Printing Office, Washington, DC, 1990), p. 176.
9. K. DeWitt, "Eighth graders' math survey shows no state is 'cutting it'," *New York Times*, 7 June 1991, p. 1.
10. A. N. Applebee, J. A. Langer, I. V. S. Mullis, "Crossroads in American education," (Educational Testing Service, Princeton, NJ, February 1989), p. 21.
11. That is, the GNP implicit deflator for government purchases; see *Economic Report of the President* (U.S. Government Printing Office, Washington, DC, January 1991), p. 291.
12. U.S. Department of Commerce, *Statistical Abstract* (U.S. Government Printing Office, Washington, DC, 1989), p. 172.
13. D. R. Waldo *et al.*, *Health Care Financing Rev.* **10**, 114 (1989), tables 2 and 3.
14. Reported money income is a good but not perfect measure of command over goods and services because it does not include fringe benefits, such as health insurance, or income from the underground economy, nor does it exclude personal income taxes. Estimation of the effects of these variables on the true net income available to households is very difficult, and even more difficult if separate estimates for children and adults are required.
15. Because the data gathered by the Bureau of the Census through the Current Population Surveys differs slightly from that gathered in the decennial censuses, the 1988 figures were adjusted to census levels by linking changes in the Current Population Survey results between 1980 and 1988 to the 1980 census levels. The number of persons in the samples are: 175,123 in 1960, 197,345 in 1970, 220,916 in 1980, and 155,654 in 1988.
16. Alternative calculations in which each child is weighted as some fraction of an adult, for example, 0.75 or 0.50, show that the trends over time that are discussed here are not sensitive to assumptions about the "adult equivalence" of children unless the assumption is changed appreciably from one year to another. We have no basis for making such changes.
17. That is, the GNP implicit deflator for personal consumption expenditures [*Economic Report of the President* (U.S. Government Printing Office, Washington DC, January 1991), p. 290].
18. The rapid growth in the female labor force participation rate since 1960 is accounted for primarily by women in households with children. Participation rates among childless women have always been high and show little change. Participation rates of older women whose children no longer live with them have shown only modest increases since 1960.
19. The purpose of this calculation is to show the contribution of women's earnings to the income available to children, not to suggest that women should not have paid jobs.
20. This statistical adjustment does not capture all the labor market and income effects of the increase in mothers taking paid jobs; to do so would require a complex model beyond the scope of this paper.
21. The weighted average of \$7640 and \$2397 is \$7273 when the weights are 93% and 7%, but only \$6644 when the weights are 81% and 19%.
22. That is, in more than 25% of the households without an adult male, women's earnings were the only source of income.
23. V. R. Fuchs, *Women's Quest for Economic Equality* (Harvard Univ. Press, Cambridge, 1988), p. 111.
24. Even if the mandate legislation is gender-neutral, the Swedish experience indicates that many more women than men will use the benefits ["A land where father (sometimes) is left holding the baby," *Sweden Now* **6**, 27 (1986)].
25. *Beyond Rhetoric: A New American Agenda for Children and Families*, Final Report of the National Commission on Children (U.S. Government Printing Office, Washington, DC, 1991).
26. Financial support for this work was provided by the Andrew W. Mellon Foundation. Helpful comments from V. Foster, A. Garber, E. King, E. Lewit, R. Olshen, and M. Shuchman are also gratefully acknowledged.

Fermi Surfaces, Fermi Liquids, and High-Temperature Superconductors

W. E. PICKETT, H. KRAKAUER, R. E. COHEN, D. J. SINGH

Recent experimental results are beginning to limit seriously the theories that can be considered to explain high-temperature superconductivity. The unmistakable observations of a Fermi surface, by several groups and methods, make it the focus of realistic theories of the metallic phases. Data from angle-resolved photoemission, positron annihilation, and de Haas–van Alphen experiments are in agreement with band theory predictions, implying that the metallic phases cannot be pictured as doped insulators. The character of the low energy excitations ("quasiparticles"), which interact strongly with atomic motions, with magnetic fluctuations, and possibly with charge fluctuations, must be sorted out before the superconducting pairing mechanism can be given a microscopic basis.

Of all the macroscopic properties that arise from the quantum nature of electrons in solids, superconductivity is the most striking. The complete disappearance of electrical resistivity at and below the superconducting critical temperature T_c results from the appearance of a coherent, macroscopic quantum state in which individual electrons can no longer dissipate energy. Accompanying the onset of superconductivity is the expulsion of magnetic fields from the superconductor and the widely reported facility for levitation of superconductors above magnets, or vice versa. For the 75 years after superconductivity was discovered in 1911, the phenomenon required very cold temperatures, within 25 K of absolute zero. Nevertheless, concerted scientific study has provided us with a large family of superconducting materials, and the theory of conventional superconductivity (*1*) is well established.

W. E. Pickett and D. J. Singh are in the Complex Systems Theory Branch, Naval Research Laboratory, Washington, DC 20375–5000. H. Krakauer is in the Department of Physics, College of William and Mary, Williamsburg, VA 23187–8795. R. E. Cohen is at the Geophysical Laboratory, Carnegie Institution of Washington, 5251 Broad Branch Road, NW, Washington, DC 20015–1305.

The breakthrough in high temperature superconductivity (*2*) that has appeared in the perovskite-derived copper oxides (cuprates) and bismuth oxides (bismuthates) was remarkable and unexpected. At present the highest T_c is 125 K in $Tl_2Ba_2Ca_2Cu_3O_{10}$, which is easily achieved using liquid nitrogen. This value is five times higher than known before Bednorz and Müller (*2*) in 1986 discovered superconductivity in cuprates. The bismuthate $Ba_{0.6}K_{0.4}BiO_3$ has T_c ~35 K, 50% higher than previously known. During the previous several decades the maximum value of T_c had increased steadily but very slowly, and the breakthrough naturally raised a wide variety of speculations about its microscopic origin. More recently, theorists have returned to more fundamental questions: Do these materials present a "novel state of matter," or are they rather "novel materials" that manage to wring a much higher critical temperature from established processes? In this article we review the evidence concern ing what has grown into something of a controversy since the discovery of high-temperature superconductivity: the character of the normal state.

The reason (other than the spectacular superconductivity) for the broad theoretical speculations about these superconductors is that many of the copper oxide superconductors have a sister compound (Fig. 1), typically differing by the removal or replacement of one atom in the unit cell, that is a non-superconducting magnetic insulator. Regions of magnetic, insulating behavior and metallic, superconducting behavior are separated narrowly at low temperature. Combined with the strong quasi-two-dimensional character of the cuprates, these features provide many possible origins for unusual properties such as high-temperature superconductivity. The bismuthate class of superconductors, while similar in many ways to the cuprates, are not quasi-two-dimensional (2D) and display no magnetism. These distinctions imply either that the high T_c mechanism is not related to two-dimensionality or magnetism in either class of material, or that the mechanism is fundamentally different in the two classes.

