Single Spin Superconductivity

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A spin-compensated half-metallic antiferromagnetic is shown to allow a new, type of superconductivity in which only one spin channel is superconducting. This $S = 1$ triplet pairing state that arises from a unique type of normal state will differ markedly from conventional, heavy fermion, or high temperature superconductors. Characteristics of such a state are outlined, and guidelines for making promising candidates are presented. [S0031-9007(96)01366-X]

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Conventional, heavy fermion, and high temperature superconductors, although having very different superconducting states, are all spin compensated, i.e., spin-up (↑) and spin-down (↓) electrons participate equally in forming the superconducting state. More precisely, electrons pairs are formed within a complex consisting of ↑ and ↓ states, on opposite sides of the Fermi surface ($\vec{k}_F; -\vec{k}_F$) so the quasiparticle and quasihole pairs have zero net momentum and, in the simplest instance, zero spin $S = 0$. These pairs mutually interact and form the superconducting condensate. Ideal diamagnetism (the Meissner effect) arises because the superconducting condensate resists the encroachment of magnetic fields. The interaction between the magnetic vector potential and charge of the condensate drives orbital currents, producing screening fields that oppose the advance of a magnetic field, and allows only entrance of the field above some critical field H_c. Strong competition between superconducting condensates and magnetic fields is a prime source of difficulty in finding widespread applications of superconductivity.

This antagonistic connection between superconductivity and magnetism is intriguing, especially because these two phases of matter are the two macroscopically evident manifestations of the quantum mechanical behavior of electrons. In this Letter we point out a new aspect of the intimate interplay between magnetism and superconductivity: the development of an antialignment of spins with vanishing total moment (and zero macroscopic magnetic field) that allows the possibility of a new type of superconducting state of triplet pairs in one spin channel only, which we call single spin superconductity (SSS). A scheme for designing the requisite properties into a compound is outlined.

Half-metallic (HM) ferromagnetism (FM) has been gaining visibility, due partially to the prediction that the so-called "colossal magnetoresistance" manganites (viz. $La_{1-x}Ca_xMnO_3$) will show HMFM behavior [1,2]. HMFM is a FM state in which one spin channel is metallic while the other spin channel is insulating. CrO_2 is the simplest example of a HMFM [3]. This condition is an uncommon occurrence, but the origin of HMFM character is easy to understand: exchange splitting may cause (only) one of the pair of spin-split d bands to overlap another set of bands (such as oxygen p bands), giving one metallic channel, while the Fermi level lies within a charge-transfer gap in the other insulating channel. Several properties of a HMFM are unusual: (i) because the insulating channel has filled bands, and there are an integral number of electrons/(unit cell), the spin moment is an *integer* N_S; (ii) electronic transport is 100% spin polarized; (iii) there is zero Pauli spin susceptibility reflecting magnetic rigidity, due to the fact that there are no ↓ spin states at low energy to allow field-induced spin flips [4].

It can occur that the HMFM type of band structure can arise, but that $N_S \equiv 0$: the number of ↑ and ↓ electrons are equal. Such a material has been called a HM antiferromagnetic (AF) [5] but since there is no symmetry operation (translation plus spin flip) that connects the ↑ and ↓ bands, it is qualitatively different from the usual AF. A model example is pictured in Fig. 1. Without the half-metallic nature (the gap in a one spin channel) a ferrimagnet may have zero moment by accident, but this occurrence is vanishingly improbable. With the HM character, vanishing moment becomes a real possibility. In many regards the HMAF will behave as a HMFM:

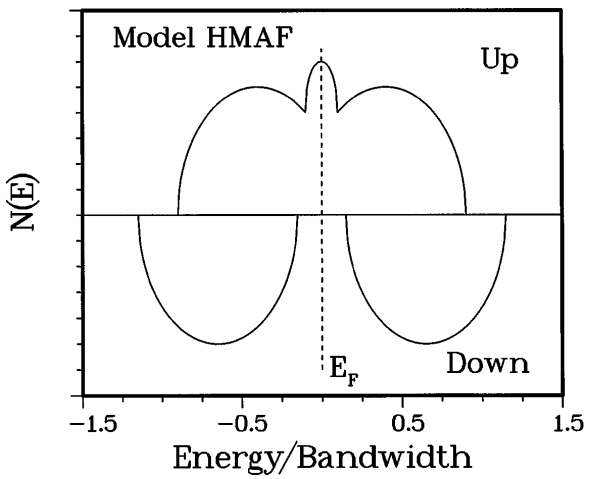

FIG. 1. Density of states (DOS) of a model HMAF, with semicircular DOS representing individual bands. Up spin bands are centered at ± 0.40 and overlap, while down spin bands are centered at ± 0.65 and are gapped and insulating.

metallic with 100% spin-polarized transport, zero spin susceptibility, and no Stoner continuum.

