GRAIN BOUNDARIES

Guilty as charged

The electrical current that can be carried by a high-temperature superconductor is known to be sharply reduced by grain boundaries in the superconductor. A state-of-the-art calculation shows that this arises because of the accumulation of charge at the grain boundary.

James K. Freericks

Ever since the 1986 discovery of high-temperature superconductivity by Bednorz and Mueller[1], there has been promise of emergent new technologies. These fall into three main categories: low-cost current-carrying wires, passive electronic devices, and high-speed active digital electronics. Microwave notch filters are already in use in cell-phone towers, but the largest application of conventional superconductors in industry has come in the form of superconducting wires for magnets, such as those used for most magnetic resonance imaging machines. For these purposes, high-temperature superconductors fall short, because the critical current is exponentially reduced by the presence in the superconductor wires of grain boundaries — where nanometre-sized crystals meet at odd angles as the bulk crystal forms.

Enormous effort has been expended on growing superconducting tapes with small-angle grain boundaries, but this approach is not yet commercially viable for most applications (although it is used, for example, in current fault limiters and generators). A theoretical understanding of why the current is so sensitive to the grain-boundary mismatch is a longstanding problem in high-temperature superconductivity — but it has now been solved. As they report in *Nature Physics*, Siegfried Graser and colleagues[2] have shown definitively that it is accumulated charge at the grain boundary that causes the exponential decrease of the current with grain-boundary angle.

The atoms that form a solid crystal structure tend to lie in well-placed locations that repeat periodically through space, similar to the stacking of cannon balls. In a real material, however, the crystal is often composed of a very large number of small crystallites, which meet at the wrong angles where they touch, destroying the periodicity of the material. These 'grain boundaries' are characterized by the mismatch angle created between the crystal faces.

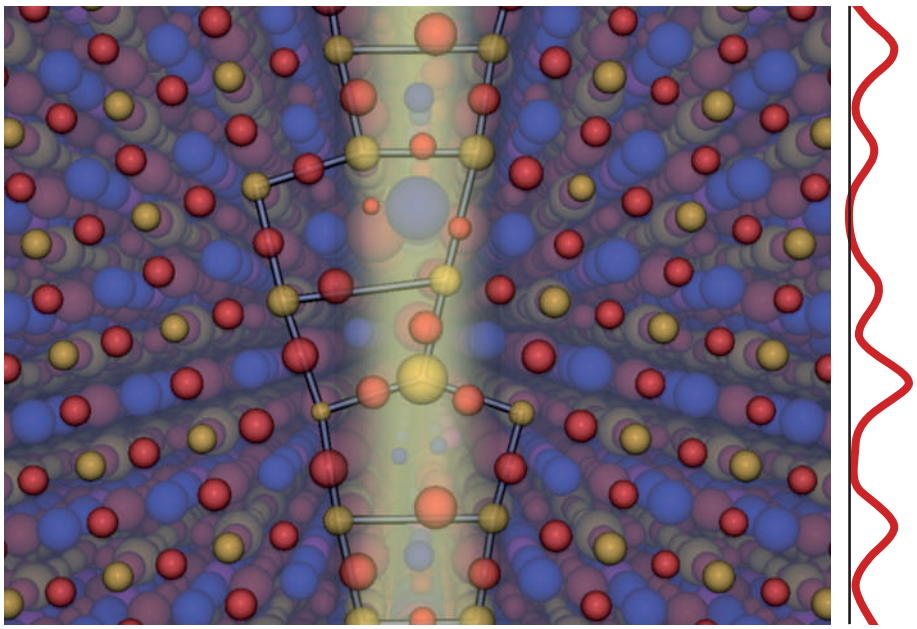

Figure 1 | Charge barrier. Grain boundaries form during crystal growth, for example, of the superconductor $YBa_2Cu_3O_{7-\delta}$ — shown here with a mismatch angle of 27.6°. The coloured circles highlight a plane, the size of each circle representing the charge around the ion; yellow circles are copper, red oxygen, blue barium and purple yttrium. (Deeper layers are in muted colours.) The change in the electronic charge around the grain boundary (shaded yellow) is illustrated by the amplitude of the charge modulation (red line, right) along a vertical cut through the grain boundary. Graser *et al.*[2] have now proved the connection between the charge at the boundary and the suppression of current in the superconductor. Figure courtesy of Siegfried Graser (Univ. Augsburg).

One would not naively expect grain boundaries to become charged, as the entire crystal is electrically neutral, and constituents of the material are uniformly distributed through the material, including near the grain boundaries. But, because of the mismatch between the crystals, bonds between different atoms can be broken and atomic positions can move around, leaving the possibility for the average charge of the electron clouds to vary in the area of the grain boundary. This is precisely what happens in a high-temperature superconductor made of yttrium, barium, copper and oxygen, as shown in Fig. 1.

High-temperature superconductors are notoriously sensitive to electronic charge: their parent compounds are insulators, and only become superconductors when the concentration of oxygen is changed, leading to a change in the number of electrons. The superconducting transition temperature and critical current vary significantly with the electron concentration.