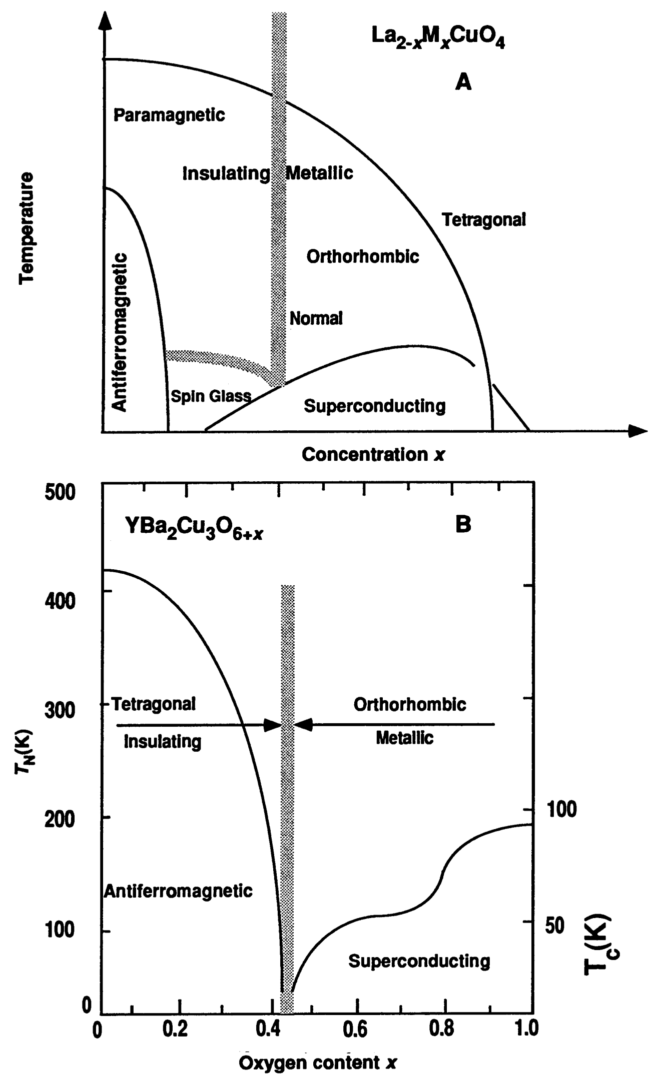


Fig. 1. Schematic concentration-temperature phase diagrams of the copper oxide based high temperature superconductors, showing insulating-metallic boundaries, magnetic-nonmagnetic boundaries, and structural transitions, in addition to the regime of high temperature superconductivity. (**A**) The $La_{2-x}M_xCuO_4$ type, M = Sr or Ba, where the maximum T_c occurs at fractional doping x; (**B**) $YBa_2Cu_3O_{6+x}$ type characteristic of the highest T_c materials, where the maximum T_c occurs for a stoichiometric compound.

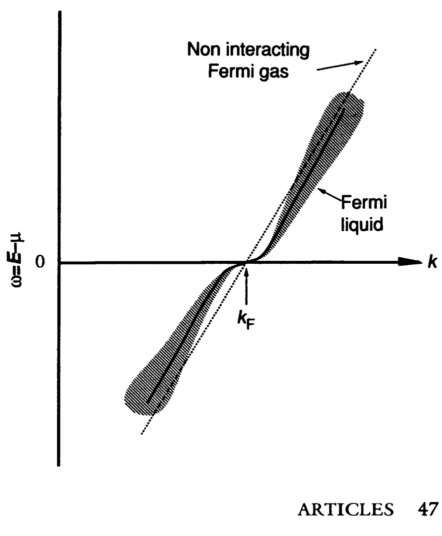
The Issue: Fermi Liquid, or Something Else?

The central question relates to the character of the normal state of the cuprates and bismuthates, with a secondary question being whether or not these two classes are fundamentally the same. During the 60 years since quantum mechanics was first applied to periodic solids, an understanding of the conventional metallic state, the Fermi liquid, has been developed in exquisite detail. This feat is remarkable in itself, considering that the problem involves an enormous number of electrons interacting strongly with each other and with atomic nuclei.

The Fermi liquid. The phenomenological Landau Fermi liquid picture (*3*) applies to metallic solids in which the low-energy excitations called quasiparticles (QPs) that determine its properties at low temperature and its response to low-frequency probes are analogous to those of a corresponding system of non-interacting electrons. These QPs are strongly modified ("renormalized") by the many-electron interactions and by interaction with the quantized atomic vibrations called phonons, and may lack the full intensity of an excitation of the fermion gas. In many ways, however, a QP behaves as a single electron. The lack of intensity appears as a wave-function renormalization factor $Z < 1$, with the "missing" intensity spread smoothly over energies away from the QP energy.

Luttinger (*4*) has justified Landau's phenomenological picture by showing that a periodic metal will have a Fermi surface, and its low energy behavior can be elucidated without detailed knowledge of the interactions. The infinite-order perturbation theory used by Luttinger is a widely accepted and highly developed formalism for describing quantum many-body systems, and the result may well be more general than the convergence of perturbation theory. This conventional Fermi liquid (cFL) picture of Landau and Luttinger provides explicit predictions: (i) there is a "Fermi surface" in momentum (**k**) space that encloses a known volume and to which the low energy excitations are confined, (ii) there is a discontinuity in the momentum distribution $n(\mathbf{k})$ across the Fermi surface, and (iii) the complex QP self-energy $\Sigma(\mathbf{k}, \omega) = \Sigma' + i\Sigma''$, which characterizes the degree of renormalization, satisfies specific requirements at the lowest energies ω: in three dimensions the real part Σ' is linear in ω, reflecting a mass renormalization, and the imaginary part Σ'' (giving the excitation's decay rate) is quadratic. Two-dimensional behavior (possibly relevant because of the layered structures of the cuprates) is similar if the Fermi surface is circular. This general behavior is illustrated in the QP dispersion curve shown in Fig. 2. The theory also provides the temperature dependence of thermodynamic properties, and the frequency of dynamic processes, in the asymptotic region $T \to 0$, $\omega \to 0$. The predicted

Fig. 2. Schematic plots of the quasiparticle band structure for a free Fermi gas and for a conventional Fermi liquid. The horizontal line denotes the Fermi energy, and k_F is the Fermi wavevector. The renormalized quasiparticle mass is enhanced (decreased slope at the Fermi energy) and broadened (denoted by hashed lines).



behavior applies below the degeneracy temperature T_F, which may be very low, and below a corresponding energy $\omega_F \sim k_B T_F$.

There is already striking experimental confirmation that the Fermi liquid concept in solids is an extremely robust one. The "heavy fermion" metals, based on *f*-electron atoms such as Ce or U, display extremely vigorous interactions between conduction electrons, local spin fluctuations, and charge (valence) fluctuations. Their thermodynamic and transport properties below 100 K can be exceedingly strange. Yet the ones that remain paramagnetic metals down to the lowest temperatures finally settle down into a highly renormalized, but nevertheless conventional, Fermi liquid regime (*5*). If any of these metals were to become superconducting above their degeneracy temperature, their properties would appear to call for a non-Fermi liquid description, when in fact the Fermi liquid regime simply had not been reached. Especially for the high T_c materials such complications should be kept in mind; in several cases T_c is greater than 100 K and the Fermi liquid regime, if it exists, may not have been reached at this temperature.

Complementary to the effort to systematize the metal near the ground state is the attempt to calculate properties of the system over a much wider energy range. Model Hamiltonians are often applied to this problem, but the past two decades have seen the development of sophisticated methods beginning solely from the periodically arranged constituent nuclei of the system and a quantum mechanical description of the electrons (that is, from "first principles"). Density functional theory (DFT) (*6*), commonly referred to simply as "band theory," is by far the most widely applied such approach. It is a highly ambitious approach, dealing with the full Hamiltonian and the precise structure. It provides a rigorous method for certain ground-state properties: the energy, the charge density, and the spin density, and it provides band energies and wavefunctions that are approximations (very often good ones) to QP bands and wavefunctions.

The spin-polarized version of band theory is not sufficiently accurate to predict (*7*) the observed antiferromagnetic insulating state for those layered cuprate compounds that are insulating (and are not superconductors). This shortcoming is a result of the local-density approximation for exchange-correlation energies. The local approximation, and the resulting local-density band structure, are remarkably good in general but are less accurate in some interesting materials, especially in materials where strong magnetic tendencies are present. Because most high T_c cuprates (but not bismuthates) have antiferromagnetic sister phases that local-density theory does not describe, its application to the metallic phases has also been suspect.

In spite of its shortcomings in the magnetic insulating phases, local-density band theory has proven to be not only reasonable but in fact very accurate in predicting from first principles a number of properties (*8*) of the metallic cuprates and bismuthates, such as lattice constants and atomic positions within the cell, phonon frequencies, structural instabilities, and electric field gradients. Any improvement, if one is necessary, must not change these predictions much. Band theory also provides an enormous amount of detail (*7*) about a system, such as the QP band energies and wavefunctions and their characters, including possible contributions from what are often viewed as "inactive" ions. In Fig. 3 we illustrate the Fermi surface predicted (*9*) by band theory for $YBa_2Cu_3O_7$. It is not at all a simple surface, because not one but four QP bands cross the Fermi energy. The surfaces are "electron-like" in some regions and "hole-like" in others, with the result that simple parabolic-band expressions cannot be used to evaluate properties such as the Hall coefficient and the Drude plasma energy.

A crucial question to be decided is to what extent, if any, these "band quasiparticles" provide at least a semiquantitative description of the excitations of metallic cuprates; failure to describe the antiferromagnetic insulators does not rule out a reasonable description of the metallic phase if the phases are fundamentally different. If the bands are qualitatively correct, then the band picture may be a good one upon which to build in remaining many-body effects via a self-energy correction.