The central idea of this Letter is that, since the HMAF nature can enforce vanishing spin moment, there is no obstacle (macroscopic magnetic field) to superconductivity appearing in the metallic channel. A HMAF with a pairing interaction would provide the first example of a SSS. With usual notation [6], and taking the metallic channel as $\uparrow$, the reduced Hamiltonian is

$$H_{\rm red} = \sum_k \epsilon_{k\uparrow} a^\dagger_{k\uparrow} a_{k\uparrow} - \frac{1}{2}\sum_{kk'} V_{kk'} a^\dagger_{k\uparrow} a^\dagger_{-k\uparrow} a_{-k\uparrow} a_{k\uparrow}, \quad (1)$$

where $V_{kk'} = \langle k\uparrow, -k\uparrow | V | k'\uparrow, -k'\uparrow\rangle$ is the pairing interaction. The $\downarrow$ channel is insulating and contributes nothing to low energy processes.

The general pairing theory can be adapted, and the following consequences appear. Pairing occurs in only in the metallic $\uparrow$ channel, leading to spin triplet pairs $S = 1$. Fermionic antisymmetry requires that the orbital pair wave function must be odd, with "$L = 1$" being the simplest possibility. The conventional symmetry analysis [7–9] is restricted considerably, since the spin asymmetry already breaks time-reversal symmetry ($\mathcal{T}$) in the normal state. Magnetocrystalline anisotropy (MCA), through spin-orbit coupling, fixes the spin direction to the lattice in the normal state, and if the MCA energy is large spin-rotation invariance S is removed because the spin is fixed to the lattice. However, the MCA energy is likely to be the smallest energy scale for the 3D-based materials we consider (smaller than the superconducting gap), and thus will be a minor perturbation [10]. We suppose there is a center of inversion of the crystal, so parity is a quantum number.

The surviving symmetries are simply the crystal point group $\mathcal{G} = \mathcal{R} \times \mathcal{I}$ ($\mathcal{R}, \mathcal{I}$ are the proper rotation group and inversion, respectively), the combination $S_\pi \mathcal{T}$ of time reversal followed by a spin rotation through π (which becomes simply complex conjugation), and gauge ($\mathcal{A}$) symmetry. The number of possible superconducting states is thus considerably more limited than in ^{3}He, where the continuous S and $\mathcal{R}$ symmetries, and $\mathcal{T}$, $\mathcal{I}$, and $\mathcal{A}$ symmetries lead to numerous allowed broken symmetry triplet pairing phases. Triplet pairing has been studied extensively (because of its occurrence in ^{3}He), but only for cases of identical triplet condensates in both spin channels (or the generalization [11] to include spin-orbit coupling in possible heavy fermion realizations).

The center of inversion requires that $\mathcal{I}\phi_k$ be degenerate with ϕ_k and associated with $-\vec{k}$. (ϕ_k is a single particle eigenstate.) This ensures that the Fermi surface has inversion symmetry, so zero momentum $(\vec{k}, -\vec{k})$ pairing is possible. Fermionic anticommutation requires that the order parameter $\hat{\Delta}_k = \sum_{k'} V_{kk'} \langle a_{k'\uparrow} a_{-k'\uparrow}\rangle$ be odd in $\vec{k}$, giving the expansion

$$\hat{\Delta}_k = \vec{q}\cdot\vec{v}_k f_1(k) + \sum_{\alpha\beta\gamma} Q^{\alpha\beta\gamma} v_{k,\alpha} v_{k,\beta} v_{k,\gamma} f_3(k) + \cdots. \quad (2)$$

Here $f_1, f_3, \ldots$ are symmetric functions of $\vec{k}$, and q_α and $Q^{\alpha\beta\gamma}$ are $\vec{k}$-independent expansion coefficients. We use the velocity $\vec{v}_k$, which is more appropriate than the standard choice of $\vec{k}$ because it is has the proper lattice symmetry and is generalizable to multiple Fermi surfaces of arbitrary shape [12]. The higher symmetry superconducting states are characterized by the vector $\vec{q}$, with possibilities such as an axial state $(0, 0, 1)$ ($\hat{\Delta}_k \propto v_{k,z}$) and a helicity pair $(1, \pm i, 0)$. The $\vec{q} = (1, \pm i, 0)$ helicity states, with $\hat{\Delta}_k \propto v_{k,x} \pm i v_{k,y}$ would have point nodes where the Fermi surface is perpendicular to the spin direction: $v_{k,x} = v_{k,y} = 0$. Such a state would have characteristic spectral and thermodynamic signatures at very low temperature, and a phase of $\hat{\Delta}$ that increases by 2π in following a contour around the node, implying boojumlike singularities [13]. A full symmetry analysis is necessary to enumerate the allowed unconventional pairing symmetries.

