation for LeBoeuf and colleagues' Hall-effect findings[1] is that these processes can show up as a reconstruction of the Fermi surface: if the electrons can complete a full circle in the Hall field before the stripe pattern changes, the quantum oscillations that the authors observe will arise.

move through the crystal, producing a flow of positive electric charges, or 'holes'.

The authors[1] investigate a point in YBCO known as 1/8 filling, which lies slightly below the doping level at which the superconducting transition temperature is highest. In this configuration, there is, on average, one additional hole for every eight copper atoms in the copper–oxygen plane of the material. Together with the underlying magnetism of the copper atoms, this leads to a periodic, stripe-like modulation of the otherwise homogeneous charge distribution. Several anomalous characteristics associated with incipient spin or charge order had already been found around 1/8 filling in practically all cuprates[2–4].

The new experiments[1] were in several respects extreme, requiring both great advances in materials preparation techniques[5,6] and the maintenance of temperatures near absolute zero at magnetic fields almost one million times stronger than Earth's magnetic field. The chosen probe was the Hall effect, a phenomenon first noted by the American physicist Edwin Hall in 1879. This effect occurs when electric currents are deflected in a weak magnetic field by means of the Lorentz force. Electrons and holes move in opposite directions, causing a build-up of charge — and therefore voltage — at right angles to both the direction of current flow and the magnetic field. The sign of the Hall voltage shows whether the current is predominantly carried by electrons (negative voltage) or by holes (positive).

In strong magnetic fields and in samples sufficiently clear of crystal defects, the electrons and holes can race around in complete circles. The Russian physicist Lev Landau pointed out in 1930 that the energy associated with this circular motion is quantized. The Hall voltage then undergoes so-called quantum oscillations when the energy of the quantized racetracks matches the energy corresponding to an extreme cross-sectional area of the material's Fermi surface. Extremely pure samples are needed to observe this subtle, but important, facet of the electronic structure, because the quantum oscillations are extremely sensitive to defects that kick the electrons out of their race-track.

LeBoeuf and colleagues' new offering[1] closely follows their previous work[7], in which they also used the Hall technique to probe YBCO superconductors. So what's new? Before, they observed quantum oscillations in an overall negative Hall voltage, but attributed them to hole pockets. The sign of the voltage must either have been intrinsic to the hole-doped material (in which a positive Hall voltage would be expected), but of unidentified origin, or have indicated the presence of vortices of supercurrents circulating around a flux line of the applied magnetic field[8]. Only now have the authors pinned down the change of sign of the Hall signal from positive to negative as being intrinsic. They have thus identified an inherent contradiction: the charge carriers in YBCO have a split personality between electron-like and hole-like behaviours. This observation immediately raises the questions of where the electron pockets come from, and why there are no quantum oscillations of the holes.

One obvious answer to this question is provided by the order that occurs in the spin and charge density of conduction electrons in the metal chromium[9]. Here, electron pockets may be produced by the 'reconstruction' of the Fermi surface through a density wave. Figure 1 shows what, by analogy, might be going on in YBCO: the periodicity initially imposed by the charge modulation at 1/8 filling could eventually introduce a new periodicity in density, and thus in the lattice, and hence a reconstructed Fermi surface. An abundance of experiments suggests that such a density wave would be dynamic, yet, for the Hall effect and quantum oscillations, the electron-like behaviour may still be coherent, whereas the hole-like behaviour (perhaps because of the underlying timescales) is incoherent, and thus invisible. Even bearing in mind that the conjecture[1] of a density wave is based on data taken at very strong magnetic fields, the prospect that a density wave can connect a modulation of charge or spin density in real space with a modulation seen in the Fermi surface, a phenomenon of momentum space, is truly exciting.

This work also offers an opportunity for comparison with other unconventional, but low-temperature, superconductors. Perhaps the fastest growing class are the f-electron or heavy-fermion superconductors, of which more than 30 have so far been identified. In many of those systems in which quantum oscillations have been observed, a reconstruction of parts of the Fermi surface topology has been spotted precisely when applied pressure tunes the superconductivity to be strongest[10]. Just as LeBoeuf *et al.*[1] might well have shown for YBCO, the conduction electrons in f-electron superconductors seem to have a split personality — not between electron-like and hole-like behaviours, but between itinerant and localized electron states. Besides their impact on high-temperature superconductivity *per se*, the latest results also hit on a more general issue: why does superconductivity seemingly emerge in the presence of schizophrenic conduction electrons? ■

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