Applying an extension beyond the local-density prescription by excluding the self-interaction of an electron when it is in a localized state, Svane and Gunnarsson (*10*) have uncovered an antiferromagnetic, insulating solution for La_2CuO_4 (as well as for the insulating transition metal monoxides) that corresponds closely to the experimental findings. In the metallic phase, such as for $YBa_2Cu_3O_7$, the solutions may revert to the standard local-density Fermi liquid

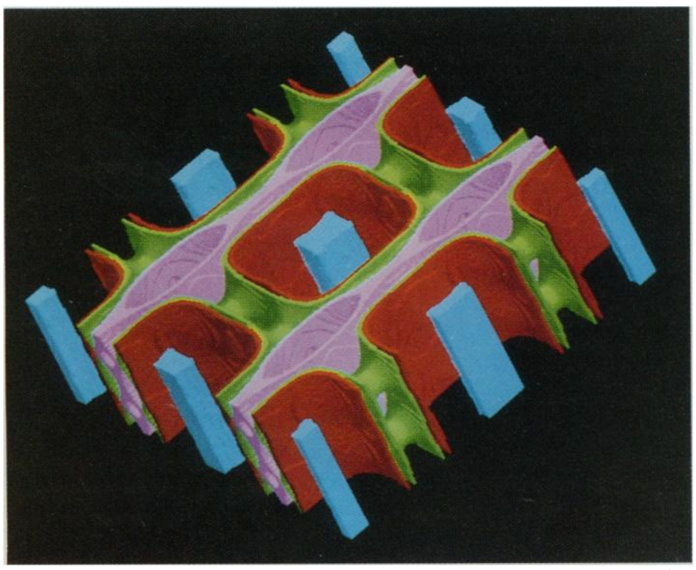


Fig. 3. Three dimensional picture of the calculated Fermi surfaces of $YBa_2Cu_3O_7$, slightly broadened and extended periodically. Roughly speaking, the red and green surfaces are derived from the two CuO_2 layers (bonding and antibonding combinations), the pink surfaces arise from the CuO chains, and the smaller blue cylinders contain both layer and chain character. (Image produced on Sun Sparc 2 with Sun Vision.)

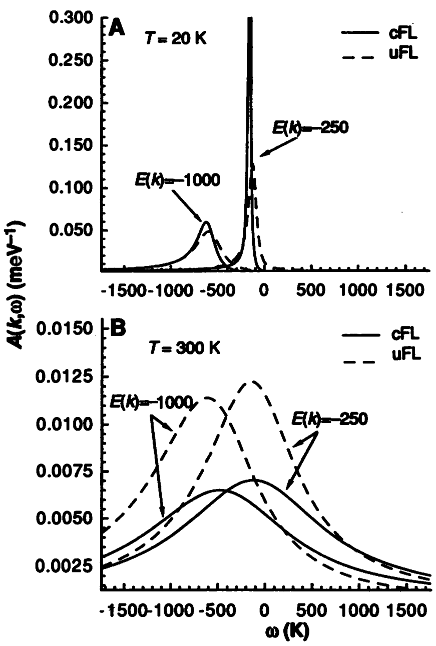


Fig. 4. Representative spectral densities for conventional (solid lines) and unconventional (dashed lines) Fermi liquids, illustrating the differences that may however be difficult to distinguish experimentally, since absolute intensities are not obtained. The spectral density measures the intensity of an excitation versus energy, and reflects the broadening arising from strong interactions between electrons. The top (**A**) and bottom (**B**) panels denote very low temperature and room temperature, respectively, and in each panel the spectral density for two different momenta (corresponding to unrenormalized binding energies of 250 K and 1000 K) are shown.

solution, as they have found (correctly) for the metal VO. If this turns out to be the case, and further analysis of the insulating phase shows the description to be realistic, this theoretical development will remove the most commonly held reservation toward the band viewpoint.

Unconventional states having Fermi surfaces. A generalization of the Fermi liquid concept is that of an unconventional Fermi liquid (uFL), based on a self-energy that differs from the cFL form discussed above. The alternative form that is most often discussed has a QP decay rate Σ'' at $T = 0$ that is linear (rather than quadratic) in both $|\omega|$ and the real part $\Sigma' \sim \omega\log|\omega|$. Discussion of such behavior goes back at least to Shekhtman (*11*). One scenario for the high T_c materials, called the "marginal" Fermi liquid by Varma *et al.* (*12*), was motivated by unusual normal-state properties observed in many cuprates: linear-in-T resistivity, linear-in-ω tunneling conductance, unusual nuclear magnetic resonance (NMR) relaxation behavior, the flat Raman scattering background, and thermal conductivity. Virosztek and Ruvalds (*13*) have shown that a band structure with strong Fermi surface nesting (scattering between parallel regions of Fermi surface) leads to a "nested" Fermi liquid form of the QP self-energy and behavior at low ω and T essentially like the uFL form mentioned above.

Although the elementary excitations at nonzero ω and T are still quasiparticles in the uFL picture, at very low ω and T where Fermi liquid theory makes specific predictions of power-law behavior of excitations, their behavior follows the different asymptotic form given above (*14*). A qualitative difference is that the QP effective mass diverges logarithmically as ω, $T \rightarrow 0$, and the QP intensity Z vanishes logarithmically at the Fermi surface. Although this behavior seems strikingly different from the conventional one, the resulting spectral density differs only subtly from its cFL counterpart except very near $T = 0$, where it is dominated by the relatively large broadening as ω, $T \rightarrow 0$. The difference rapidly becomes less important as T increases. Spectral densities illustrating the differences are pictured in Fig. 4.

Alternatives. A metallic periodic solid need not necessarily be a Fermi liquid, even an unconventional one, although there seem to be no accepted physical counterexamples at present. (Bipolaronic materials may be the nearest possibility.) Possible conditions under which a breakdown of the Fermi liquid state might occur are not clear; low dimensionality with its strong nesting and van Hove singularities are the most widely discussed possibilities for inducing exotic behavior.

A standard alternative to the quasiparticle picture arises from consideration of the Hubbard Hamiltonian, which was suggested for the high T_c materials in the expectation that on-site Coulomb interactions are dominant and that the model would describe the insulating and lightly doped-insulator regime. This picture has led to conjectures that a Fermi liquid picture of the metallic phases is not viable, either because of strong interactions or possible instabilities of the 2D electronic system. The Hubbard model describes particles hopping, with bandwidth W, on a lattice whose sites have a single available state for each spin. Only opposite-spin particles interact, and then only when on the same site, with energy U. This model is intended to capture some of the more striking behavior of crystals displaying either magnetic or "highly correlated" behavior. Although very little about this model has been firmly established, it is suggested to provide a surfeit of novel phenomena, which can be searched for in condensed matter systems. With respect to real materials, the Hubbard model shows some peculiarities; due to the lattice formulation and the simple, on-site interaction, it displays extra local symmetries (*15*), and its spectrum is bounded above.

One view of its role is that, as was previously successful for Bardeen, Cooper, and Schrieffer (*1*) with their reduced BCS Hamiltonian, one might hope to identify the essential interaction in its simplest form and work out the consequences. In fact the BCS interaction is a highly anomalous (non-local, infinite-range) attraction that is not like the one actually responsible for conventional superconductivity. The microscopically justified theory of the conventional electron-phonon coupled superconductors was presented in detail by Scalapino, Schrieffer, and Wilkins (*16*). The simple BCS model "works" because the fundamental process is pairing of quasiparticles near the Fermi surface, the BCS reduced interaction reproduces such a pairing, and that is all that matters in the weak-coupling limit.

Although simple in form, the Hubbard model has proven exceedingly difficult to sort out, at least when $U/W > 1$. Although many studies had suggested that, away from half filling, this model describes a Fermi liquid unless U/W is very large, even this qualitative result is now being reconsidered. On one hand, some studies (*17*) have used the Hubbard model to motivate a cFL description of the cuprates. On the other hand, there has been a variety of suggestions (see below), based on ideas stemming from the infinite U or negative U Hubbard models, of ground states differing from the (conventional or unconventional) Fermi liquid, and that these might persist to more physical values of U. Recent numerical studies (*18*) suggest that, for physical values $U \sim W$ and well away from half filling, the Hubbard model in two dimensions behaves in a cFL-like fashion, while near half filling more complicated behavior can appear, arising from nesting or from critical points in the band structure (van Hove singularities).

