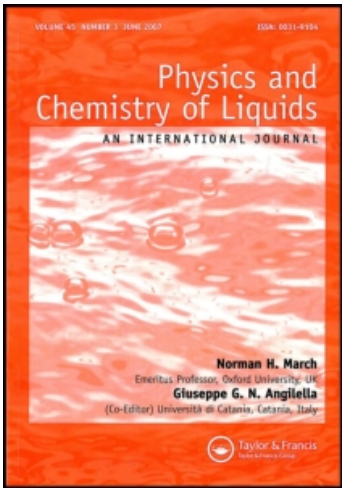

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Review: Luttinger or fermi liquids versus topological superconductivity

G. G. N. Angilella[a]; N. H. March[bc]; R. Pucci[a]; R. H. Squire[d]
[a] Dipartimento di Fisica e Astronomia, Istituto Nazionale per la Fisica della Materia, Università di Catania, Catania, Italy [b] Oxford University, Oxford, England [c] Department of Physics, University of Antwerp (RUCA), Antwerp, Belgium [d] Department of Natural Science, Marshall University, Belle, WV, USA

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Review

LUTTINGER OR FERMI LIQUIDS VERSUS TOPOLOGICAL SUPERCONDUCTIVITY

G.G.N. ANGILELLA[a,*], N.H. MARCH[b,c], R. PUCCI[a] and R.H. SQUIRE[d]

[a]*Dipartimento di Fisica e Astronomia, Università di Catania, and Istituto Nazionale per la Fisica della Materia, UdR di Catania, Corso Italia, 57, I-95129 Catania, Italy;* [b]*Oxford University, Oxford, England;* [c]*Department of Physics, University of Antwerp (RUCA), Antwerp, Belgium;* [d]*Department of Natural Science, Marshall University, 901, W. DuPont Ave., Belle, WV 25015, USA*

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Superconductors, classified by materials, embrace at least four broad groups: (i) BCS metals and alloys; (ii) heavy Fermion materials; (iii) high-T_c cuprates and (some) organic compounds, and (iv) fullerides. Broadly speaking, in classes (i) and (iv), with (i) possibly embracing the recent discovery of superconductivity in MgB_2 with $T_c \sim 40\,K$, electron liquids flow through essentially non-magnetic lattices and the electron-phonon interaction is a key component of the mechanism for Cooper pairing. In classes (ii) and (iii), plus the low-T_c material Sr_2RuO_4, electron or hole liquids flow through assemblies with magnetic spin fluctuations. The nature of the normal state in class (iii) is not yet universally agreed, both Fermi or Luttinger liquids remaining viable to date, the former, however, with the formation of precursor $2e$ Bosons somewhat above T_c. Our own studies reveal some common ground between classes (ii) and (iii), involving coherence lengths and effective masses, as well as non-*s*-wave pairing, though the interactions leading to pairing almost certainly have different physical origins in these two groups. Finally, topological superconductivity is reviewed. It is argued that such a treatment of a topological superfluid could eventually deepen the understanding of the class (iv) fullerides. Resonating valence bond theory, used by Anderson and co-workers as an, of course, approximate strongly-correlated electron technique for high-T_c cuprates, can itself be re-written in the form of topological superconductivity, as discussed especially by Wiegmann and collaborators.

*Corresponding author. E-mail: Giuseppe.Angilella@ct.infn.it

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1. BACKGROUND AND OUTLINE

In previous studies, we have focussed on the high-T_c cuprates, with special attention being given to electron or hole liquids flowing through assemblies with antiferromagnetic backgrounds. Some experimental tests, on the normal state of high-T_c materials, involved the product of the in-plane electrical resistivity and the nuclear spin-lattice relaxation time. While Fermi liquid theory, based on electron or hole liquids flowing through assemblies with such spin fluctuations leads to a prediction which can be tested, one material $YBa_2Cu_4O_8$, for which experimental data is available deviates markedly from the Fermi liquid prediction as T approaches the superconducting transition temperature T_c from above (see Fig. 4). This was suggested to be due to the formation of **r**-space precursor Bosons [1–3], and the major review by Timusk and Statt [4] concluded that this picture remained viable when confronted with a much wider body of experimental evidence. Furthermore, in subsequent theoretical work by one of us [5], using spin glass theory in which a Luttinger liquid phase (see Section 2 for details of this 'phase' of electrons) is known to exist [6], it was shown that while the theoretical prediction was different from the Fermi liquid result [see Eq. (6)], it may provide a considerable experimental challenge to make a decisive choice between the two predictions.

Our aim in the present review is different from the previous studies reported above, and we shall begin with a very brief, and it seems to us at the time of writing, essentially straightforward, materials classification of superconductors. Thus, we assert that superconducting materials embrace at least four broad classes as follows:

i. BCS metals and alloys;
ii. Heavy Fermion materials;
iii. High-T_c cuprates plus (some) organic superconductors;
iv. Alkali-metal doped fullerites.

A few months after the important finding of MgB_2 as a superconductor with T_c as high as 39 K [7], i.e. well above the commonly accepted

limit allowed by BCS theory and strong-coupling generalizations thereof, recent determination of the phonon density of states in MgB_2 via neutron scattering [8,9] allowed us to establish that such material may still fit into category (i) above.

The other comment we need to make here concerns class (iii). The fact that some organic compounds fit nicely along with the high-T_c cuprates in the 'materials' classification above has been emphasized especially by McKenzie [10]. His figure of the phase diagram of some such organic compounds under pressure has been redrawn in Fig. 1 (see also [11,12]). As he stresses, the phase diagram has considerable similarity to that of the high-T_c cuprates, provided the independent

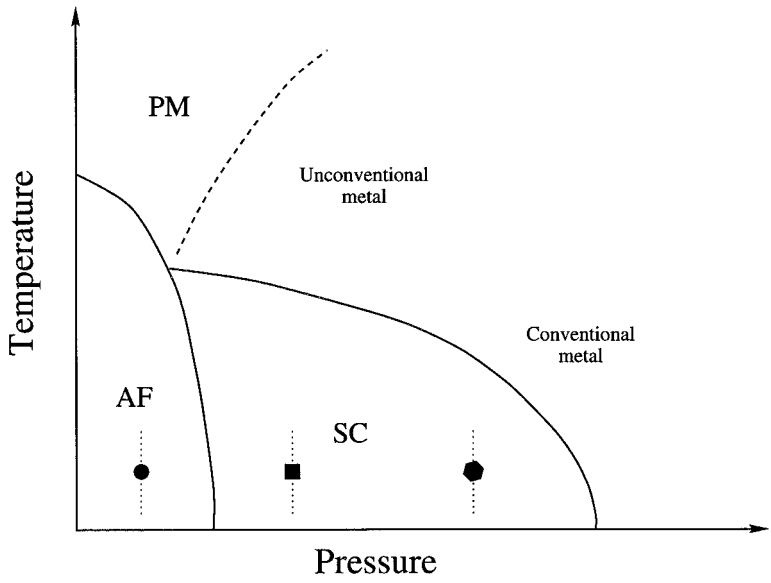


FIGURE 1 Schematic phase diagram of the κ-(BEDT-TTF)$_2$-X organic superconductors, redrawn from Ref. [10]. Such a phase diagram is similar to that of the high-T_c cuprate superconductors, with hydrostatic pressure playing the role of doping. SC denotes the superconducting phase, AF and PM denote the antiferromagnetic and paramagnetic insulating phases, respectively. Kanoda [11,12] suggested that the application of hydrostatic pressure is to be related to a variation of U_{eff}/W, where U_{eff} is an effective on-site (dimer) Coulomb interaction and W the in-plane band-width. The symbols schematically indicate the positions of the organic compounds with X=Cu[N(CN)$_2$]Cl, Cu[N(CN)$_2$]Br, Cu(NCS)$_2$ (left to right) according to their ambient pressure ground-state properties. See also [15] for a generalization of such a phase diagram, embracing further electronic as well as structural instabilities at intermediate temperatures.

variable 'pressure' in Fig. 1 for the organic superconductors is replaced by 'doping' in the high-T_c cuprates.[1]

In the present review, we shall discuss the nature of these broad classes of materials in terms of a first-principles theory classification, having three different fundamental bases. Two of them, Fermi and Luttinger liquids, have been briefly referred to above and some of their predictions will be taken up in Section 2. The third area, 'topological superconductivity', is discussed in Section 4.

1.1. Cooper Pairing in Conventional and Unconventional Superconductors

Besides these three areas of basic theory, a lot of attention will be devoted to pairing mechanisms and the symmetry of the order parameter. While this is dealt with at length in Section 3, we close this Introduction by anticipating some points to be more fully developed below.

It is now established beyond reasonable doubt that category (i) superconductors correspond to Cooper *s*-wave pairing, whereas the 'unconventional' superconductors, heavy Fermion, high-T_c cuprates and some organic salts have non-*s*-wave pairing. The name 'heavy Fermion', it should be added here (see [16]), implies that in category (ii) materials the normal state is a Fermi liquid, but with effective mass m^*, which is very large ($m^*/m_e \approx 100$).

As already mentioned above, while in BCS materials Cooper pairing only takes place below T_c, in the high-T_c cuprates there is a body of evidence reviewed fully by Timusk and Statt [4] that points to the formation of ($2e$) **r**-space Bosons somewhat above T_c.

Turning briefly to category (iv), in which delocalized electrons from the alkali metal dopants flow through a lattice of C_{60} buckyballs, Gunnarsson [17] has given an authoritative review that concludes that superconductivity in fullerides has its origins in electron–lattice interaction. In the penultimate section of the present review, we

[1] An underlying electronic topological transition in the single-particle spectrum may be responsible of the nonmonotonic dependence of T_c on doping or pressure both in the high-T_c cuprates and in the organic quasi-2D superconductors [13,14].

shall return to the doped fullerite category as a possible area where 'topological superconductivity' may come into its own.

2. SOME THEORETICAL PREDICTIONS FOR FERMI OR LUTTINGER LIQUID NORMAL STATES

Let us begin by comparing and contrasting some theoretical predictions for (a) Fermi-liquid and (b) Luttinger-liquid properties of the normal states of superconductors. Then we immediately encounter the crucial role of dimensionality D.

