PERSPECTIVES: SUPERCONDUCTIVITY

The True Colors of Cuprates

J. E. Hirsch

In the early days of superconductivity, researchers expected that superconductors, by analogy with good metals, would be particularly good reflectors of high-frequency radiation. However, no changes in reflectivity in the visible range were detected when metals were cooled below their superconducting transition temperature (T_c) (*1*, *2*). Half a century later, Molegraaf *et al.* report on page 2239 of this issue (*3*) that at least some superconductors appear to follow the original expectation. The results have important implications for the theory of high-T_c superconductivity.

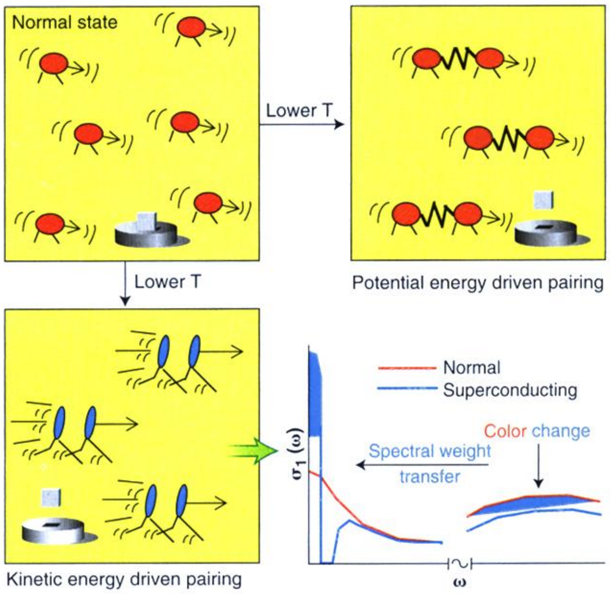
The search for enhanced reflectivity was abandoned when the Bardeen-Cooper-Schrieffer (BCS) theory of superconductivity was developed (*4*). BCS theory rests on the realization that superconductivity results when electrons pair up into "Cooper pairs," which can condense into a coherent state that is insensitive to impurities and imperfections and conducts electricity without resistance, and that the pairing is mediated by interactions of electrons with "phonons," the quanta of ionic vibrations of the crystal.

According to BCS theory, electrons form pairs with binding energy $2\Delta \approx k_B T_c$. Photons of energy $<2\Delta$ can therefore not be absorbed and optical absorption is inhibited at low frequencies (far infrared and microwave). This suppression of low-frequency optical absorption in superconductors has been detected experimentally (*5*). This spectral weight is transferred to a zero-frequency absorption δ-function that describes transfer of kinetic energy to the supercurrent; the equality of the spectral weight in the δ function and the spectral weight lost by the opening of the superconducting energy gap is referred to as the low-frequency optical sum rule (5).

The interaction between electrons and phonons that mediates Cooper pair formation can give rise to changes in absorption at frequencies $2\Delta + \hbar\omega_0$, where ω_0 is a phonon frequency in the infrared spectrum. However, no mechanism exists in BCS theory for changes in optical absorption in the visible range, and no attempts to measure superconductivity-induced "color changes" were undertaken for many years.

Enter the high-T_c cuprates. These remarkable materials, discovered in 1986 (*6*), exhibit superconductivity at much higher temperatures than their conventional counterparts. Charge carriers in high-T_c cuprates form Cooper pairs when they superconduct, but the pairing mechanism responsible for the high transition temperatures remains controversial. It is generally agreed that the conventional electron-phonon pairing mechanism cannot explain cuprate superconductivity, because the energy scale of lattice vibration frequencies is too small to explain transition temperatures as high as 160 K.

In BCS theory, the potential energy of the Cooper pairs is lowered through their interactions with the phonons. The kinetic energy increases slightly, but the lowering of the potential energy is larger, providing the condensation energy that stabilizes the superconducting state. To explain pairing in cuprates, new mechanisms have been envisaged in which the carriers lower their kinetic energy upon pair formation (*7*, *8*). Such kinetic-energy-driven superconductors would exhibit qualitatively new features in their optical properties—a "violation" of the low-frequency optical sum rule (*9*, *10*) and a "change in color" (*9*), that is, a change in high-frequency optical absorption—when the material becomes superconducting.