Widely discussed alternatives to Fermi liquids include the resonating valence bond possibility (*19*) (superposition of spin-singlet electron pairs distributed over a range of separations), the anyon/flux phase states (*20*) characterized by a loss of time-reversal symmetry, and the bipolaron picture (*21*) in which charge carriers bind into pairs to form bosonic, rather than fermionic, excitations. For the first two of these possibilities the theories are incomplete, in terms of the existence (or not) of something like a Fermi surface and of how thermal, transport, and optical properties would differ from a Fermi liquid, so references to these possibilities will perforce be limited to their few anticipated properties.

There have been serious attempts to proceed to more realistic extended Hubbard models (*22*), with $U/W \sim 1$ and intersite interactions that are not negligible. Since the excitations move primarily on the oxygen ions while the strongest interactions are located on the Cu ions, it seems that even the simplest realistic model must contain more than a single site per cell. Understanding extended Hubbard models is more difficult than for the single-band case, so the predictions also remain undecided. As models are made more realistic the spontaneous broken symmetry solutions (such as anyon phases) seem to be more difficult to obtain (*23*), so it is probably realistic to anticipate that extended Hubbard models with imperfect nesting and smeared out van Hove singularities as well as more interactions will have a stronger tendency toward cFL behavior than the standard Hubbard model.

The Experiments: Fermi Surfaces and Quasiparticle Bands

There are three primary experimental methods of measuring Fermi surfaces: de Haas–van Alphen (dHvA) and related effects, angular correlation of annihilation radiation (ACAR) from positrons annihilating with electrons, and angle-resolved (direct and inverse) photoelectron spectroscopy (ARPES and ARIPES, respectively). The dHvA experiments measure oscillations in electronic properties arising from electrons orbiting the Fermi surface in resonance with an applied magnetic field. Completed orbits require long mean free paths, which normally require clean, stoichiometric crystals and low temperatures. High T_c cuprates would seem to be ill-suited to the application of dHvA techniques, due to the short mean free path (arising from relatively poor sample quality); nevertheless results have now been reported.

The resolution of the other two methods is considerably reduced from that of dHvA, but the Fermi surface geometry is obtained more directly. Due to the short escape depth of the excited electron (a few atomic layers), photoemission spectroscopy (PES) is extremely sensitive to atomic arrangements at the surface of the sample. This presents problems for the study of the bulk electronic structure of cuprates, with the complications including problems with sample surface quality and the possibility of surface states that can be confused with bulk states.

ACAR spectra measure the electron-positron momentum density, which has discontinuities at momenta **p** corresponding to the Fermi surface. Complications for the ACAR method are (i) lattice imperfections (possible positron trapping at defects or grain boundaries), (ii) low count rates, and (iii) character of the positron wave-function: if, for example, it avidly avoids the Cu-O layers, then layer-derived Fermi surfaces may be "invisible" to positrons. Fortunately, the quasi-2D structure of the cuprates provides simplifications. First, the Brillouin zone dimension is small perpendicular to the Cu-O layers, and the expected dispersion is much less in this direction, so the surfaces should be roughly "cylinders" of arbitrary cross-sectional shape, as are the calculated Fermi surfaces of Fig. 3. Second, the layered structure and strong anisotropy of the cuprates make it easy to prepare the (001) surface or to orient small crystals as necessary.

ARPES. A breakthrough in the study of $EuBa_2Cu_3O_{7-y}$ was reported by List *et al.* (*24*) who found after cleaving a single crystal in vacuum at low temperature (20 K) that oxygen leaves the surface at temperatures as low as 80 K. This established that all previous PES data (in which no Fermi cutoff was found) and any taken since without similar precautions reflect properties of an oxygen-deficient insulating surface layer rather than the metallic bulk. Subsequently Arko *et al.* (*25*) reported identifying the Fermi edge in $YBa_2Cu_3O_{6.9}$, and since then clear Fermi edges have been seen in both direct and inverse PES of many cuprate superconductors. Olson *et al.* (*26*) established that the Fermi edge of $Bi_2Sr_2CaCu_2O_8$ is precisely the same shape as that of Pt, for temperatures from 100 K to 250 K. Taken together, these results establish that metallic cuprates have a sharp cutoff at the Fermi level, consistent in detail with the fermionic excitations of a Landau Fermi liquid. This fact poses severe problems for the bipolaron picture.

ARPES studies designed to search for band-like dispersion of the spectral peaks have been carried out by several groups. The most extensive investigation of Fermi surface band crossings in $YBa_2Cu_3O_7$ has been reported by Campuzano *et al.* (*27*) whose investigations at about 40 different angles revealed Fermi surface crossings that coincided closely with the predictions of band theory in all respects (Fig. 5). Several ARPES studies of $Bi_2Sr_2CaCu_2O_8$ have been reported. The Karlsruhe-Kiel group (*28*) reported both direct and inverse ARPES results, finding a band that crosses the Fermi surface where band calculations predict two degenerate (within experimental resolution) Cu-O layer bands to be, and two bands near and at the zone edge M point where band theory predicts Bi-O derived bands. Olson *et al.* (*26*) observed the Cu-O band, with the point of Fermi surface crossing in excellent agreement with the Karlsruhe-Kiel group and with band predictions. By depositing an Au overlayer on the surface (a Bi-O layer), Wells *et al.* (*29*) have verified the Bi-O character of pieces of the Fermi surface predicted by band calculations to be Bi-O related states. Takahashi *et al.* (*30*) observed two bands within 0.5 eV below E_F, the uppermost in agreement with the ARPES data mentioned above. The origin of the other band is not clear. An ARIPES study by Bernhoff *et al.* (*31*) mapped out a number of dispersive bands above E_F that show similarity to band calculations, although there are shifts relative to the band energies and extra spectral peaks, perhaps due to surface states. The one observed Fermi surface crossing agrees with both ARPES results and band calculations.

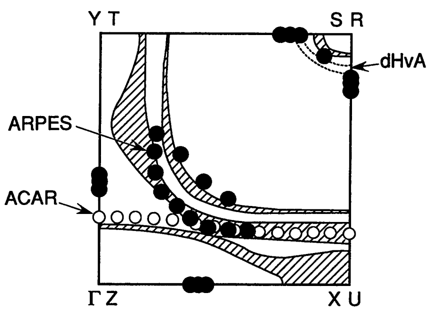


Fig. 5. Cross section in the (k_x,k_y) plane (*9*) of our calculated Fermi surface for $YBa_2Cu_3O_7$, together with the ARPES data of Campuzano *et al.* (*27*) (solid circles), the ACAR data (open circles), and dHvA data (dashed lines at upper right). The hashed areas represent those values of (k_x,k_y) for which there is a Fermi surface for some value of k_z; thus the width of the hashed area reflects the k_z dispersion of the band at that point in the plane. The dHvA data are presented as suggested by Fowler *et al.* (*36*). The data points that lie on large circular arcs correspond to the two Cu-O layer-derived Fermi surfaces, which are the red and green surfaces in Fig. 3. The data points near the $S(R)$ point correspond to the blue sheet in Fig. 3.

ACAR. Very high statistics ACAR spectra (*32*) from the University of Texas-Livermore collaboration and the Argonne group, obtained from detwinned $YBa_2Cu_3O_7$ crystals, provide convincing evidence for the flat Cu-O chain-derived Fermi surface sheet, precisely as expected from local density band calculations, as pictured in Fig. 5. In agreement with expectations based on our calculations of positron wavefunctions (*33, 34*) which showed little overlap of the positron density with the Cu-O planes, the researchers found no evidence for the plane-derived Fermi surfaces. Thus not only the position of the bands, but also their character, is borne out by the ACAR data.