As a canonical model of interacting electrons, it is helpful to start from the homogeneous electron liquid, or jellium. This is a model of a metal going back essentially to Sommerfeld in the early days of quantum mechanics [18]. Instead of the granular ions in real metals such as Na or Cu, one smears out the positive charge into a non-responsive uniform neutralizing background (or jelly) in which electrons move but correlated by Coulomb repulsion energy e^2/r_{ij} between electrons i and j at separation r_{ij}. The model has a single parameter r_s, the mean interelectronic spacing, related to the uniform density ρ_0 of the electron liquid by

$$\rho_0 = \frac{3}{4\pi r_s^3}. \tag{1}$$

2.1. Momentum Distribution

2.1.1. Fermi Liquid in $D = 3$ Dimensions

Figure 2 shows first of all the usual Fermi distribution $n(\mathbf{p})$ at $T = 0$ (dashed line). It is unity for $p \leq p_F$, with p_F denoting the Fermi momentum, and is zero for $p > p_F$. This is the limit $r_s \to 0$, or the extreme high density limit in which kinetic energy completely dominates.

As interactions are 'switched on', or equivalently r_s becomes greater than zero, electrons are promoted to states outside the Fermi sphere of radius p_F, leaving holes inside (solid lines of Fig. 2, for $r_s = 1$–3; after [19]; compare [18]). All this discussion is for dimensionality $D = 3$. The important points to make are:

i. The discontinuity in $n(\mathbf{p})$ at $p = p_F$ is reduced, but not removed, by the electron-electron interactions.

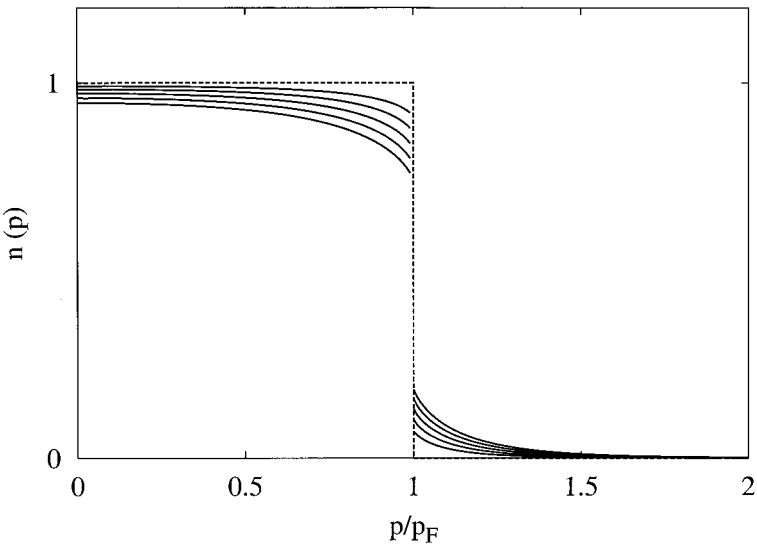


FIGURE 2 Momentum distribution $n(\mathbf{p})$ for a Fermi gas at $T = 0$ (dashed line). Momentum distributions for a high-density Fermi liquid, for $r_s = 1$–3 (solid lines; after [19]; compare [18]).

ii. In the region of high momentum, the 'tail' of $n(\mathbf{p})$ decays as $\sim p^{-8}$ [20,21], the magnitude of this inverse eighth power term involving linearly the electron pair correlation function, for the paired spin case under discussion, at coincidence. This value varies with the mean interelectronic spacing r_s, a simple formula having been constructed for the pair function at coincidence by Overhauser [22].

2.1.2. Luttinger Liquid in Dimensionality $D = 1$

Let us turn to the case when $D = 1$, in the same jellium model. This, in essence, will reveal the prime characteristic of the so-called Luttinger liquid [23–25]. Again we focus on the momentum distribution $n(\mathbf{p})$.

We follow below the study of $n(\mathbf{p})$ around the Fermi momentum p_F due to Holas and March [26]. They asked the question in a model related to, but differing in detail from jellium: does the Fermi momentum distribution in the presence of electron–electron repulsion reflect the Fermi momentum of the non-interacting homogeneous electron gas? The Holas–March study took, as a starting point, the $D = 1$

many-body investigation of Ovchinnikov and Zabrodin [27]. These latter workers obtained the form of the translationally invariant first-order density matrix $\gamma(|\mathbf{r}-\mathbf{r}'|)$, but far from the diagonal $\mathbf{r}=\mathbf{r}'$ (apart from normalization)

$$\gamma(|\mathbf{r}-\mathbf{r}'|) \equiv \gamma(R) = (\rho R)^{-\nu}\cos\left(\tfrac{1}{2}\pi\rho R + \phi_0\right), \tag{2}$$

with $R = |\mathbf{r}-\mathbf{r}'|$. By use of Fourier transform techniques, Holas and March could prove that $n(\mathbf{p})$ still, in the presence of strong electron-electron interactions characterized by the index ν and phase ϕ_0 in Eq. (2), had non-analyticity at the Fermi momentum p_F of the original non-interacting homogeneous electron gas, the non-analytic component $n^{\text{non-anal}}(p)$ having the explicit form, with $\mathbf{p} = \hbar\mathbf{k}$,

$$n^{\text{non-anal}}(p) = C_F|k-k_F|^{\nu-1}\left[\tan\left(\tfrac{1}{2}\pi\nu\right) + \tan(\phi_0)\, sgn(k-k_F)\right]. \tag{3}$$

The result Eq. (3) is displayed in Fig. 3, for $\nu = 9/8$ and for three values of the phase ϕ_0. Though, at first sight, it might appear that

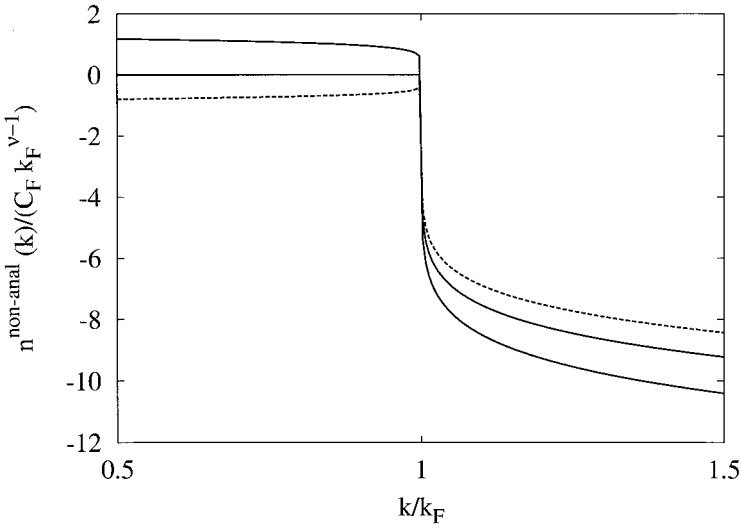


FIGURE 3 Non-analytic contribution $n^{\text{non-anal}}(p)$ to the momentum distribution $n(\mathbf{p})$ of a jellium in dimensionality $D = 1$, Eq. (3), for $\nu = 9/8$ and $2\phi_0/\pi = 1.1, 1.125. 1.15$. One recognizes that the behaviour of $n^{\text{non-anal}}(p)$ changes from monotonic to non-monotonic, as the Fermi momentum is traversed, depending on whether $|\tan\phi_0| \gtrless |\tan(\frac{1}{2}\pi\nu)|$ (compare [26]).

the discontinuity persisted at $k = k_F$, close inspection of Eq. (3) shows that it in fact is zero but that important non-analyticity persists.

Thus, the conclusion of Holas and March was that, in contrast to $D = 3$, the Fermi liquid case discussed in Section 2.1.1 above, there is no longer a discontinuity, though 'memory' of the 'Fermi surface' in the non-interacting case remains. This removal of the discontinuity in the original homogeneous free Fermi gas at $D = 1$ by switching on any arbitrarily weak interaction is the prime characteristic of the Luttinger liquid.

2.1.3. 'Singular' Fermi liquids in $D = 2$

The properties of a strongly correlated electron liquid in dimensionality $D = 2$ have been extensively debated during the last few years, especially in connection with the unusual features exhibited by the "normal" (*i.e.*, non superconducting) state of the quasi-2D high-T_c cuprates (see [28] for a very recent review, where the term 'singular' Fermi liquid is coined for this novel correlated state of electron assemblies in 2D). Such properties include, in particular, the functional form of the momentum distribution $n(\mathbf{p})$ and the possibility itself of defining a Fermi surface, since $n(\mathbf{p})$ is expected to be smooth at $p = p_F$ (or, equivalently, $Z = n(p_F^-) - n(p_F^+) \to 0$), and quasiparticles are ill-defined objects.

The issue of dimensional crossover from a Luttinger liquid in $D = 1$ to a Fermi liquid in $D = 3$ has been addressed by Castellani *et. al.* (see [29] for a review). They employ a nonperturbative diagrammatic approach, allowing to recover exact Ward identities in continuous dimensionality $1 < D < 2$. They find that charge and spin obey asymptotically valid conservation laws down to $D = 1$ (see, however, [30]). Therefore, for $1 < D < 2$ the low-energy properties can be described by a "tomographic" Luttinger model [31,32], defined as an angular sum over 1D Luttinger liquids, each intersecting the 2D Fermi surface in a 'left' and 'right' Fermi point.

A viable proposal for a strongly correlated electron liquid in 2D is that of a "generalized" metal, retaining some features of a Fermi-liquid picture, such as the existence of a volume-conserving Fermi surface, in agreement with Luttinger theorem, and some features of the Tomonaga–Luttinger model, such as spin-charge separation or,

more generally, electron fractionalization (see Section 4). A possible realization of such a model for anisotropic, quasi-2D systems such as the high-T_c cuprates or the quasi-2D organic conductors would be characterized by confined coherence [33] within the 2D entities (the CuO_2 planes or the bis(ethylenedithio) tetrathiafulvalene (BEDT-TTF) planes, respectively), instead of confined quasiparticles. Some of its features, including a possible shape of the momentum distribution function, may be derived from a suitable Ansatz for the low-lying properties of the spectral function [34]. However, a consistent derivation of a non-Fermi liquid theory in 2D from the microscopic point of view is still lacking, to date [28].