In a SSS the supercurrent is 100% spin polarized, and opens the possibility of spin-polarized Josephson junctions. Combined with magnetic normal metals, HMFMs, or magnetic insulators, the SSS would allow new magnetoelectronic configurations that have not been considered previously. Interest in high current density applications naturally leads one to question whether the SSS will be influenced (adversely, as a consequence of the Meissner effect) as strongly by magnetic field $\vec{H}$ as are conventional superconductors. Conventionally, the coupling of the vector potential to the orbital current (i.e., the charge) of the electrons is dominant; coupling to spin is less important at moderate fields. Because of the axial nature of pairing in a SSS (and in analogy with ^{3}He [14]), the response to a field and in particular the phase boundary $H_c(T)$ will depend on $\vec{H}\cdot\hat{z}$. Measuring a direction dependence of $H_c(T; \hat{H})$ could be one of the most straightforward ways of identifying this unconventional state and its axial direction. Another way of identifying this unconventional state would be by tunneling into a conventional s-wave superconductor. Such tunneling would be disallowed, both due to symmetry differences and because spin $\downarrow$ carriers cannot be transported through the HM material.

The symmetry of the HMAF, with spin-orbit coupling, leads to a net orbital moment, and the resulting field would oppose conventional superconductivity. However, the symmetry of the SSS order parameter allows a spontaneous orbital moment (see [8,13]) that would cancel the intrinsic orbital moment and lead to vanishing total macroscopic field. Therefore a normal state orbital moment can be tolerated, and canceled, by a SSS state.

We turn now to the question of finding a SSS. To promote HMAF (the normal state precursor of SSS) character in a crystalline material, one should observe the following guidelines: (a) the crystal must be magnetic with chemically distinct (i.e., symmetry unrelated) spin channels having antialigned atomic moments (see Fig. 1); (b) to obtain an insulating ↓ channel, the ↓ states on neighboring active ions (viz. transition metal ions) should be separated in energy by an amount comparable to the bandwidth, as this will promote both band insulating behavior and Mott or charge transfer insulating tendencies; (c) to obtain a metallic ↑ channel, the ↑ conduction states on neighboring active ions should be separated in energy by considerably less than the bandwidth; (d) to obtain vanishing net magnetic moment, the moments on ions with spin down must sum to the same value as the moments on ions with spin up; (e) to encourage insulating behavior in a cubic material, AF preferably should be of a bipartite (e.g., rocksalt or zinc blende) type of arrangement, with ↑ spins surrounded by ↓ in each of the three directions; (f) ionic radii and charges should differ as much as possible to promote well ordered crystals with high sublattice integrity; (g) strong electron-phonon coupling should be sought, since the half-metallic nature of the normal state rules out pairing by single-magnon exchange [4].

Criteria (a)–(e) can be achieved in the simplest way with two types of ions whose on-site energy separation $\epsilon_1 - \epsilon_2$ is comparable to their intra-atomic exchange splitting Δ_1 and Δ_2 (not to be confused with the order parameter $\hat{\Delta}_k$ above). Letting ion 1 of the pair of ions be the one with highest energy ($\epsilon_1 > \epsilon_2$), then one achieves the conditions

$$B\text{: } \epsilon_{+,1} = \epsilon_1 - \Delta_1/2 \approx \epsilon_2 + \Delta_2/2 = \epsilon_{-,2}, \quad (3)$$

for the ↑ channel, and

$$A\text{: } \epsilon_{-,1} = \epsilon_1 + \Delta_1/2 \gg \epsilon_2 - \Delta_2/2 = \epsilon_{+,2}, \quad (4)$$

for the ↓ channel. Here + (−) denotes the majority (minority) component; recall that for antialigned moments a spin ↑ electron is majority on one site and minority on the next. This simple picture will actually be much more complicated, first by crystal field splitting, which may be comparable to Δ (see below), second, by the dependence of Δ_j on the moment of ion j, third, by interaction with oxygen ions that leads to strongly spin-dependent hybridization, [2] and, fourth, by the multiband nature of real materials.