Many theories anticipate the layer-derived bands (and Fermi surfaces) to be more closely related to superconductivity, and therefore more important to identify, than the chain-derived surface seen experimentally. Calculations (*33, 34*) predict that positrons would be better probes of layer-derived Fermi surfaces in $Bi_2Sr_2CaCu_2O_8$ ($T_c > 80$ K), and that $Tl_2Ba_2CaCu_2O_8$ ($T_c > 100$ K) is even more promising. Two groups (*35*) have reported ACAR studies on a single, untwinned crystal of $Bi_2Sr_2CaCu_2O_8$ ($T_c = 90$ K). Such Bi-based crystals are orthorhombic due to a structural modulation in the Bi-O layers, so data projection was required before comparison with the band predictions for the idealized tetragonal structure. Chan *et al.* (*35*) find evidence for the Bi-O portion of the Fermi surface, and some indication of the Cu-O planar Fermi surface predicted by band calculations.

dHvA. From the earliest times of consideration (that is, four years ago) it has seemed inconceivable that dHvA oscillations could ever be seen in cuprate samples, which are not precisely stoichiometric and have $T_c \sim 100$ K. Remarkably, two reports of observations (*37*) of oscillations in $YBa_2Cu_3O_7$ have now appeared. The Los Alamos group has used an explosively-powered flux-compression system to produce magnetic fields above 100 T lasting a few tens of microseconds. For aligned crystals cooled to ~2 K, they observed three oscillations, reflecting cross-sectional areas corresponding to magnetic fields of 0.5, 0.8, and 3.5 kT. Using more conventional methods, the Tohoku-Osaka collaboration made measurements in steady fields up to 27 T, and reported a single oscillation whose area is in excellent agreement with the smallest of the orbits found by the Los Alamos group.

The two smaller orbits (a few percent of the Brillouin zone area) correspond closely to the smallest Fermi surface orbits predicted by band calculations, so we have sketched them in on Fig. 5 in this place. Higher fields or cleaner samples will be required before the larger area, layer-derived surfaces can be observed by dHvA. According to the calculations, the measured surfaces centered at $S(R)$ in Fig. 5 arise from a combination of states associated (*7, 9*) both with the Cu-O chains and the bridging oxygen near the CuO_2 layers, reflecting coherent participation of chain and layer states at the Fermi surface. This interpretation also requires a three-dimensional Fermi surface with dispersion (small but not negligibly so) perpendicular to the Cu-O layers, conflicting with pictures requiring extremely weakly coupled 2D layers.

Band metals, not doped insulators. The ARPES data clearly show dispersing, Cu-O layer-related bands crossing the Fermi surface, the unmistakable sign of Fermi liquid-like behavior. The ACAR data vividly reveal the Cu-O chain-related band, indicating metallic character of the chain. The dHvA data reflect the remaining piece of predicted Fermi surface, the hybridized layer-chain Fermi surface. All of the Fermi surface data strongly support the predictions of band calculations, and all of the calculated surfaces [predicted four years ago (*7, 9*)] in $YBa_2Cu_3O_7$ have been seen. Effective masses are no doubt altered from the band masses (as is always the case), but rather than detracting from the band picture, these results tend to support it by suggesting that masses and related quasiparticle properties should be obtained by including a substantial but standard (in principle) self-energy correction to band quasiparticles as in other normal metals. Moreover, the ARPES and ACAR data have verified the character of the Fermi surfaces predicted by band theory.

The spectroscopic data now clarify one of the long-standing points of contention: Is the high T_c metallic phase to be regarded as a band metal, as band theory predicts, or a doped insulator, as the phase diagram has led many to accept? Direct and inverse photoemission studies, as well as electron energy loss spectroscopy, indicate a continuous spectral density from below and above, vanishing only at the common Fermi cutoff, indicating no gap near the Fermi level. The Fermi surfaces are large and obey Luttinger's theorem, rather than being small and enclosing a fraction of one carrier as in a doped semiconductor. The specific predictions of most alternative pictures are not yet established, but the band picture is in excellent agreement with Fermi surface geometries and characters.

The Fermi Liquid: Conventional or Unconventional?

The data discussed above mandate that a theory of the high T_c materials begins with the Fermi surface. The finding that the measured Fermi surfaces are predicted correctly by band theory provides both general implications and strong specific constraints. The exotic models (anyons, flux phases), which are suggested to arise in strongly correlated systems, can hardly be expected to apply to metals whose Fermi surfaces are predicted correctly by band theory. Moreover, it can be surmised immediately that the self-energy, relative to the local density bands, must be essentially k-independent parallel to the Fermi surface, otherwise it would alter the Fermi surface.

Considering the dynamic processes that are neglected in local density theory, this conclusion is especially significant. A wide variety of experiments, as well as local-density–based calculations (*8*), demonstrates that certain phonons are strongly coupled to QPs at the Fermi surface, but it has long been known that lattice vibrations do not affect the Fermi surface itself. But there are several other considerations. First, magnetic fluctuations have been seen in $YBa_2Cu_3O_{7-y}$. As the oxygen deficiency y decreases and T_c increases, the fluctuations lose much of their coherence and move to higher energy (*38*), implying that for ideal ($y = 0$, $T_c = 93$ K) materials they may be nearly incoherent. Even so, with Fermi surface nesting the resulting self-energy could be dispersive. Second, Egami and collaborators (*39*) have found that the Cu-O layers contain pronounced short-range disorder, with atoms lying off their ideal lattice sites in an incoherent fashion. Third, there may be charge fluctuations, of which little is known at present. Like electron-phonon coupling, none of these effects is included in the band calculations. Evidently these interactions, some of which may be strong, leave the Fermi surface unchanged from the band theory prediction. As mentioned, this will be the case if they lead to a self-energy that may be strongly ω dependent but must be very weakly **k** dependent parallel to the Fermi surface. The self-energies that have been discussed within most of the uFL pictures satisfy this constraint.

Low ω, *low* T *experiments.* Now that sample quality has generally improved over that of the "early days," there has grown to be an accepted body of experimental data "characteristic" of the normal state of these materials. We now address these properties and their implications for the two pictures (cFL or uFL) of the normal state.

Electronic transport. The resistivity $\rho(T)$ in many of the materials shows a linear temperature dependence from just above T_c to 500 to 800 K, although others, such as $YBa_2Cu_4O_8$ and $Nd_{2-x}Ce_xCu_4$, show nonlinear behavior. Initially suggested to be very strange, it has since been found that similar behavior over a wide temperature range can result not only from scattering from phonons but from several other possible mechanisms. That the linearity extends down to 10 K in the $Bi_2Sr_2CuO_6$ material (*40*) is unusual; that the linearity extends so high in temperature is also unusual if one expects "resistivity saturation" to occur as happens in conventional 3D metals. The uFL picture accounts qualitatively for this behavior, but without identifying the scattering mechanism or accounting for the lack of saturation.

But implications of the resistivity may not be so simple. Sundqvist and Andersson (*41*) have questioned whether the linearity of ρ is the proper transport question to address: When the large volume coefficient of resistivity of the cuprates is accounted for, $\rho(T)$ at constant volume is not linear, but rather only $\rho(T)$ at constant (atmospheric) pressure. At constant volume (which is what standard theories address), ρ is concave downward, consistent qualitatively with behavior seen in conventional metals, although ρ itself is unusually large.

Moreover, linear (isobaric) $\rho(T)$, though common, is not universal. This appears clearly in $YBa_2Cu_4O_8$ ($T_c = 80$ K), which is stoichiometric and much more stable than the more widely studied $YBa_2Cu_3O_7$ material, but is structurally similar, having only an extra Cu-O "chain." Its resistivity is concave downward (*42*) above ~200 K, typical of behavior observed in conventional metals with strong electron-phonon coupling. Massidda *et al.* (*43*) have found that band-theory-based transport theory incorporating only scattering by phonons accounts for the data on $YBa_2Cu_4O_8$, and that disagreement in $YBa_2Cu_3O_7$ is not as serious as suggested by earlier studies. To summarize, the resistivity is not fully understood, but it is not obviously inconsistent with either the cFL or uFL pictures.

Quasiparticle behavior. One of the best means to test theories would be to measure directly the quasiparticle linewidths all around the Fermi surface. This is not at all easy. The most direct procedure is to use ARPES at the highest resolution and at low T, enabling in principle imaging at the lowest possible excitation energies and identification of the linewidth (inverse decay rate). However, even the recently improved energy resolution (approaching 15 meV ~ 180 K) has not been sufficient to resolve the questions, and the onset of the superconducting state further complicates spectroscopy very near the Fermi surface.