2.2. Resistivity and Nuclear Spin Lattice Relaxation Time Related to Q-Dependent Susceptibility

The work of Egorov and March [1] took as its starting point the two-dimensional Fermi liquid theory of Kohno and Yamada for a liquid of charged Fermions flowing through an antiferromagnetic background [35]. Essential input from Kohno and Yamada's work [35] was that

$$\rho_{ab} \propto T^2 \chi(\mathbf{Q}), \tag{4}$$

where ρ_{ab} is the in-plane resistivity and $\chi(\mathbf{Q})$ the magnetic susceptibility of the lattice, at the antiferromagnetic wave vector $\mathbf{Q}$ [$\mathbf{Q} = (\pi/a, \pi/a)$ below, with a the lattice spacing of a square lattice], while

$$(TT_1)^{-1} \propto \chi(\mathbf{Q}), \tag{5}$$

with T_1 the spin lattice relaxation time [35]. It was then straightforward to eliminate $\chi(\mathbf{Q})$ from Eqs. (4) and (5) above, and obtain the correlation

$$\rho_{ab} T_1 \propto T, \tag{6}$$

which applies to the normal state, *i.e.* for $T > T_c$ [1].

3. SYMMETRY OF THE ORDER PARAMETER: EXPERIMENTAL SIGNATURES OF UNCONVENTIONAL (NON-*s*-WAVE) PAIRING IN SUPERFLUID STATES

The relevance of the symmetry properties of the paired state and, in general, its space variation cannot be overemphasized. This section will therefore discuss the current understanding concerning the pairing symmetry of the superconducting materials listed in classes (i)–(iv) above, invoking experimental information whenever feasible.

All the main macroscopic phenomena characterizing superconductivity, such as perfect electrical conductivity and the Meissner effect (see also Section 4.1), require that off-diagonal long-range order (ODLRO) is established in going into the superconducting state [36]. In conventional (class (i) materials), as well as in high-T_c, superconductors, this is realized by *pairing* below a definite temperature T_c.[2] Indeed, a number of experiments, such as flux quantization, Shapiro steps in I–V characteristics, and Andreev scattering indicate that condensation occurs in pairs of charge $2e$ [37]. This implies that the anomalous expectation value

$$b_{\mathbf{k}} = \langle c_{-\mathbf{k}\downarrow} c_{\mathbf{k}\uparrow} \rangle, \tag{7}$$

is nonzero in the superconducting state. Here, $c_{\mathbf{k}\sigma}$ is a fermionic annihilation operator in the state labelled by wavevector $\mathbf{k}$ and spin projection σ, and $\langle \ldots \rangle$ denotes a thermal average. The superconducting gap $\Delta_{\mathbf{k}}$ is related to the pair amplitude of Eq. (7) by $\Delta_{\mathbf{k}} = \sum_{\mathbf{k}'} V_{\mathbf{k}\mathbf{k}'} b_{\mathbf{k}'}$, where $V_{\mathbf{k}\mathbf{k}'}$ is the pairing potential.

In BCS-like theories, where the normal state is assumed to be a Fermi liquid, $\Delta_{\mathbf{k}}$ is directly related to the anomalous self-energy and to the spectrum $E_{\mathbf{k}}$ of the Bogoliubov excitations through

$$E_{\mathbf{k}}^2 = \xi_{\mathbf{k}}^2 + |\Delta_{\mathbf{k}}|^2 \tag{8}$$

(see, e.g., [38]), where $\xi_{\mathbf{k}} = \varepsilon_{\mathbf{k}} - \mu$ is the single-particle dispersion relation in the normal state, relative to the chemical potential μ.

In theories where the normal state is *not* a Fermi liquid, such a relationship does not hold, in principle, and even the fact that $\Delta_{\mathbf{k}}$ obeys a

[2]See however, Section 3.5, which strongly points to the possibility of precursor **r**-space Boson formation near to, but above T_c in specific high-T_c cuprates.

BCS-like self-consistent gap-equation might be questioned. Indeed, the occurrence of an energy gap in the low-lying excitation spectrum and the onset of ODLRO are, in general, different phenomena, which correspond to widely different energy scales $k_B T^* \gg k_B T_c$ in the underdoped, short coherence length cuprates [39,40].[3] An energy gap and an order parameter, describing spontaneous breaking of global $U(1)$ gauge invariance and phase coherence in the superconducting state, are therefore *different* quantities, which happen to coincide and open simultaneously, i.e. at the same transition temperature T_c, in BCS theory. The continuous evolution of the pseudogap into the superconducting gap in underdoped cuprates, as shown by ARPES experiments in the high-T_c bilayer cuprate Bi-2212, suggest however that an intimate relationship is shared by the two [41].

A possible relationship between the superconducting phase and other ordered phases at intermediate temperatures above T_c has been recently evidenced also in some quasi-2D organic superconductors [15], the larger energy scale $k_B T^*$ here corresponding to a spin density wave developing over quasi-1D patches of the Fermi surface of such compounds. In particular, such observations allowed Müller *et al.* [15] to generalize the schematic phase diagram sketched in Fig. 1 in order to embrace an intermediate temperature ordered phase occurring for $T_c \ll T \lesssim T^*$ over a considerable pressure range, which reminds of the pseudogap region in the high-T_c cuprates phase diagram.

The symmetry properties of $\Delta_{\mathbf{k}}$, and to a certain extent its overall $\mathbf{k}$-dependence, are however logically independent of the microscopic nature of the normal state [42]. On the other hand, the order parameter (OP) contains important information on the microscopic origin of the paired state.

In BCS theory (relevant certainly to class (i) materials, and possibly to class (iv)), the OP is a constant over a narrow shell around the Fermi level, $\Delta_{\mathbf{k}} = \Delta_0 \theta(|\xi_{\mathbf{k}} - \hbar\omega_D|)$, its width being given by the Debye frequency ω_D. This is a clear consequence of the phonon-mediated nature of the pairing interaction [43]. In the generalized framework of Eliashberg theory for strongly coupled superconductors [44]

[3]Quite the opposite happens in Abrikosov–Gor'kov so called 'gapless' superconductors in presence of magnetic impurities, which are examples of low-temperature superconductivity characterized by an order parameter, but no gap.

(see also [45,46], and [47] for a recent, up-to-date review), the gap $\Delta(\omega)$ acquires a frequency dependence, which can be viewed in BCS materials as an image of the phonon density of states $F(\omega)$.

Analogously, the **k**-dependence of the superconducting order parameter $\Delta_{\mathbf{k}}$ in the high-temperature superconductors is expected to retain the overall essential information of the underlying pairing mechanism. The latter statement may be specified within the assumption of a Fermi-liquid normal state (plus possible precursor $2e$ Boson formation above, but near to, T_c) and in the mean-field approximation through a definite relation between the pair wave-function and the superconducting gap (see, e.g., App. B in [48], and [49]).

Due to our limited access to the microscopic physics governing the onset and the properties of the superconducting state, the symmetry of the order parameter poses severe restrictions on the available theoretical frameworks. As an example, interlayer tunneling of pairs characterizes in a very special way the **k**-dependence of the order parameter, and many relevant physical properties [50].

3.1. *d*-Wave Pairing Symmetry in Superconducting Fluids

Since only global gauge symmetry is spontaneously broken in going into the superconducting state, the order parameter must transform according to an irreducible representation of the crystal point group. One has 'conventional' superconductivity when the order parameter is invariant under the full Hamiltonian symmetry group. In particular, it must be invariant with respect to crystal rotations and translations, as well as spin rotations and time reversal. This is all true in BCS theory, whose order parameter is isotropic.

'Unconventional' pairing involves an order parameter which is invariant only with respect to a group lower than the Hamiltonian full symmetry group. Unconventional pairing in strongly correlated fermionic systems is indeed observed in superfluid ^{3}He, where the paired state is a p-wave triplet, and possibly in the heavy-fermion superconductors UPt_3 and UBe_{13} (see Section 3.4) [51]. The possible paired states for an orthorhombic or a tetragonal lattice, like in most cuprate superconductors, can be therefore labelled according to the irreducible representations of the corresponding crystal point groups, viz. D_{2h} and D_{4h} [37,52].

Some proposed pairing mechanisms, based on magnetic fluctuations, critically rely on the possibility that the order parameter assumes different sign (i.e., changes its phase) in different sectors of the first Brillouin zone [48]. Therefore, the earlier quest for 'unconventional' pairing in the cuprates was aimed at evidencing *nodes* in the order parameter.

Indirect evidence for nodes can be inferred from the anomalous behaviour of several measurable quantities as a function of temperature, in the low temperature regime (see [37] for an earlier review). Such experiments include the measurement of the specific heat and thermal conductivity, spin susceptibility and nuclear spin relaxation, as well as penetration depth, which for some time stood as an evidence in favour of *s*-wave superconductivity, until the effect of impurity scattering was duly taken into account.

Within a BCS-like framework, taking anisotropy into account, all such quantities may be readily expressed in terms of integrals of expressions involving the excitation spectrum $E_{\mathbf{k}}$ of Eq. (8) over the first Brillouin zone. An asymptotic expansion for low temperatures then shows that their T-dependence varies whether or not $E_{\mathbf{k}}$ is allowed to vanish, i.e. whether or not $\Delta_{\mathbf{k}}$ has nodes on the Fermi surface. In general, one finds that such expressions show a polynomial dependence on T as $T \to 0$ if $\Delta_{\mathbf{k}}$ vanishes on the Fermi surface, the order of such polynomials depending upon the dimensionality of the $\mathbf{k}$-space available for integration and the topological character of the nodes (viz. isolated nodes, nodal lines, nodal surface areas) [53]. On the contrary, an 'activated' behaviour $\propto \exp(-\beta\Delta_{\min})$ is predicted if $\Delta_{\mathbf{k}}$ has no nodes on the Fermi surface, as in BCS theory [37,51]. Here, $\Delta_{\min} = \min_{\mathbf{k}} E_{\mathbf{k}} > 0$ denotes the minimum gap in the excitation spectrum. More specific asymptotic behaviours have been predicted within several models for extended $d_{x^2-y^2}$-wave pairing, which give rise to deviations from the simple power-law at some intermediate temperature, connected to a characteristic energy scale of the model [54,55].

3.2. Probing the Phase of the Order Parameter by Experiments on Electron or Hole Superfluids

It was not until quite recently that unconventional superconductivity with predominant $d_{x^2-y^2}$ symmetry pairing was experimentally

established in the cuprates. In order to probe the phase of the order parameter, recourse has been made to a completely different class of experiments, probably among the most elegant and sophisticated ever devised in condensed matter physics. All of them exploit the Josephson effect in quantum phase interferometers, designed in such a way as to probe the relative phase of different materials, or of a single material along different directions.