Two routes to pairing and superconductivity. In the conventional route (**upper right**), carriers lower their potential energy upon pairing. In the new route (**lower left**), carriers lower their kinetic energy upon pairing, they become lighter and can propagate more easily. In both cases optical spectral weight at low frequencies is rearranged due to the opening of the superconducting energy gap. Only in the latter case is optical spectral weight transferred from the high-frequency visible region to the low-frequency region.

The kinetic energy of charge carriers depends on their effective mass. Carriers that interact strongly with other carriers or other degrees of freedom have a large effective mass and cannot respond well to low-frequency electric fields; hence, the low-frequency optical absorption is small, and optical absorption occurs mostly at high frequencies. If the effective mass decreases upon pairing, optical spectral weight is transferred from high (optical) to low frequencies; the decrease in high-frequency absorption causes the "color change." As the effective mass decreases, the carriers can delocalize better and the kinetic energy decreases.

In 1999, Basov *et al.* performed optical experiments and detected a small lowering of kinetic energy in the interlayer transport of high-T_c cuprates (*11*). This finding provided some support for the interlayer tunneling mechanism (ILT) (*7*), in which the condensation energy arises from interlayer pair delocalization. Unfortunately, Moler *et al.* (*12*) and Tsvetkov *et al.* (*13*) had previously shown that ILT could provide no more than 1% of the condensation energy in certain cuprates. As a result, ILT is no longer considered a viable mechanism for cuprate superconductivity (*14*).

Molegraaf *et al.* provide convincing evidence for optical conductivity changes in the visible range, which track the opening of the superconducting energy gap. The authors do not directly measure the expected violation of the low-frequency sum rule that should accompany this effect. However, recent measurements by Santander-Syro *et al.* (*15*) show precisely that effect in the infrared spectrum. Both Molegraaf *et al.* and Santander-Syro *et al.* quantify the amount of kinetic energy lowering at ~1 meV per Cu atom. This lowering is much more than is required to account for the condensation energy of this material (~100 μeV per Cu atom) (*16*). This is, however, not surprising: an increase in potential energy should occur simply because of Coulomb repulsion between members of a Cooper pair, which should be substantial because of the short coherence length in the cuprates and should partially compensate for the kinetic energy lowering.

These results place strong constraints

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on theories of high-T_c superconductivity. A successful theory needs to explain the physical origin of the kinetic energy lowering and the magnitude, temperature-, and doping-dependence of the observed kinetic energy lowering. It must explain the physical origin of the high-energy scale that gives rise to the observed optical changes in the visible range, and elucidate the mechanism by which the remarkable coupling between this high-energy scale and the low-energy scale of the superconducting energy gap occurs.

Theories that ascribe the pairing mechanism to a magnetic exchange coupling predict an increase of kinetic energy upon pairing (*17*). They thus appear to be inconsistent with the new findings. Theories based on stripes (*18*) and spin-charge separation (*14*) may be consistent with the findings. Kinetic energy lowering has been predicted by these theories, but its expected magnitude must be quantified and the physical origin of the high-energy scale clarified. In the theory of hole superconductivity (*8*), pairing gives rise to lowering of the effective mass of hole carriers, and various predicted consequences (*9*, *19*) appear to be consistent with the reported observations. According to this theory, the same phenomena should also occur in other superconductors (*20*). New theories based on kinetic energy lowering will undoubtedly be formulated.

A new, qualitatively different paradigm for superconductivity is emerging. Carriers pair not because they are happy "being" together, as in the BCS paradigm, but because they are happy "moving" together, even if they are uncomfortable in each other's presence. It is like carpooling with someone one dislikes. The results of Molegraaf *et al.* show that kinetic-energy-driven superconductors, heretofore a theoretical construct, exist. Given that superconductors are defined by the enhanced ability of the carriers to propagate and thereby conduct electricity, this new paradigm makes eminent sense.