Olson *et al.* (*26*) have extracted linewidths from their data on $Bi_2Sr_2CaCu_2O_8$, after removing background and modelling the (non-negligible) nonzero angular resolution, obtaining a linear width $\Gamma(\omega) \sim 0.6\omega$ in the range $40 < \omega < 300$ meV, ostensibly consistent with the uFL picture. However, our recent calculations indicate (*44*) that linear linewidths due to phonon scattering occur in the range $10 < \omega < 80$ meV, requiring spectroscopies to go below $\omega < 10$ meV to obtain the form of the limiting (cFL or uFL) behavior.

Raman scattering. A strong, structureless Raman background has been observed in many of the high T_c cuprates and in the bismuthate (*45*) $Ba_{1-x}K_xBiO_3$. It arises from electronic scattering and is symmetry specific. According to Slakey *et al.* (*46*) the B_{1g} symmetry response follows closely the form assumed for the uFL picture, while that of A_{1g} symmetry follows a less unusual relaxation form. Investigating these forms down to low temperature is interrupted by the onset of superconductivity. Monien and Zawadowski (*47*) have shown that the band structure of $YBa_2Cu_3O_7$ allows interband Raman scattering down to very low energy, which could show up as a Raman background. To oversimplify, the Raman background provides support for the uFL picture, but it is not understood in detail within this theory nor is it necessarily inconsistent with cFL behavior.

Magnetic resonance. The NMR spin-lattice relaxation time T_1 for high T_c materials has been widely discussed as reflecting something different than a conventional Fermi liquid. The expression for a Fermi liquid is the Korringa relation $1/T_1T$ = constant, and indeed this behavior is followed by the oxygen and yttrium nuclear spins, thereby appearing to necessitate a cFL state (*48*). The T-dependence of the planar Cu T_1 is more complicated, and was one argument (*12*) for adopting a uFL outlook. However, the Korringa prediction quoted above assumes a completely innocuous Fermi liquid, whereas the cuprates represent a richer Fermi liquid with strong spin fluctuations, confined primarily to the Cu atoms. For such a system, that is, a renormalized cFL, the Korringa theory can be generalized (*49*) to account for the crystal structure and magnetic fluctuations, with the result that T_1 should behave in the manner observed. Thus cFL theory can account for the Cu NMR data, while it would be difficult to explain the (conventional) oxygen and yttrium behavior within a uFL picture.

Circular birefringence. The "flux phases" of the 2D *t-J* model and the anyon models support regimes in which time reversal and 2D reflection symmetry are broken. A prime feature of the broken time reversal symmetry is the possibility of circular dichroism and birefringence. These optical effects have been searched for by AT&T, Stanford, and German groups (*50*). Positive results have been reported by the AT&T and German groups for both $YBa_2Cu_3O_7$ and $Bi_2Sr_2CaCu_2O_8$, while the Stanford group reported no sign of circular activity on a variety of $YBa_2Cu_3O_7$ samples. In addition, the AT&T group has found circular dichroism in samples of $Ba_{1-x}Rb_xBiO_3$, a non-copper material with the cubic perovskite structure. These experimental results are confusing at best, but the discovery of the effect in a 3D non-cuprate material indicates that theories based on the dominance of two-dimensionality (flux phases, anyons) cannot provide a unified explanation of the data. Another difficulty for the pictures based on overwhelming two-dimensionality is that, in the best $YBa_2Cu_3O_7$ samples, the resistivity ρ_c perpendicular to the Cu-O layers is metallic, indicating good coupling of carriers across layers that would invalidate the assumptions (strict two-dimensionality) underlying an anyonic description. The critical temperature itself is observed to be insensitive to the behavior of ρ_c.

There are two further experimental indications that the anyon picture is untenable. First, persistent currents indicative of coherent quantum tunneling between conventional and high T_c superconductors have been observed (*51*), whereas this would not occur between a conventional superconductor and an anyon superconductor. Second, an anyon phase would give rise to magnetic fields arising from the spontaneously occurring fluxoids. Muon spin resonance (*52*) experiments have put an upper bound on such fields that is well below what the theory predicts. Thus experimental evidence is close to ruling out an anyon phase.

The Theoretical Situation: Moving Toward Resolution

The quantitative successes of first principles band theory that are now evident demonstrate that we are closer to a predictive theory of the normal phase of the high-temperature superconductors than could have been expected even one year ago. We do not imply that remaining questions are simple. Self-energy corrections away from the Fermi surface may be substantial, and formulating a realistic theory of dynamic processes and the resulting self-energy will be the next step in unravelling the mysteries of the high-temperature superconductors. Magnetic fluctuations are likely to give important contributions and their effects are not well understood.

The bands at the Fermi surface themselves indicate other processes that need further consideration, of which we mention two. First, the degree of Fermi surface nesting can be evaluated directly using the quantity (*53*)

$$\xi(Q) = \sum_{\mathbf{k}} \delta(E_{\mathbf{k}} - E_F)\delta(E_{\mathbf{k}+\mathbf{Q}} - E_F) \quad (1)$$

that measures the phase space available for scattering a QP from any point $\mathbf{k}$ on the Fermi surface to another point $\mathbf{k} + \mathbf{Q}$ also on the Fermi surface. For $La_{1.85}Sr_{0.15}CuO_4$, we have found that this nesting indeed peaks strongly at the zone corner X point (Fig. 6), and it is also strongly peaked all along the (q, q, k_z) direction for all k_z. The consequences of this strong nesting are not yet fully understood, but this behavior of $\xi(Q)$ is much like that assumed by Virosztek and Ruvalds (*13*) in their "nested Fermi liquid" model, suggesting that the treatment of many-body effects beyond, but built upon, band theory could lead in some cases to behavior similar to that of a uFL.

A second feature of the band structures near the Fermi level is that, in several of the compounds, there are interband transitions extending down to $\omega = 0$. The consequences are not fully understood, even though this sometimes occurs in standard metals. These low energy excitations could affect the resistivity as well as the Raman background. Whether such low energy interband transitions occur generally enough in high T_c materials to be a plausible explanation is not clear.

Another consideration for the cuprates is crystal quality, and the degree of true crystalline order even for stoichiometric crystals. Neutron scattering determinations of the (nuclear) pair distribution function for several cuprates (*39*) indicate that Cu and O atoms in the layers are not placed simply as diffraction experiments suggest, but rather that there are out-of-plane displacements of both atoms. These local distortions are without long-range order, so they do not contribute in diffraction determinations of the structure except to add to the statistical distributions ("ellipsoids") derived from structural refinements. A consequence of this innate disorder could be to add an intrinsic broadening (weakly dependent on ω and T) to the QP peak, thereby making the near-Fermi-surface properties scale differently from a cFL state even though there is nothing intrinsic in

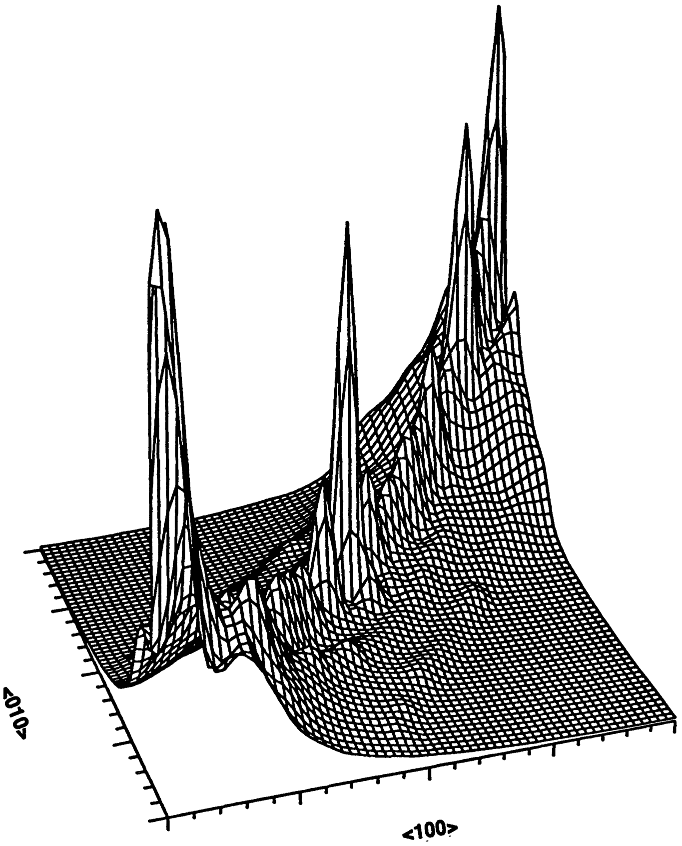


Fig. 6. Surface plot in the two dimensional plane $\mathbf{Q} = (q_x, q_y, 0)$ of the Fermi surface nesting factor $\xi(\mathbf{Q})$ for $La_{1.85}Sr_{0.15}CuO_4$, which reflects the number of allowed transitions for a quasiparticle scattering on the Fermi surface through momentum-transfer $\mathbf{Q}$. The transitions are concentrated near the Γ-X diagonal line (Γ is the near corner).

the electronic system to drive it away from cFL behavior.