Earlier experiments were carried on HIS Josephson junctions, where 'H' denotes a HTSC material (most frequently, YBCO), 'S' a conventional, *s*-wave superconductor (usually, Pb), and 'I' an insulating barrier in between. Such measurements evidenced the presence of excess states within the region where BCS theory would predict a fully formed, isotropic gap. Moreover, additional features appear also farther from the gapped region. Such features are most likely related to the gap anisotropy, as well as to the details of the junction and of the tunneling process.

The availability of top quality HTSC single crystals has allowed the performance of quantum interference experiments in dc SQUIDs with two HIS junctions [56], single junction modulation [57], and tricrystal ring magnetometry in epitaxially grown SQUIDs across zero, two, or three grain boundaries of YBCO [58] and Tl-2201 [59].

In the original experiment performed by the group of Van Harlingen [56], a SQUID loop was obtained by closing the two ends of a thin Pb film either on the same edge, or at the two corner sides of a YBCO single crystal, parallel to the *a* and *b* directions, respectively. The total supercurrent flowing along the loop is modulated by the trapped flux of the external magnetic flux, in units of the flux quantum, plus a phase shift δ, which is always zero in the edge-junction configuration, and $0 \leq \delta \leq \pi$ in the corner-junction configuration (see [60] for a review). One expects either $\delta = 0$ or $\delta = \pi$, corresponding to a purely isotropic, or to a purely *d*-wave order parameter, respectively. As in a double-slit optical interferometer experiment, Wollman *et al.* [56] were thus able to evidence an order parameter at least with predominant $d_{x^2-y^2}$ symmetry character ($\delta \lesssim \pi$) [56].

Wollman *et al.*'s original results [56] were confirmed by a subsequent experiment, in which the 'Fraunhofer' modulation in the supercurrent maximum was measured as a function of the magnetic flux trapped

in a single YBCO-Pb corner-junction [57]. Again, the result is strongly dependent on the pairing symmetry of the order parameter, unambiguously supporting unconventional superconductivity with pronounced d-wave symmetry character, possibly with an admixture of an s-wave component.

The results of Van Harlingen's group were soon confirmed by the experiments of Tsuei *et al.* [58] in YBCO, and in Tl-2201 [59]. Epitaxial films of YBCO were grown on an appropriate substrate in the shape of rings, each one crossing either zero, two, or three grain boundaries, respectively. At a grain boundary, the crystal orientation changes, corresponding to a 'frustrated' HIH junction, in the sense that the phase difference which minimizes the coupling energy at the Josephson junction is π, instead of zero [61]. Owing to the mutual orientation of the crystals at the grain boundaries, one expects that an integral or an half-odd integral multiple of the flux quantum is to be trapped in a ring interrupted by zero or two (an even number of), or by three (an odd number of) junctions, which is indeed observed experimentally [58,59].

The current understanding of the symmetry of the paired state of the quasi-2D organic salts κ-$(ET)_2$-X is still unsettled. Here, ET is the organic molecule BEDT-TTF, and X denotes an anion, such as $Cu[N(CN)_2]Cl$, $Cu[N(CN)_2]Br$, $Cu(SCN)_2$, or I_3 [62,63]. The absence of an Hebel–Slichter peak in NMR data, a power-law low-temperature behaviour of the inverse nuclear spin-lattice relaxation time $T_1^{-1} \propto T^2$, and a T-linear low-temperature dependence of the thermal conductivity, all provide indirect evidence of nodes in the OP of such class (iii) materials. Moreover, evidence against phonon-mediated pairing in κ-$(ET)_2$-X organic superconductors has been recently reported [64], based on the high-pressure dependence of the electron-phonon coupling constant extracted from optical and Raman scattering experiments. The latter finding suggests that a purely or dominantly electronic mechanism may be at work in the organic superconductors.

Indeed, theory has long ago predicted [65] that $d_{x^2-y^2}$-wave superconductivity in κ-$(ET)_2$-X may be driven by spin fluctuations [66–69], while a d_{xy}-wave OP may be substained by charge fluctuations in the θ- and β''-phases of the same class of compounds [70,71]. However, recent high-resolution specific heat measurements

in κ-$(ET)_2$-$Cu[N(CN)_2]Br$ still stand in favour for a fully gapped, isotropic superconducting state [72], while the actual orientation of the gap nodes in κ-$(ET)_2$-X – should the OP eventually turn out to be anisotropic – is still an open issue [73].

3.3. Mixed Symmetry

The onset of superconductivity at $T = T_c$ is characterized by a spontaneous breaking of $U(1)$ global gauge symmetry. Taking into account the restrictions enforced by the underlying lattice structure, and barring accidental degeneracies, one expects that such a transition corresponds to a nonzero contribution to the energy gap $\Delta_{\mathbf{k}}$ coming from only one, well defined, irreducible representation of the crystal point group, say $\Delta_{\mathbf{k}} = \Delta_{\mathbf{k}}^{(1)}$, at $T \lesssim T_c$. Such a result has very general grounds in Ginzburg–Landau theory (see, e.g., [49]), and is well-known in extended BCS-like mean-field calculations [74]. It has also been rederived by Siringo *et al.* [75] in the context of a renormalization group approach to anisotropic superconductors.

As temperature decreases further below some characteristic temperature $T_m < T_c$, the symmetry of the superconducting state may be lowered, which is accompanied by the opening of a new contribution $\Delta_{\mathbf{k}}^{(2)}$ adding up to the total order parameter as

$$\Delta_{\mathbf{k}} = \Delta_{\mathbf{k}}^{(1)} + e^{i\theta}\Delta_{\mathbf{k}}^{(2)}, \tag{9}$$

where θ is the relative phase difference. The two contributions $\Delta_{\mathbf{k}}^{(1)}$ and $\Delta_{\mathbf{k}}^{(2)}$ generally belong to different irreducible representations of the crystal point group, which motivates the terminology of 'mixed symmetry' superconducting phase. It must be stressed that this does not correspond to any new superconducting transition: The order parameter $\Delta_{\mathbf{k}}$ related to the breaking of $U(1)$ global gauge symmetry is already different from zero, and the addition of new contributions would only correspond to condensation of Cooper pairs in other available channels. Furthermore, any new contribution $\Delta_{\mathbf{k}}^{(2)}$ maintains the scalar character of the order parameter[4].

[4]It is therefore an abuse of terminology that of referring to a new 'component' of the order parameter, even when the latter is not a vector, in the sense of Section 3.4.

However, assuming that $\Delta_{\mathbf{k}}^{(2)}$ opens smoothly at T_m, i.e. with $\Delta_{\mathbf{k}}^{(2)}(T = T_m) = 0$, the crossover into a mixed symmetry phase would be accompanied by 'features' in thermodynamic quantities, such as a second peak in the specific heat at constant volume, C_V, as is observed in the heavy Fermion compound UPt_3 (see, e.g., [76] and Section 3.4), or by a change of slope in the magnitude of $\Delta_{\mathbf{k}}$ as a function of T. In principle, the occurrence of a crossover to a mixed superconducting phase is not forbidden by Ginzburg–Landau theory, but the observation of features such as a second peak in C_V would be made difficult by the much reduced value of T_m with respect to T_c (see also [50]).

General symmetry considerations restrict the possible values of the relative phase difference θ between the two gap contributions in Eq. (9) to $\theta = 0$ or π, or $\theta = \pi/2$ or $3\pi/2$. The latter cases imply a breaking of time reversal symmetry (TRS). Such is the case when the superconducting state characterized by the OP $\Delta_{\mathbf{k}}$ is not equivalent to that characterized by the complex conjugate OP $\Delta_{\mathbf{k}}^*$ [77–79]. Clear evidence of TRS breaking in the superconducting state of Bi-2212 has been reported by Krishana *et al.* [80] from measurements of magnetothermal conductivity. The occurrence of a low-temperature mixed symmetry phase has been numerically investigated on a square lattice as a function of various parameters [50,81–84]. Such studies allowed to classify the possible additional gap component opening at $T = T_m$ according to its symmetry properties. A renormalization group analysis (see [85] and refs. therein) leaves out the $d_{x^2-y^2} + is$- and $d_{x^2-y^2} + id_{xy}$-wave symmetries as the only possible candidates, whereas further comparison with ARPES data suggests that the latter one be the most favourable possibility. A quantum phase transition at $T = 0$ from a purely $d_{x^2-y^2}$- to a TRS-breaking mixed $d_{x^2-y^2} + id_{xy}$-wave symmetry phase has been reviewed and discussed with reference to its observability in the cuprates by Vojta and Sachdev [85] (but see also [86]). Given the gain in superconducting condensation energy afforded by a new, generally TRS-breaking component of the OP, Sigrist [87] argued that "the presence of such [mixed] states is rather a rule than an exception in unconventional superconductors" (see also [88]).

Reliable evidence for symmetry mixing has been quite recently provided by experiments carried out on high-quality single-crystal

samples. Some experiments probe the phase anisotropy directly, exploiting ARPES or tunneling techniques, as follows:

a. The different temperature dependence of the gap amplitude observed by Ma *et al.* [89] in Bi-2212 along the $\Gamma - M$ and $\Gamma - X$ directions in ARPES experiments has been interpreted by Betouras and Joynt [90] as evidence for an $s + d$ mixed symmetry ground state (see also [83,84]).
b. Josephson tunneling experiments, analogous to those performed by Wollman *et al.* [57] in corner-junction Pb-YBCO SQUIDs, were carried out by Kouznetsov *et al.* [91]. They studied the dependence of the critical current on the magnitude and the orientation of an external magnetic field applied to a Pb junction located across a twin boundary of a YBCO single crystal along the *c*-axis. The modulation patterns of the current evolve with the applied field orientation from a Fraunhofer-like shape, characterized by a local maximum at zero field, to an anti-Fraunhofer-like shape, characterized by a local minimum at zero field. Kouznetsov *et al.*'s results [91] are strongly suggestive of a mixed $s + d$-wave superconducting ground state, with predominant *d*-wave pairing.
c. A conceptually analogous class of tunneling experiments have been extensively discussed by Klemm *et al.* (see [92,93] and refs. therein). They take into account a *c*-axis *twist* junction, formed by the two halves of a Bi-2212 single crystal cleaved between a pair of BiO layers, rotated with respect to each other of an angle ϕ_0, and eventually fused back together. They show that the critical current of Josephson tunneling between mixed states in the two edges, with predominant *d*-wave symmetry, would show a remarkable dependence on ϕ_0.