Using state-of-the-art computational techniques, Graser *et al.*[2] first construct the fully relaxed atomic positions of the atoms at a particular grain boundary. Next, they find the electronic charge

associated with the grain boundary, and then they formulate a model for the superconductivity to determine the current that flows through the device. In this model, they see current that often flows in the wrong direction, and that the net current clearly shows an exponential suppression with grain-boundary angle, even for large-angle grain boundaries. Previous theories that focused on how the *d*-wave superconducting order parameter was mismatched across the grain boundary[3–5], or how grain boundaries create insulating regions[6], cannot show this exponential suppression for large-angle grain boundaries.

Now that we understand the underlying reason for the suppression of the current, can we find ways to alleviate it and make a technologically viable wire? It is well known that calcium moves preferentially along, and can reduce the charge at, a grain boundary, thereby increasing the current[7]. Expect the next generation of calculations, then, to examine how calcium doping on a grain boundary could mend the distribution of charge and improve the supercurrent flow. ❐

James K. Freericks is in the Department of Physics, Georgetown University, 37th and O Street NW, Washington, DC 20057, USA.
e-mail: freericks@physics.georgetown.edu

References

1. Bednorz, J. G. & Mueller, K. A. *Z. Phys. B* **64,** 189–193 (1986).
2. Graser, S. *et al. Nature Phys.* **6,** 609–614 (2010).
3. Sigrist, M. & Rice, T. M. *J. Phys. Soc. Jpn* **61,** 4283–4286 (1992).
4. Sigrist, M. & Rice, T. M. *J. Low Temp. Phys.* **95,** 389–393 (1994).
5. Yokoyama, T., Sawa, Y., Tanaka, Y. & Golubov, A. A. *Phys. Rev. B* **75,** 020502 (2007).
6. Gurevich, A. & Pashititskii, E. A. *Phys. Rev. B* **57,** 13878–13893 (1998).
7. Hammerl, G. *et al. Nature* **407,** 162–164 (2000).

MATHEMATICAL PHYSICS

Mutual stimulation

"The miracle of the appropriateness of the language of mathematics for the formulation of the laws of physics is a wonderful gift which we neither understand nor deserve", wrote Eugene Wigner in the closing paragraph of his 1960 essay *The Unreasonable Effectiveness of Mathematics in the Natural Sciences*. But the application of mathematics to problems in physics can also, in turn, bring wider recognition to otherwise little-known mathematical concepts. Jean Mawhin and André Ronveaux describe a beautiful example of such interplay — the role of Laguerre polynomials in the study of the hydrogen atom (*Arch. Hist. Exact Sci.* **64,** 429–460; 2010).

Laguerre polynomials famously describe the radial part of the solution of the Schrödinger equation for hydrogen-like atoms. In 1926, Erwin Schrödinger (right, with Werner Heisenberg and Paul Dirac, left) published a series of articles on 'quantization as an eigenvalue problem', in which he solved his equation for a single electron evolving in a Coulomb potential. However, in the first paper, as Mawhin and Ronveaux write, Schrödinger used a "nowadays almost forgotten method for obtaining the wave equation for the hydrogen atom". It was only in the second article — received by *Annalen der Physik* a month after the first — that Schrödinger started to make use of Laguerre polynomials. (Indeed, later, in the French translation of his book *Abhandlungen zur Wellenmechanik*, Schrödinger advised the reader to forget his first approach.) The third paper of the series, in which Schrödinger introduces his famous perturbation method, contains an appendix detailing the properties of generalized Laguerre polynomials.

MAX-PLANCK INSTITUTE COURTESY OF AIP EMILIO SEGRE VISUAL ARCHIVES

Ever since, Laguerre polynomials have appeared in textbooks whenever the Schrödinger equation is discussed. The same is not true, however, for solutions to the Dirac equation, the relativistic equation describing the hydrogen atom. Solutions expressed in terms of Laguerre polynomials were found shortly after Dirac's seminal 1928 paper, but seem to have been widely forgotten. Dirac himself didn't solve the equations exactly in his paper, only approximately. Complete solutions came shortly afterwards, first from Walter Gordon and, independently, Charles Galton Darwin, and later from the British mathematician Frederick Bernard Pidduck, who in 1929 explicitly used Laguerre polynomials to solve the equations — a contribution that, Mawhin and Ronveaux say, is often overlooked.

Laguerre polynomials owe much of their popularity to their role in the formal description of the hydrogen atom. Throughout the eighteenth and nineteenth centuries, a number of celebrated mathematicians made important contributions to the exploration of what we know today as Laguerre polynomials, including Joseph Louis Lagrange, Niels Henrik Abel, Robert Murphy, Pafnuty Chebyshev and, of course, Edmond Laguerre. But as these polynomials had few uses in classical mathematical physics, it was only with the advent of quantum mechanics that they rose, at last, to prominence.

ANDREAS TRABESINGER