No doubt most of these complications will be addressed in the near future, and intense investigation of unconventional or novel electronic behavior will continue. The inescapable conclusion is that any of these theoretical pursuits must be consistent with the measured Fermi surfaces and with nearby excitations to be considered viable possibilities. We have not addressed the question of superconductivity at all here, but the implication is clear: Theories based on (conventional or unconventional) Fermi liquid theory are reasonable possibilities, while those that are inconsistent with a Fermi surface are no longer viable alternatives. This still leaves a wide variety of possibilities: conventional strong phonon coupling (perhaps generalized to account for anharmonicity) and purely electronic ("excitonic") mechanisms are both being studied widely, and magnetic pairing mechanisms are not ruled out by the data discussed above. Now that the picture of the normal state is being clarified, the emphasis can soon shift back to the unsolved questions posed by the superconductivity itself.

REFERENCES AND NOTES

1. J. Bardeen, L. N. Cooper, J. R. Schrieffer, *Phys. Rev.* **108**, 1175 (1957).
2. G. Bednorz and K. A. Müller, *Z. Physik B* **64**, 189 (1986).
3. See for example D. Pines and P. Nozieres, *The Theory of Quantum Liquids* (Benjamin, New York, 1966).
4. J. M. Luttinger, *Phys. Rev.* **119**, 1153 (1960).
5. Z. Fisk *et al.*, *Science* **239**, 33 (1988); P. A. Lee, T. M. Rice, J. W. Serene, L. J. Sham, J. W. Wilkins, *Comments Condensed Matter Phys.* **12**, 99 (1986).
6. R. O. Jones and O. Gunnarsson, *Rev. Mod. Phys.* **61**, 689 (1989).
7. W. E. Pickett, *ibid.*, p. 433.
8. R. E. Cohen, W. E. Pickett, H. Krakauer, *Phys. Rev. Lett.* **62**, 831 (1989); *ibid.* **64**, 2575 (1990); K. Schwarz, C. Ambrosch-Draxl, P. Blaha, *Phys. Rev.* **B42**, 2051 (1990); C. O. Rodriguez *et al.*, *ibid.*, p. 2692.
9. H. Krakauer, W. E. Pickett, R. E. Cohen, *J. Supercond.* **1**, 111 (1988); W. E. Pickett, R. E. Cohen, H. Krakauer, *Phys. Rev.* **B42**, 8764 (1990).
10. A. Svane and O. Gunnarsson, *Phys. Rev. Lett.* **65**, 1148 (1990); *Europhys. Lett.* **7**, 171 (1988).
11. A. Z. Shekhtman, *Zh. Eksp. Teor. Fiz.* **59**, 957 (1970) [*Sov. Phys.-JETP* **32**, 521 (1971)].
12. C. M. Varma, P. B. Littlewood, S. Schmitt-Rink, E. Abrahams, A. E. Ruckenstein, *Phys. Rev. Lett.* **63**, 1996 (1989).
13. A. Virosztek and J. Ruvalds, *Phys. Rev.* **B42**, 4064 (1990); J. Ruvalds and A. Virosztek, *ibid.* **B43**, 5498 (1991).
14. A related anomalous (one dimensional) fermion system is known: the "Tomonaga-Luttinger liquid." In one dimension the great restriction on states available for scattering can lead to a system in which there is still a Fermi surface with a QP-like behavior nearby, but instead of having logarithmic vanishing of the QP intensity as the Fermi surface is approached, it vanishes as a power law (a stronger type of unconventionality) [A. Luther and I. Peschel, *Phys. Rev.* **B9**, 2911 (1974); D. Haldane, *J. Phys. C* **14**, 2585 (1981)]. It has been suggested [P. W. Anderson, *Phys. Rev. Lett.* **64**, 1839 (1990)] that exceedingly strong interactions and/or two dimensionality may lead to a breakdown of conventional Fermi liquid behavior into this unconventional, Tomonaga-Luttinger liquid behavior. For the purposes of this paper we include this possibility also as a uFL.
15. C. N. Yang, *Phys. Rev. Lett.* **63**, 2144 (1989); S. Zhang, *ibid.* **65**, 120 (1990).
16. D. J. Scalapino, J. R. Schrieffer, J. W. Wilkins, *Phys. Rev.* **148**, 263 (1966).
17. K. Levin, J. H. Kim, J. P. Lu, Q. Si, *Physica* **C175**, 449 (1991); H. Kohno and K. Yamada, *Prog. Theor. Phys.* **85**, 13 (1991).
18. J. W. Serene and D. Hess, in *Proceedings of the Miami Workshop on Electronic Structure and Mechanisms for High Temperature Superconductivity*, J. Ashkenazi, S. E. Barnes, F. Zuo, G. C. Vezzoli, B. M. Klein, Eds. (Plenum, New York, 1991); J. W. Serene and D. Hess, *Phys. Rev.* **B44**, 3391 (1991).
19. P. W. Anderson, *Science* **235**, 1196 (1987).
20. R. B. Laughlin, *ibid.* **242**, 525 (1988).
21. R. Micnas, J. Ranninger, S. Robaszkiewicz, *Rev. Mod. Phys.* **62**, 113 (1990); D. Emin, *Phys. Rev. Lett.* **62**, 1544 (1989); P. Prelovsek, T. M. Rice, F. C. Zhang, A. Klostermann, *Physica* **148B**, 268 (1987).
22. A. K. McMahan, J. F. Annett, R. M. Martin, *Phys. Rev.* **B42**, 6268 (1990); M. S. Hybertsen, M. Schlüter, N. E. Christensen, *ibid.* **B39**, 9028 (1989).
23. M. Rasolt and G. Vignale, *Phys. Rev. Lett.* **65**, 1498 (1990).
24. R. S. List *et al.*, *Phys. Rev.* **B38**, 11966 (1988).
25. A. J. Arko *et al.*, *ibid.* **B40**, 2268 (1989).
26. C. G. Olson *et al.*, *ibid.* **B42**, 381 (1990).
27. J. C. Campuzano *et al.*, *Phys. Rev. Lett.* **64**, 2308 (1990).
28. R. Manzke, T. Buslaps, R. Claessen, M. Skibowski, J. Fink, *Phys. Scripta* **41**, 579 (1990); G. Mante *et al.*, *Z. Phys. B* **80**, 181 (1990).
29. B. O. Wells *et al.*, *Phys. Rev. Lett.* **65**, 3056 (1990).
30. T. Takahashi *et al.*, *Physica B* **165 & 166**, 1221 (1990); T. Takahashi *et al.*, *Nature* **334**, 691 (1988).
31. H. J. Bernhoff, K. Tsushima, J. M. Nicholls, *Europhys. Lett.* **13**, 537 (1990).
32. H. Haghighi *et al.*, *Phys. Rev. Lett.* **67**, 382 (1991); L. C. Smedskjaer, A. Bansil, U. Welp, Y. Fang, K. G. Bailey, in *Proceedings of the Workshop on Fermiology of High T_c Superconductors* (Argonne National Laboratory, Argonne, IL, 1991); H. Haghighi *et al.*, in *Proceedings of the Miami Workshop on Electronic Structure and Mechanisms for High Temperature Superconductivity*, J. Ashkenazi, S. E. Barnes, F. Zuo, G. C. Vezzoli, B. M. Klein, Eds. (Plenum, New York, 1991).
33. E. C. von Stetten *et al.*, *Phys. Rev. Lett.* **60**, 2198 (1988); D. Singh, W. E. Pickett, R. E. Cohen, H. Krakauer, S. Berko, *Phys. Rev.* **B39**, 9667 (1989).
34. D. Singh, W. E. Pickett, E. C. von Stetten, S. Berko, *Phys. Rev.* **B42**, 2696 (1990); S. Massidda, *Physica C* **169**, 137 (1990).
35. L. P. Chan, D. R. Harshman, K. G. Lynn, S. Massidda, D. B. Mitzi, *Phys. Rev. Lett.* **67**, 1350 (1991); P. E. Mijnarends, A. F. J. Melis, A. W. Weeber, A. A. Menovshy, K. Kadowaki, *Physica C* **176**, 113 (1991).
36. C. M. Fowler *et al.*, in preparation; J. L. Smith *et al.*, in *Proceedings of the Miami Workshop on Electronic Structure and Mechanisms for High Temperature Superconductivity*, J. Ashkenazi, S. E. Barnes, F. Zuo, G. C. Vezzoli, B. M. Klein, Eds. (Plenum, New York, 1991).
37. G. Kido *et al.*, in *Advances in Superconductivity III*, H. Kajimura and H. Hayakawa, Eds. (Springer-Verlag, Tokyo, 1991), p. 237.
38. J. Rossat-Mignod *et al.*, *Physica B* **169**, 58 (1991).
39. B. H. Toby, T. Egami, J. D. Jorgensen, M. A. Subramanian, *Phys. Rev. Lett.* **64**, 2414 (1990).
40. S. Martin, A. T. Fiory, R. M. Fleming, L. F. Schneemeyer, J. V. Waszczak, *Phys. Rev.* **B41**, 846 (1990).
41. B. Sundqvist and B. M. Andersson, *Solid State Commun.* **76**, 1019 (1990).
42. J. Schoenes, J. Karpinshi, E. Kaldis, J. Keller, P. de la Mora, *Physics C* **166**, 145 (1990).
43. S. Massidda, J. Yu, K. T. Park, A. J. Freeman, *Physica C* **176**, 159 (1991).
44. W. E. Pickett, *J. Supercond.* **4**, 397 (1991).
45. S. Sugai, Y. Enomoto, T. Murakami, *Solid State Commun.* **72**, 1193 (1989).
46. F. Slakey, M. V. Klein, J. P. Rice, D. M. Ginsberg, *Phys. Rev.* **B43**, 3764 (1990).
47. H. Monien and A. Zawadowski, *Phys. Rev. Lett.* **63**, 911 (1989).
48. H. Alloul, T. Ohno, P. Mendels, *ibid.*, p. 1700.
49. A. J. Millis, H. Monien, D. Pines, *Phys. Rev.* **B42**, 167 (1990); J. P. Lu, Q. Si, J. H. Kim, K. Levin, *Phys. Rev. Lett.* **65**, 2466 (1990); H. Kohno and K. Yamada, *Prog. Theor. Phys.* **85**, 13 (1991).
50. K. B. Lyons *et al.*, *Phys. Rev. Lett.* **64**, 2949 (1990); S. Spielman *et al.*, *ibid.* **65**, 123 (1990); H. J. Weber *et al.*, *Solid State Commun.* **76**, 511 (1990); K. B. Lyons *et al.*, *Phys. Rev.* **B43**, 11408 (1991).
51. G. T. Yee, J. P. Collman, W. A. Little, *Physica C* **261**, 195 (1989); M. N. Keene,