Some experiments probe the phase anisotropy indirectly, involving the observation of the low-temperature behaviour of measurable quantities, as below

d. Shrikanth *et al.* [94,95] report of features in the complex conductivity σ and the penetration length $\lambda \propto (\mathrm{Im}\,\sigma)^{-1/2}$ in YBCO as a function of temperature that may be explained by the opening of an additional superconducting channel at a temperature below T_c.
e. Nemetschek *et al.* [96] have recently reviewed many experimental results from Raman spectroscopy of YBCO, Bi-2212, Hg-1212,

and Hg-1223, again claiming for symmetry mixing between an *s*- and a *d*-wave contribution (see [96] and refs. therein). In particular, they recognize that the relative amount of mixing may depend on doping within a given material, and that "spontaneous breakdown of *d*-wave symmetry may be rather universal in high-T_c compounds." Indeed, recent theoretical findings [97,98] indicate that a phase transition from a rotationally invariant (*s*-wave or $\ell = 0$) to an unconventional *d*-wave ($\ell = 2$) superconducting ground state (allowing for a possible crossover through a mixed phase) should be expected on quite general grounds, and may be related to the BCS to Bose–Einstein crossover as a function of doping [99].

f. Measurements of the temperature dependence of the thermal conductivity κ of Bi-2212 single crystals in a magnetic field by Krishana *et al.* [80] suggest that an applied magnetic field may induce a crossover from a purely *d*-wave to a mixed $d_{x^2+y^2} + id_{xy}$-wave or $d_{x^2+y^2} + is$-wave symmetry order parameter [83,84]. In particular, this would imply breaking of time-reversal invariance [80].

The above review of experimental data is indeed suggestive that the actual symmetry of the superconducting paired state in a class (iii) HTSC is a material-specific property, depending on the details of its electronic properties as well as of the interaction [100]. However, it should be expected, on rather general grounds, that the symmetry of the order parameter crosses over from one symmetry to another, characterized by a lower lattice symmetry, depending on structural and compositional details (e.g., on doping or disorder), or on external effects, such as pressure or an applied magnetic field. In intermediate regions of the phase diagram, such a crossover should allow room for a mixed symmetry phase, possibly characterized by a spontaneous breaking of time reversal symmetry.

3.4. Spin-Triplet Pairing

Cooper pairing characterized by a nonzero total spin has been long known to occur in the A-phase of superfluid ^{3}He [101]. Among the unconventional superconductors, the most likely candidates to

spin-triplet pairing are the heavy Fermion compounds UPt_3 and $U_{1-x}Th_xBe_{13}$ $(0.018 < x < 0.045)$ [16,51], belonging to class (ii) above, and Sr_2RuO_4, characterized by a T_c as low as 1.5 K [102]. Since the OP for such materials has to take into account also for the spin degrees of freedom, as well as of **k**-space anisotropy, it is usually written as a (complex) vector $\mathbf{d}(\mathbf{k})$, orthogonal to the plane defined by the two parallel spins in a Cooper pair, and such that $\mathbf{d}(-\mathbf{k}) = -\mathbf{d}(\mathbf{k})$, in order to ensure a globally odd pair wave-function. In terms of the vector OP, the superconducting energy gap $\Delta_{\mathbf{k}}$ at the wave-vector **k**, now a 2×2 matrix in spin space, can be expressed as

$$\Delta_{\mathbf{k}} = i(\sigma \cdot \mathbf{d}(\mathbf{k}))\sigma_y, \tag{10}$$

with $\sigma = (\sigma_x, \sigma_y, \sigma_z)$ the Pauli matrices. Given the (usually **k**-independent) direction of such a vector OP, its overall **k**-space symmetry and temperature dependence can be factorized as

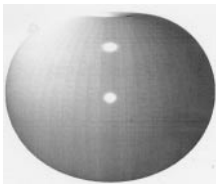
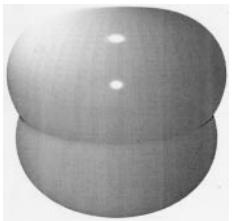
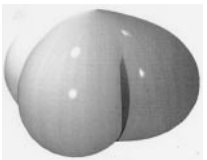
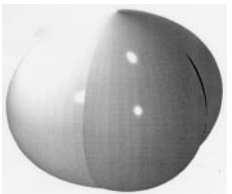
$$\mathbf{d}(\mathbf{k}) = \Delta(T)\varphi(\mathbf{k})\hat{\mathbf{d}}. \tag{11}$$

Some of the current nomenclature for the several orbital symmetries proposed for pairing in the heavy Fermions and the ruthenates are summarized in Table I.

It is important to remark that not all of the triplet OPs listed in Table I do actually present node lines, also depending on dimensionality of the Fermi surface (cf. Table I). Therefore, indirect evidence of unconventional superconductivity from the low-temperature behaviour of electronic properties is more difficult to assess, than in cases where a scalar OP is appropriate, as for the cuprates.

In order to probe (a) the vector character, and (b) the actual symmetry (occurrence and location of nodes in **k**-space) of the OP, one is then led to consider experiments where (a) the internal spin degrees of freedom are coupled to an external magnetic field or that associated to magnetic impurities, and (b) a directional probe is used. Evidence for (nodeless) *p*-wave spin-triplet pairing in the heavy Fermion (class (ii)) compounds UPt_3 and $U_{1-x}Th_xBe_{13}$ is provided by a comparable pair-breaking effect induced by both magnetic and nonmagnetic impurities, by a substantially T-independent spin susceptibility in a magnetic field perpendicular to **d**, as well as by experiments implying

TABLE I Nomenclature and **k**-space anisotropy of some spin-triplet gap functions, that have been suggested to describe the pairing state of the heavy Fermion compounds and of Sr_2RuO_4, both in the case of a 3D (upper row) and of a quasi-2D or cylindrical Fermi surface (lower row). The middle row indicates d_z as a suitable (complex) polynomial in the components of wave-vector **k**, as in atomic physics, being $d_x = d_y = 0$ in all cases. It should be emphasized that the occurrence of point or line nodes depends on the effective dimensionality of the Fermi surface. For example, a *p*-wave OP is gapless in 2D, whereas it has two point nodes [along the (001) direction] in 3D

p-wave [51]	*f-wave ('3D' model) [103]*	$f_{x^2-y^2}$*-wave [104]*	f_{xy}*-wave [105]*
			
$k_x + ik_y$	$k_z(k_x + ik_y)^2$	$(k_x^2 - k_y^2)(k_x + ik_y)$	$k_x k_y(k_x + ik_y)$
			

spontaneous TRS breaking [$\mathbf{d}(\mathbf{k}) \not\equiv \mathbf{d}^*(\mathbf{k})$] (see also [76,87,106] for recent reviews).

The current understanding is still less settled for Sr_2RuO_4. While spin–singlet pairing seems to be ruled out, and several electronic properties exhibit power-law behaviours at low temperature, thus suggesting the presence of nodes in the gap, the actual orientation of the nodal lines is yet to be determined. Among the various possible symmetries proposed theoretically (see Table I), the observed dependence of the thermal conductivity as a function of in-plane magnetic field rotation seems to point towards $f_{x^2-y^2}$-wave orbital symmetry [107,108]. Given the structural analogies of Sr_2RuO_4 with the prototypical high-T_c cuprate, La_2CuO_4, such a possibility is quite appealing, since it would imply a (vector) OP with nodes directed as for a $d_{x^2-y^2}$-wave (scalar) OP.

3.5. Superconducting Transition Temperatures and Coherence Length in Non-*s*-Wave Pairing Materials Correlated with Spin-Fluctuation Mediated Interaction

In early work, Egorov and March [1] discussed electron or hole liquids flowing through assemblies with antiferromagnetic spin fluctuations, and proposed the correlation Eq. (6) above between the in-plane electrical resistivity ρ_{ab} and the nuclear-spin lattice relaxation time T_1. This relationship has been tested on the underdoped high-T_c cuprate $YBa_2Cu_4O_8$ with T_1 extracted from ^{63}Cu NMR data, and is appropriate somewhat above the superconducting transition temperature (Fig. 4, redrawn from Fig. A.7.5.1 on p. 355 of [109], and [3]).

More recently, the present authors [110] have demonstrated that T_c for non-*s*-wave pairing superconductors, and in particular for heavy Fermion materials and high-T_c cuprates, correlated with coherence length and effective mass (see Fig. 5). The very recent and apparently quite different studies of Abanov *et al.* [46], and prior to that, of Monthoux and Lonzarich [45], are here brought into close contact with our earlier work [110].

Following [45], in Section 3.5.1, we briefly summarize the essential input in the treatments of spin-fluctuation mediated pairing in [45,46]. Anticipating that, we stress at the outset that the common

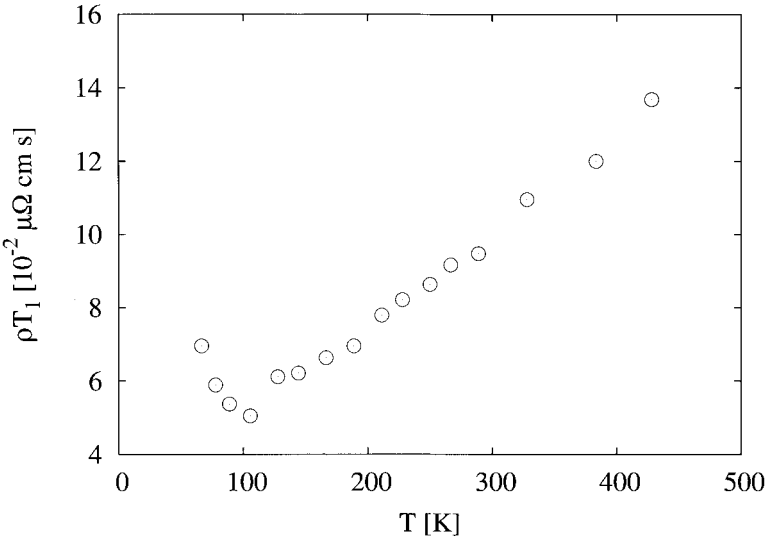


FIGURE 4 Plot of product $\rho_{ab}T_1$ versus temperature T for normal state of high-T_c compound $YBa_2Cu_4O_8$ (redrawn from [1]).

feature in [45,46] is a characteristic thermal energy $k_B T_{sf}$ associated with a spin-fluctuation temperature T_{sf}. Section 3.5.2 connects the work on T_{sf} in [45,46] with our own studies on coherence length [110].