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PERSPECTIVES: PALEOCLIMATE

Blowing Hot and Cold

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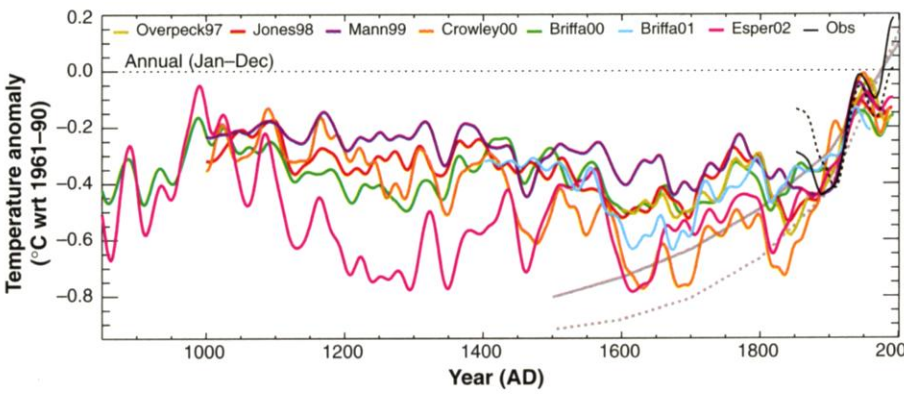
Hiding behind a rather dry title, Esper *et al.*, on page 2250 of this issue, provide a new and important vision of the detailed course of changing temperatures throughout the last millennium (*1*). Their analysis is based exclusively on tree-ring records from 14 locations spread over much of the northern extratropics. Though virtually all previous Northern Hemisphere temperature reconstructions use at least some tree-ring data, the authors use many new data and a processing technique that provides a largely independent history of widespread tree-growth variations, which they scale against modern temperature observations to estimate the relative magnitude of past temperature changes.

The new record differs in several respects from that highlighted in the Synthesis of the Third Assessment Report of the Intergovernmental Panel on Climate Change (IPCC) (*2*), which focused on the 1000-year reconstruction of Mann *et al.* (see the purple line in the figure) (*3*). This record has a smaller amplitude of century-to-century variability and is consistently at, or near, the upper limit of the range of alternate records produced by other researchers (*4–8*).

The curve from Esper *et al.* (pink line) shows a pronounced cold phase in the 17th century, in qualitative agreement with the other records and especially with a record of borehole temperature data (see the figure) (*9*), more so when the latter are first gridded to reduce bias due to regional concentrations of these records. The borehole data (and data from Mann *et al.*) are interpreted as indications of true annual temperatures, incorporating both warm season and cold season signals. All records in the figure have been calibrated assuming that they portray annual warmth. It is possible, however, as Esper *et al.* state, that their tree-growth data are more influenced by summer than winter conditions. This affects not only their own record but also a number of the tree-ring series used in other reconstructions shown in the figure.

To place their record on an absolute scale and allow direct comparison of past temper-



Records of past climate. Solid colored lines indicate seven reconstructions of Northern Hemisphere climate: yellow, (*4*); red, (*5*); purple, (*3*); orange, (*6*); green, (*7*); blue, (*8*); and pink (*1*). All records were re-calibrated with linear regression against 1881–1960 mean annual temperature observations averaged over land areas north of 20°N, and the results smoothed with a 50-year filter. The black dotted line shows the estimate that would be made if the predictor was observed warm-season temperatures from the same region, highlighting the difference between warm-season and annual temperature changes during the observed record. Black solid line: smoothed observations, truncated in 1993 when the record of Esper *et al.* ends. Gray lines: annual temperature changes estimated from Northern Hemisphere borehole temperature profiles [dotted line, unweighted average of many sites (*9*); solid line, records gridded before averaging].

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