T. J. Jackson, C. E. Gough, *Nature* **340**, 210 (1989).
52. R. F. Kiefl *et al.*, *Phys. Rev. Lett.* **64**, 2082 (1990).
53. W. E. Pickett, H. Krakauer, R. E. Cohen, *Physica B* **165 & 166**, 1055 (1990).
54. This paper is dedicated to the memory of Stephan Berko, a good friend and a pioneer in the positron spectroscopy of Fermi surfaces. W.E.P. acknowledges the hospitality of the Cavendish Laboratory, Cambridge, England, where much of this paper was written. We thank J. W. Serene for thoughtful comments on the manuscript. We acknowledge the support of two national supercomputer centers where most of our calculations have been carried out: the Cornell National Supercomputing Facility (IBM 3090 computer grants to W.E.P., H.K., D.J.S.) and the National Center for Supercomputing Applications (Cray 2 grant to R.E.C.). H.K. was supported by NSF grant no. DMR-90-22588, W.E.P. and D.S. were supported by the Office of Naval Research, and R.E.C. acknowledges support from the Carnegie Institution of Washington.

Molecular Code for Cooperativity in Hemoglobin

GARY K. ACKERS,* MICHAEL L. DOYLE, DAVID MYERS, MARGARET A. DAUGHERTY

Although tetrameric hemoglobin has been studied extensively as a prototype for understanding mechanisms of allosteric regulation, the functional and structural properties of its eight intermediate ligation forms have remained elusive. Recent experiments on the energetics of cooperativity of these intermediates, along with assignments of their quaternary structures, have revealed that the allosteric mechanism is controlled by a previously unrecognized symmetry feature: quaternary switching from form T to form R occurs whenever heme-site binding creates a tetramer with at least one ligated subunit on each dimeric half-molecule. This "symmetry rule" translates the configurational isomers of heme-site ligation into six observed switchpoints of quaternary transition. Cooperativity arises from both "concerted" quaternary switching and "sequential" modulation of binding within each quaternary form, T and R. Binding affinity is regulated through a hierarchical code of tertiary-quaternary coupling that includes the classical allosteric models as limiting cases.

A MAJOR DISCOVERY OF MODERN BIOCHEMISTRY WAS THAT proteins act as molecular switches to regulate metabolic reactions (*1, 2*). Intracellular control of enzymic activity is often brought about by multimeric assemblies of enzyme subunits that undergo changes in the conformation (tertiary structure) and the arrangement of intersubunit contacts (quaternary structure) in response to the binding of substrates and other "regulatory" molecules. These alterations in protein structure either enhance or diminish binding affinities and thus regulate the concentrations of product. Cooperativity, or "self-regulation," is manifested when the binding of a ligand species alters the affinity for subsequent binding of the same ligand. The protein brings this about by acting as a transducer of free energy: favorable increases in binding energy are "paid for" by (unfavorable) decreases in the free energies of subunit interaction and conformational rearrangement within the protein itself. This transduction of free energy between binding sites and conformational states is reciprocal; after ligand dissociation the original protein structure is restored.

Studies on the structural and functional properties of tetrameric hemoglobin have had a pivotal role in the development of concepts to explain cooperativity and regulation by allosteric enzymes and other multisubunit proteins. The hemoglobin molecule was awarded the rank of "honorary enzyme" by Monod, in recognition that it displays the essential features of allosteric regulation yet maintains the comparative simplicity desired in a model system. Hemoglobin thus had a significant role in the development of the classical theories for allosteric regulation during the 1960s by Monod *et al.* (MWC) (*3*) and by Koshland *et al.* (KNF) (*4*). These models were based on concepts of "concerted" (all or none) versus "sequential" (ligand-induced) processes, respectively. They have provided sharply contrasting frameworks for understanding how regulatory behavior can arise from protein conformational changes coupled to subunit interactions and ligand binding (Fig. 1).

Hemoglobin has also played a major role in the progress toward understanding the detailed structural basis of allosteric regulation, beginning with the pioneering work of Perutz on crystallographic structures of unligated and fully ligated tetramers [see (*5*) for an extensive review of allosteric structures]. The hemoglobin molecule continues to be the object of an immense range of studies on the structural, dynamic, spectroscopic, energetic, clinical, and engineering issues of protein structure and function, for which no attempt at review will be made here. In this article we describe recent findings on properties of the intermediate-state species (partially ligated tetramers) that shed new light on the origins of hemoglobin cooperativity (*6–12*) and the rules whereby heme-site ligation generates cooperativity through tertiary and quaternary switches.

How can it be that the allosteric mechanism of hemoglobin is not completely understood, given the vast amount of effort that has gone into the problem over a number of years? Highly cooperative systems greatly suppress the populations of molecular forms that lie on the pathway between the initial and final states, which makes it extremely difficult to study the properties that may reveal features critical to an understanding of the overall mechanism. The same "conspiracy" is encountered in attempts to understand the mechanisms of protein folding and of nucleated polymerization by filamentous protein assemblies. The recent discovery that hemoglobin quaternary structure is controlled by the specific configuration of ligated subunits within the tetrameric molecule (7) could only arise from studies on the different intermediate species at each degree of ligation.

The authors are in the Department of Biochemistry and Molecular Biophysics, Washington University School of Medicine, St. Louis, MO 63110.

*To whom correspondence should be addressed.