3.5.1. Spin-Fluctuation Temperature Related to T_c in p- and d-Wave Superconductivity in Quasi-2D Metals

Essential input into both [45,46] is a form of the retarded generalized magnetic susceptibility $\chi(\mathbf{q}, \omega)$. Quite specifically, in [45] the phenomenological form

$$\chi(\mathbf{q}, \omega) = \frac{\chi_0 \kappa_0^2}{\kappa^2 + \hat{q}^2 - i[\omega/\eta(\hat{q})]} \tag{12}$$

is assumed. Here, κ^{-1} and κ_0^{-1} are correlation lengths in units of the lattice constant a, with and without strong magnetic correlations, respectively.

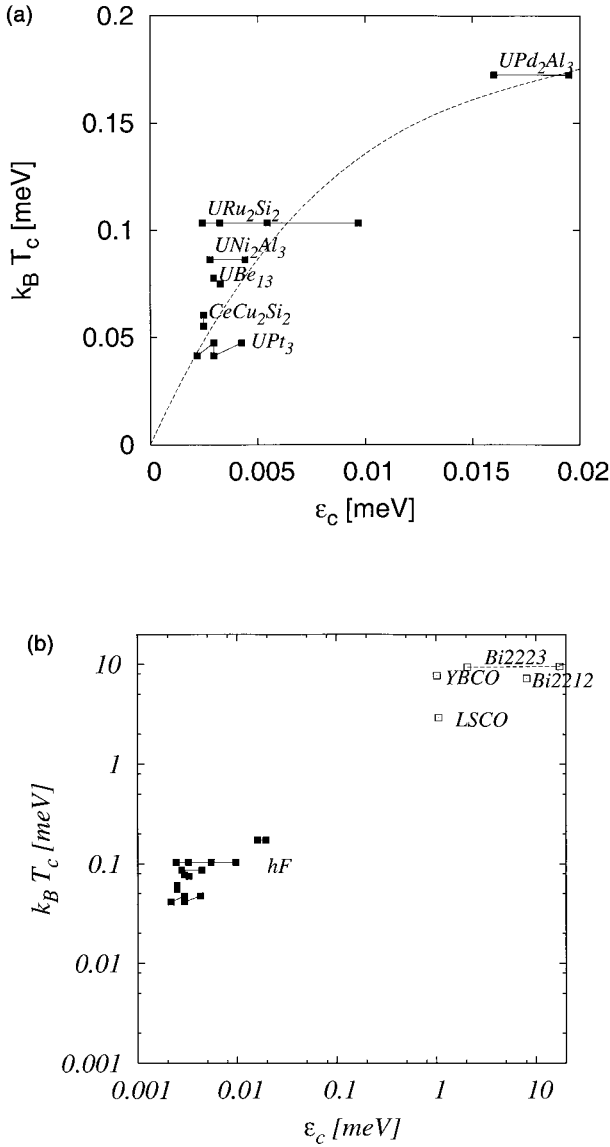


FIGURE 5 (a) Thermal energy $k_B T_c$ corresponding to superconducting transition temperature T_c versus characteristic energy $\epsilon_c = \hbar^2/(m^*\xi^2)$, Eq. (18), with m^* the effective mass and ξ the coherence length, for six heavy Fermion compounds. The dashed curve should be regarded mainly as a guide to the eye. (b) log–log plot of panel (a), but now with high-T_c cuprates in the top right-hand corner. For the cuprates, use has been made of the in-plane coherence length ξ_{ab} [110].

Monthoux and Lonzarich [45] then adopt a tight-binding form for the quasiparticle dispersion relation, and subsequently define the quantities $\hat{q}_{\pm}^2$ by

$$\hat{q}_{\pm}^2 = 4 \pm 2[\cos(q_x a) + \cos(q_y a)]. \tag{13}$$

In the case of ferromagnetic correlations, typified by the ruthenate Sr_2RuO_4 with a low $T_c \sim 1.3\,\mathrm{K}$ [102], the parameters $\hat{q}^2$ and $\eta(\hat{q})$ entering $\chi(\mathbf{q}, \omega)$ in Eq. (12) are defined as

$$\hat{q}^2 = \hat{q}_{-}^2 \tag{14}$$

and

$$\eta(\hat{q}) = T_{sf}\hat{q}_{-}, \tag{15}$$

where T_{sf} is the spin-fluctuation temperature already referred to in Section 3.5.

Monthoux and Lonzarich [45] also investigate antiferromagnetic correlations as in the d-wave paired cuprates, in which case the above parameters have the form

$$\hat{q}^2 = \hat{q}_{+}^2 \tag{16}$$

and

$$\eta(\hat{q}) = T_{sf}\hat{q}_{-}. \tag{17}$$

The final input we need to refer to here is a coupling parameter g^2 in the quasiparticle self-energy $\Sigma(\mathbf{q}, \omega)$, involving of course [see [45], Eqs. (11)–(13)] summations over wave vectors and Matsubara frequencies of $\chi(\mathbf{q}, \omega)$.

The mean-field Eliashberg equations for nearly ferromagnetic and nearly antiferromagnetic metals with a single 2D Fermi surface were then solved numerically in [45], to obtain the ratio of critical temperature T_c to spin fluctuation temperature, T_{sf}, essentially as a function of coupling strength g^2 for different values of the inverse

correlation length κ. This was done both for p-wave triplet and d-wave singlet pairing.

The major predictions of [45,46] were in accord that at strong coupling, T_c/T_{sf} exhibits saturation. For a physically reasonable range of values of κ^{-1}, the quantitative results of [45] were: (i) For p-wave triplet pairing, T_c/T_{sf} saturates at a value of 1/30, and (ii) For d-wave singlet pairing, T_c/T_{sf} has a saturation value of 1/2. This then is the point at which to make contact between these findings of [45,46] and our own study [110].

3.5.2. *Spin-Fluctuation Temperature T_{sf} and Correlation Length ξ in non-s-Wave Pairing Superconductors: Especially high-T_c Cuprates*

In [110], we exposed a relationship, for both heavy Fermion materials and for high-T_c cuprates, between the thermal energy $k_B T_c$ and another characteristic energy, ϵ_c say, for such non-s-wave superconductors, where ϵ_c was defined by

$$\epsilon_c = \frac{\hbar^2}{m^* \xi^2}, \tag{18}$$

ξ being the coherence length and m^* the effective mass (Fig. 5). We noted [110] that Uemura *et al.* [111] had already clearly recognized that m^* should enter inversely in determining the scale of $k_B T_c$.

Since Monthoux and Lonzarich [45] made their most extensive numerical investigations for the p-wave triplet pairing, let us take first the ruthenate Sr_2RuO_4, discussed at some length in [45]. From Fig. 2a of [45], for example, provided κ^2 is in the (physically reasonable) range from 0.25 to 1.0 and their quantity $g^2\chi_0/t$, with t the hopping energy, is in the physical range 10–20, then T_c/T_{sf} is in the range 0.02–0.03, which yields $T_{sf} \simeq 50\,\mathrm{K}$ for Sr_2RuO_4, compared with a 'saturation' value of 40 K for this material with $T_c \sim 1.3\,\mathrm{K}$. Abanov *et al.* [46] refer to values of $T_{sf} \sim 100\,\mathrm{K}$, so there is semiquantitative accord.

Turning to the high-T_c cuprates, the present authors [110] have pointed out that in marked contrast to the heavy Fermion materials

they also considered, $k_B T_c \sim \hbar^2/m^*\xi^2$ and from the saturation limit (ii) in Section 3.5.1, taken again from [45],

$$k_B T_c \sim \tfrac{1}{2} k_B T_{sf} \tag{19}$$

for the d-wave pairing high-T_c cuprates. Thus, one has as a consequence the order of magnitude result

$$k_B T_{sf} \sim \frac{2\hbar^2}{m^*\xi^2}, \tag{20}$$

and the coherence length ξ of the high-T_c cuprates is plainly determined by the antiferromagnetic spin-fluctuation mediated pairing, via a temperature $T_{sf} \sim 2T_c$.

Physical interpretation of the coherence length ξ resulting from d-wave singlet pairing spin-fluctuation interaction in the high-T_c cuprates We return to our earlier result [110] obtained from experimental data for the high-T_c cuprates that $k_B T_c \sim \epsilon_c$, with ϵ_c given by Eq. (18). We now add to this empirical correlation a further experimental consequence used by Monthoux and Lonzarich [45], namely that the product of the thermal energy $k_B T_{sf}$ associated with the spin-fluctuation temperature [45,46] T_{sf} with κ_0^2, the inverse magnetic correlation length squared without strong magnetic correlations, is constant, i.e.

$$k_B T_{sf} \kappa_0^2 = const. \tag{21}$$

Adopting the value in their Table V, the constant value turns out to be $\sim 8t$.

Returning to the strong coupling limit to gain further insight into the factors determining the coherence length ξ, we have

$$k_B T_c \sim \frac{1}{2} k_B T_{sf} \sim \frac{4t}{\kappa_0^2}. \tag{22}$$

Putting $\kappa_0^2 = a^2/\ell_{m0}^2$, where ℓ_{m0} is the (antiferro-) magnetic correlation length in the high-T_c cuprates, we find almost immediately

$$\xi \sim \frac{a}{2}\left(\frac{\hbar^2}{m^*\ell_{m0}^2}\right)^{1/2} \frac{1}{t^{1/2}}. \tag{23}$$

Physically, Eq. (23) shows that, in units of the lattice spacing a, the magnitude of the coherence length is determined by the square root of the ratio of two further characteristic energies. The first of these is the kinetic energy of localization of a carrier of mass m^* within the magnetic correlation length ℓ_{m0} determined however in the absence of strong magnetic correlations. The second energy is t, the magnitude of the hopping energy.

We can anticipate, using the additional (generally weaker!) variables $g^2\chi_0/t$ and κ^2 that, provided the range of $g^2\chi_0/t$ is limited to the physical region 10–20 (see [45]) and κ^2 is likewise restricted to the range 0.5–1, then Eq. (23) will be replaced, away from the strong coupling limit, by

$$\xi \sim \frac{a}{2}\left(\frac{\hbar^2}{m^*\ell_{m0}^2}\right)^{1/2}\frac{1}{t^{1/2}}F(g^2\chi_0/t;\kappa^2), \tag{24}$$

where F is a slowly varying function of its arguments, F becoming unity for sufficiently large values of the 'coupling strength' $g^2\chi_0/t$, with κ^2 restricted to the range quoted above.

Above, the achievement has been to bring the studies of [45,46], in which the superconducting transition temperature T_c is connected to the spin-fluctuation temperature T_{sf}, into direct contact with the work of Angilella *et al.* [110] relating k_BT_c to the characteristic energy $\hbar^2/m^*\xi^2$. For a d-wave singlet pairing mediated by antiferromagnetic spin fluctuations in the cuprates, the simple, order of magnitude relation Eq. (20) follows, showing that the coherence length ξ is determined by the interaction mediated by spin fluctuations. This is expressed, more specifically, in the language of [45], in Eqs. (23) and (24).

However, the situation regarding the relation of T_{sf} in the low T_c ruthenate Sr_2RuO_4 to the coherence length ξ is much less clear presently than in the high-T_c cuprates. This may be because of a competition between nearly ferromagnetic behavior and antiferromagnetic spin fluctuations. Experiments on $\chi(\mathbf{q},\omega)$ using both neutron scattering and NMR on this ruthenate would be valuable for furthering understanding of the origins of superconductivity, and especially the physics of the coherence length in this material. As for T_{sf} it seems to lie in the range 40–50 K. Having referred to heavy Fermion materials

in connection with [110], of the six such cases considered there, the 'anomalous' material was UPd_2Al_3 (compare Fig. 1 in [110]). It would therefore, we believe, be of interest to know more about the magnetic properties of this material, as it is well known that pure Pd is an 'almost ferromagnetic' metal (see, e.g., [112]). If it should turn out in the material UPd_2Al_3 that the assumptions underlying [45] are approximately fulfilled, we thought it of interest to construct from the *p*-wave studies of [45] a plot of T_c/t versus T_{sf}/t (see Fig. 6), by combining data from their Figs. 2–4. It is worth noting, though we expect the mechanisms generally to be different, that the shape of the present Fig. 6 parallels that of Fig. 1 of [110]. However, large numbers $\sim 10^2$ to 10^3 now appear, supporting the view that the mechanism for the majority of the heavy Fermion materials considered in [110] is quite different from the magnetic pairing confirmed here for the high-T_c cuprates.

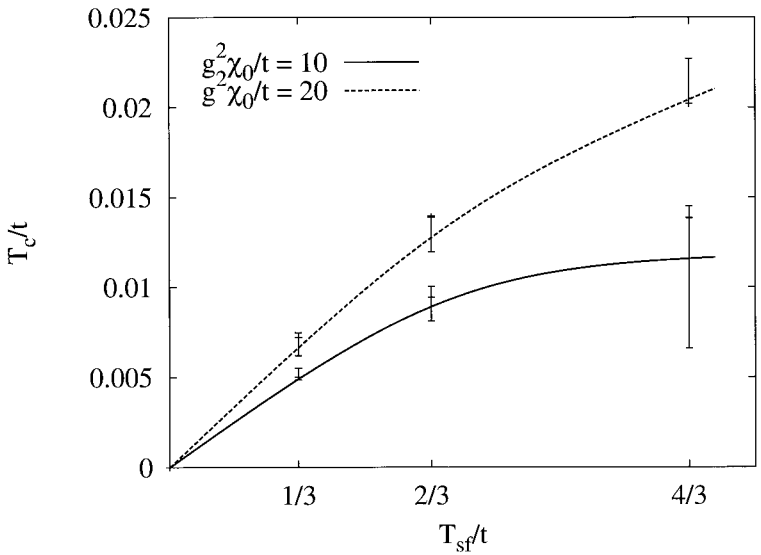


FIGURE 6 Shows plot of T_c/t versus T_{sf}/t for *p*-wave spin-triplet pairing (redrawn from [113]). This has been constructed by combining numerical data from Figs. 2–4 of [45], assuming for the parameters the physical range $10 \leq g^2\chi_0/t \leq 20$ and $0.25 \leq \kappa^2 \leq 1$. Points corresponding to the same value of T_{sf}/t and of $g^2\chi_0/t$, but to different values of κ^2, have been arranged as vertical bars. The two curves shown are guides to the eye through the choices of 'coupling strength' $g^2\chi_0/t$ of 10 and 20, and have been extrapolated through the origin.

4. TOPOLOGICAL SUPERCONDUCTIVITY

The idea of an ordered ground state with elementary excitations having topological character probably first arose in connection with the soliton theory of transport in quasi-1D conducting polymers, such as polyacetylene [114]. The normal state of such systems is known to belong to the universality class of the Tomonaga–Luttinger liquid (see Section 2.1.2), which in particular implies separation of the electron's spin and charge degrees of freedom. More generally, this aspect has been recently interpreted as an instance of electron fractionalization [115], i.e. the possibility of having fractional quantum numbers for excitations in a solid. Apart from polyacetylene, modern realizations of quasi-1D systems displaying electron fractionalization and spin-charge separation include carbon nanotubes, which can be related to fullerides, listed in class (iv) above, and Bechgaard salts [116]. In higher dimensionality, electron fractionalization has been proved particularly successful in the theory of the fractional quantum Hall effect, and gave rise to the theory of anyon superconductivity (see [117] for a brief review). In the last few years, moreover, the ideas of electron fractionalization and topological order have been employed in order to attempt at a description of the unconventional normal as well as the superconducting state of the high-T_c cuprates [118].

4.1. London Equations and Hydrodynamics of a Superfluid

In order to account for the electromagnetic properties of a superconductor, F. and H. London (1935) imposed a further constraint to the solutions of the equation of motion of a perfectly conducting charged fluid with current density $\mathbf{j} = \rho\mathbf{v}$, combined with Maxwell equations for the external electric ($\mathbf{E}$) and magnetic ($\mathbf{B}$) fields. London's equation reads:

$$\nabla \times \mathbf{j} = -\frac{n_s e^2}{mc}\mathbf{B}, \tag{25}$$

where n_s is the superfluid density ($\rho = -n_s e$; see, e.g., [119] for a derivation, and for reference to London's original papers). One major consequence of Eq. (25) is that persistent currents and magnetic

fields in a superconducting specimen can exist only within a layer of thickness $\lambda = (nc^2/4\pi n_s e^2)^{1/2}$ (London's penetration length) from the surface (Meissner effect).
The equation of motion for the current density $\mathbf{j}$ (assuming an isotropic velocity $\mathbf{v}$) can then be written as

$$\nabla\rho + \frac{1}{v^2}\frac{\partial \mathbf{j}}{\partial t} = \kappa \mathbf{E}, \tag{26}$$

which describes a compressible superfluid, with compressibility $\kappa = (\lambda v/c)^{-2}$ [120,121]. In the Lorentz gauge $\nabla \cdot \mathbf{A} + v^{-2}\partial_t \phi = 0$, both equations reduce to

$$\mathbf{j} = -\lambda^{-2}\mathbf{A}, \tag{27}$$

where $\mathbf{A}$ is the external vector potential. Indeed, replacing $\mathbf{E}$ by the gradient of pressure in Eq. (26) and $\mathbf{B}$ by a torque in Eq. (25), one recovers a complete analogy with Euler equations for an ideal compressible liquid (i.e., there is no shear modulus). Moreover, Eq. (27) allows to establish the equivalence between the Meissner effect ($\mathbf{B} = \nabla \times \mathbf{A} = 0$) and Landau's criterion for superfluidity ($\nabla \times \mathbf{v} = 0$, in any simply connected region). Such equivalence is made possible by the identification of the mechanical momentum $m\mathbf{v}$ of a superfluid particle with the electromagnetic momentum $2e\mathbf{A}/c$ of a Cooper pair of electrons.[5]

4.2. Fröhlich's One-Dimensional Model with Peierls Instability: Sliding Lattices But no Superconductivity

Landau's criterion for superfluidity does not work for 1D systems, since one cannot distinguish between a liquid and a solid by means of shear modulus in 1D. However, a few years before BCS theory, Frölich observed [122] that an incommensurate charge density wave (CDW) due to a Peierls instability would slide through a 1D metal

[5]A generalization of Landau's condition to multiply connected regions allows to take into account for vortices in a superfluid, and leads to flux quantization in a superconductor.

lattice without attenuation. Since a CDW carries an electric charge and implies a gap in the electronic spectrum, Frölich concluded that the ground state of such a 1D system is superconducting. It should be noted, however, that no true off-diagonal long-range order can develop in 1D [36], and that any finite amount of impurities is expected to pin the CDW in 1D, thus preventing Frölich superconductivity from being observed in real systems.

Charge transport by means of sliding CDW has been however reported in the quasi-2D organic salt α-$(ET)_2KHg(SCN)_4$ below $\sim 2\,K$ and under very high magnetic fields ($\gtrsim 20\,T$) [123], and the possible relevance of topological superconductivity for the quasi-2D cuprate superconductors has been recently suggested by Abanov and Wiegmann [124].

Fröhlich superconducting state in 1D lends itself as the prototype of a topologically ordered state. Topological order has been invoked as a viable mechanism for superconductivity in reduced dimensionality strongly correlated electron systems. Anyon superconductivity is an example of topological superconductivity in 2D [117]. A further example is provided by resonating valence bond superconductivity, to be discussed below (see Section 4.3).

4.3. Resonating Valence Bond Approach and Topological Superconductivity

4.3.1. Anderson's Resonating Valence Bond Approach to the High-T_c Cuprates

Senatore and March [125] have reviewed the way in which the Hubbard Hamiltonian, for large values of the on-site Coulomb interaction U, can be transformed into an antiferromagnetic Heisenberg Hamiltonian by means of a suitable unitary transformation [125]. In this connection and also in relation to the high-T_c superconductivity, it seems appropriate here to briefly review the mathematical formulation due to Anderson [126,127] of the concept of the resonating valence-bond (RVB) states first put forward by Pauling [128].

For electrons on a lattice, one can view a singlet bond or pair as the state formed when two electrons with opposite spin are localized on two distinct sites. A RVB state is a coherent superposition of such

singlet bonds; its energy is further lowered as a result of matrix elements connecting different valence-bond configurations.

Heuristically, valence bonds can be viewed as real-space Cooper pairs that repel each other, a combined effect of the Pauli principle and the Coulomb interaction. When there is one electron per site, charge fluctuations are suppressed, and one obtains an insulating state. However, as one moves away from half filling, current can flow. The assembly becomes superconducting as the valence bonds Bose condense.

Anderson [126,127], while stressing the difficulty of making quantitative calculations with RVB states, gives a suggestive representation by exploiting the Gutzwiller-type projection technique.

Clearly, a delocalized or mobile valence bond can be written as

$$\begin{aligned} b_\tau^\dagger|\Phi_0\rangle &= \frac{1}{\sqrt{N}}\left(\sum_i a_{i\uparrow}^\dagger a_{i+\tau\downarrow}^\dagger\right)|0\rangle \\ &= \frac{1}{\sqrt{N}}\left(\sum_{\mathbf{k}} a_{\mathbf{k}\uparrow}^\dagger a_{-\mathbf{k}\downarrow}^\dagger \exp(\mathbf{k}\cdot\tau)\right)|0\rangle, \end{aligned} \tag{28}$$

$b_\tau^\dagger$ being the creation operator for a valence-bond with lattice vector τ, while N is the total number of lattice sites. A distribution of bond lengths can be constructed by summing $b_\tau^\dagger$ over τ with appropriate weights. One then finds a new creation operator,

$$b^\dagger = \sum_{\mathbf{k}} c_{\mathbf{k}} a_{\mathbf{k}\uparrow}^\dagger a_{-\mathbf{k}\downarrow}^\dagger, \tag{29}$$

with the restriction

$$\sum_{\mathbf{k}} c_{\mathbf{k}} = 0, \tag{30}$$

imposed to avoid double occupancy.

Anderson proceeds by (a) allowing Bose condensation of such mobile valence bonds,

$$|\Phi\rangle = (b^\dagger)^{N/2}|0\rangle, \tag{31}$$

and by (b) projecting out the double occupancy with an infinite-U Gutzwiller projection operator $P_d = \prod_i (1 - n_{i\uparrow} n_{i\downarrow})$,

$$|\Phi_{RVB}\rangle = P_d (b^\dagger)^{N/2} |0\rangle. \tag{32}$$

One can then demonstrate that the RVB state constructed above can be obtained with simple manipulations from a standard BCS state by projecting on the state with N particles and projecting out, at the same time, the double occupancy:

$$|\Phi_{RVB}\rangle = P_{N/2} P_d \left(\frac{1}{\sqrt{1 + c_{\mathbf{k}}}} + \frac{c_{\mathbf{k}}}{\sqrt{1 + c_{\mathbf{k}}}} a^\dagger_{\mathbf{k}\uparrow} a^\dagger_{-\mathbf{k}\downarrow} \right) |0\rangle. \tag{33}$$

Baskaran *et al.* [129] have subsequently demonstrated that by treating the large-U Hamiltonian of Eq. (3.44) in [125] with a mean-field (Hartree–Fock) approximation, one obtains precisely a BCS-type Hamiltonian which, for half-filling, yields the RVB state heuristically introduced above. One could also find that $\sum_{\mathbf{k}} c_{\mathbf{k}} = 0$, $|c_{\mathbf{k}}| = 1$ and the $c_{\mathbf{k}}$ change sign across what they call a 'pseudo-Fermi surface'. The nature of the excitations from such a RVB state will not be discussed here, being referred to the original papers.

4.3.2. RVB for Topological Superconductors

A modification of the original Hubbard model [130–132], the so-called t-J model, has become widely used in the field of strongly correlated electronic assemblies. At zero doping, this model reduces to the Heisenberg Hamiltonian

$$H = \sum_{ab} J_{ab} \mathbf{S}_a \cdot \mathbf{S}_b, \tag{34}$$

with spins $\mathbf{S}_a$ and $\mathbf{S}_b$ on sublattices A and B, respectively. March and Klein [133] have compared in the present context the resonating valence bond and the Néel states (see also below). When 'doping' terms are added, the new (t-J) Hamiltonian has a hopping amplitude t_{ij} and an exchange amplitude J_{ij} which connect the nearest sites.

The total number of electrons N_e, say, is near to the lattice site number and we write below (see also [120,121])

$$N_e = N_0(1 - \bar{\rho}). \tag{35}$$

Additionally, a strong (Hubbard) interaction forbids double occupancy of sites:

$$n_i = \sum_{\sigma} c_{i\sigma}^{\dagger} c_{i\sigma} = 0 \text{ or } 1. \tag{36}$$

As well as an average spin value, two further operators [120,121] characterize the ground-state of an antiferromagnet, namely the density of energy ϵ_{ij},

$$\epsilon_{ij} = \left(\tfrac{1}{4} + \mathbf{S}_i \cdot \mathbf{S}_j\right), \tag{37}$$

and chirality, or topological order measure $W(C)$,

$$W(C) = \mathrm{Tr} \prod_{i \in C} \left(\tfrac{1}{2} + \sigma \cdot \mathbf{S}_i\right), \tag{38}$$

the σ denoting Pauli matrices, while C is a lattice contour [134–137]. The operator $W(C)$ takes on especial significance for the doped material as it determines the correlation of electronic phases at different spatial points.

This is the point at which to make contact with the RVB ideas, going back to Pauling on d-electrons in transition metals, and utilized by Anderson and co-workers in their treatment of high-T_c materials (in class (iii) above) [120,121]. In the RVB approach, the amplitude and phase Δ_{ij} of Anderson *et al.* [120,121] have the form

$$\epsilon_{ij} = |\Delta_{ij}|^2 \tag{39}$$

and

$$W(C) = \prod_{C} \Delta_{ij}. \tag{40}$$

Wiegmann and co-workers then write the hopping Hamiltonian H in terms of h_i – a dopant (hole) operator, an electron operator being represented by the product of a 'spinon' and a 'holon', namely $c_{\sigma i}h_i^\dagger$. H then has the form

$$H = t\sum_{\langle ab\rangle} h^\dagger(a)h(b)\Delta_{ab} + H.c. \tag{41}$$

Here, a and b are sites of the sublattices A and B and Δ_{ab} is given by

$$\Delta_{ab} = \left\langle \sum_\sigma c_\sigma^\dagger(a)c_\sigma(b) \right\rangle. \tag{42}$$

Wiegmann stresses that, depending on parameter values in this model, physically different regimes can be embraced. This is related closely to the conclusions of March and Klein [133], who analyze the crossover between RVB and Néel state situations. Wiegmann stresses additionally that in the latter state the modulus and phase of bonds fluctuate similarly and cannot be separated. In this Néel state, the holes form a Fermi liquid and interact weakly with spin fluctuations.

Wiegmann discusses, by invoking next a semi-classical strategy, some of the predictions flowing from the above Hamiltonian H in the RVB regime, and the interested reader is referred to his work [120,121] for further details.

5. SUMMARY AND FUTURE DIRECTIONS

Our conclusions at the time of writing can be stated as follows.

Class (i) superconductors: BCS metals and alloys are well understood, with electron-phonon interaction as the mechanism for (s-wave) Cooper pairing. In the normal state, the momentum distribution $n(\mathbf{p})$ is characteristic of a $D = 3$ Fermi liquid with a discontinuity Z at the Fermi momentum p_F, which is reduced from the free Fermi gas value of unity by electron-electron interactions. In the superconducting state, the discontinuity in $n(\mathbf{p})$ is 'rounded off' (see, e.g., [18,138]). Recent determination of the phonon density of states in

MgB_2 via neutron scattering [8,9] allows to place such material in class (i), despite its relatively high T_c. The recent study of Silkin *et al.* [139] makes interesting calculations which show that T_c can be increased in surfaces of this material.

Class (ii) and (iii) superconductors Heavy Fermion and high-T_c unconventional superconductors are characterized by pairing with $\ell > 0$: for heavy Fermion systems, p-wave pairing seems prominent, while for most high-T_c cuprates $\ell = 2$ appears very probable (see, however, the objections raised by Brandow [140]). T_c in both these categories (ii) and (iii) appears to correlate interestingly with coherence length and effective mass. But the pairing mechanisms seem quite different, the high-T_c cuprate interaction being mediated by d-wave singlet (antiferro-) magnetic fluctuations. Although the current understanding is still unsettled, several experimental findings support unconventional pairing also in the quasi-2D organic superconductors. The determination of the actual direction of the nodal lines of the OP in such compounds would allow to discern whether spin or charge fluctuations be at work in mediating the pairing interaction. A time reversal symmetry breaking triplet order parameter has been suggested for both heavy Fermion compounds and the ruthenates.

Class (iv) superconductors Alkali-metal doped fullerites, as emphasized by Gunnarsson [17], appear to be characterized by s-wave Cooper pairs arising from electron-phonon interaction, and the overall phenomenology of fullerides can be accounted for within the frame of Eliashberg theory [141].

It is our belief, at the time of writing, that there is a really firm body of evidence, firm from both experiment and theory, in support of the conclusions. However, in turning finally to propose what seem to us to be some interesting directions for future studies, we are beginning to trespass into potentially controversial areas, and so we shall be very brief.

Secondly, in the search for even higher T_c values than in the cuprates, f-wave superconductivity may be important, as our own proposed correlation of T_c (but now for the unconventional superconductors in categories (ii) and (iii)) with coherence length and effective mass suggests [110]: the term $(\hbar^2/2m)(\ell(\ell+1)/r^2)$ in the centrifugal potential energy suggesting that a factor of 2 increase in T_c would seem plausible,

since $\ell(\ell + 1)$ goes from 6 for a d-wave pairing to 12 for f-wave pairing superconductors. Of course, this assumes no 'trade-off' in (a) coherence length, and (b) effective mass (see [113]) as one passes from d-wave to f-wave pairing. Already, in the very recent literature, f-wave pairing is specifically discussed, in one case associated with an organic superconductor [142,143].

Thirdly, and entirely speculatively, can topological superconductivity come into its own in the doped fullerites (or other materials, as yet presumably unexplored)? This could take one back to the early studies by the quantum chemists, Coulson, Longuet-Higgins, Pople, and Walmsley where "misfits" were generalized to solitons in conducting polymers [114,144]. The topological nature was recognized by Jackiw and Schrieffer [145], and the result is the same topological invariant in Wiegmann's approach. But, for the moment, it is not clear what experiments could distinguish between the very convincing picture of superconductivity in the doped fullerites presented by Gunnarsson in his review [17] and the (presumably alternative) viewpoint of these materials as topological superconductors. Do we expect topological superconductivity to be an altogether new mechanism or a reformulation consistent with Gunnarsson's treatment.

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