We propose that ordered alloys of $3d$ transition metal (TM) perovskites ABO_3 provide promising candidates for SSS. In the class with trivalent A cation, e.g., La^{3+} or Y^{3+}, the metal ions are nominally 3+, which allows one to "prepare" the compound with pairs of ions with equal moments. In Table I we provide anticipated moments of TM ions in perovskite compounds in two limits. The first case is for vanishing crystal field splitting, for which the moment is simply the Hund's rule value. The second case is for a crystal field greater than the exchange splitting $\Delta \approx I_{\rm ex} m$, where $I_{\rm ex}$ is an exchange constant $\approx$0.9 eV/μ_B, [15] and m is the local moment. The perovskite structure is known to promote antialignment of spins in stoichiometric compounds and many such compounds have strong electron-phonon coupling. The structurally simpler rocksalt-type transition metal monoxides, viz. NiO, appear to be a less optimal choice. The metal ions lie on an fcc lattice, and it is not possible to satisfy requirement (d) above that each active ion be surrounded only by opposite spin nearest neighbors ("frustration"). Intermetallic compounds are however a possibility [5].

A simple candidate for a HMAF is La_2MnCoO_6, with a rocksalt ordering of the Mn and Co ions in the simple cubic perovskite lattice. If each ion (Mn^{3+} is d^4, Co^{3+} is d^6) has a Hund's rule moment of $4\mu_B$, then if directed oppositely the compound may attain a vanishing net moment. Mn^{3+}, having a lower nuclear charge, will have an on-site energy that might be of the order of 1 eV higher than that of Co^{3+} (but see

TABLE I. Nominal charge states, Hund's rule magnetic moments m (μ_B), and crystal field moments m (μ_B), for AMO_3 compounds. Ions in parentheses are uncommon. As discussed in the text, Hund's rule will not be followed if the crystal field splitting is comparable to the intra-atomic exchange splitting. "cf" and "no cf" indicates atomic moments with a normal crystal field for the perovskite structure, or negligible crystal field (Hund's rule), respectively (see text).

Compound	Ion	d^1	d^2	d^3	d^4	d^5	d^6	d^7	d^8	d^9
$A^{4+}M^{2+}O_3$	M^{2+}	(Sc)	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
	m (no cf)	1	2	3	4	5	4	3	2	1
	m (cf)	1	2	3	4	5	0	1	2	1
$A^{3+}M^{3+}O_3$	M^{3+}	Ti	V	Cr	Mn	Fe	Co	Ni	(Cu)	
	m (no cf)	1	2	3	4	5	4	3	2	
	m (cf)	1	2	3	4	3	0	1	2	
$A^{2+}M^{4+}O_3$	M^{4+}	V	Cr	Mn	Fe	Co	(Ni)			
	m (no cf)	1	2	3	4	5	4			
	m (cf)	1	2	3	4	3	0			

below). Each ion tends to Jahn-Teller instability, which will provide strong electron—phonon coupling, but any static structural distortions could complicate the picture of their electronic and magnetic structure. The difference in ionic size between the two transition metal cations is small but should tend to promote ordering (relative to disordered site occupation, which is not favorable for HMAF). The compound La_2CrNiO_6 provides an analogous possibility based on Hund's rule moments of $3\mu_B$ (see Table I).

Local spin density approximation (LSDA) calculations [16] indeed *lead to a* HMAF *solution* for La_2MnCoO_6, with antialigned Mn^{3+} and Co^{3+} moments. The metallic spins (our ↑ channel) are parallel to the Mn moment, while the Co sublattice is insulating. The local densities of states are pictured in Fig. 2. The moments are not the full Hund's rule value, being $2.7\mu_B$ rather than $4\mu_B$. Because the crystal field splitting is comparable to Δ, minority states begin to get filled before majority states are full. The HMAF character arises due to more subtle factors than suggested in (b) and (c) above. The site energy difference $\epsilon_d^{\mathrm{Mn}} - \epsilon_d^{\mathrm{Co}}$ is smaller than anticipated, but since it is spin independent, it assists in splitting the Mn t_{2g}^- and Co $e_g^+ \downarrow$ states around the Fermi level that runs through the degenerate Mn e_g^+ and Co $t_{2g}^- \uparrow$ states. Thus the outcome depends on three energy scales (site energy difference, exchange splitting, and crystal field splitting) as well as necessitating rather narrow bandwidths (small hopping amplitude t).

This positive result is very encouraging, but it is not the whole story. At the volume we have studied (perovskite lattice constant of 3.89 Å), this HMAF state is metastable; a ferromagnetic, and nearly half-metallic, state ($4.6\mu_B$ per doubled perovskite cell) with high spin Mn ($3.3\mu_B$) and low spin Co ($1.3\mu_B$) was also found and is 0.09 eV/atom lower in energy. Thus at this volume La_2MnCoO_3 does not appear to be a likely HMAF, or SSS. Calculations for La_2CrNiO_6 show it to fit the expectations of (a)–(d) above rather well (the site energy difference is ≈1.5 eV), but a HMAF situation is narrowly missed and a ferrimagnetic character with net moment of $0.3\mu_B$ results. Relaxing the cell volume might produce a HMAF.

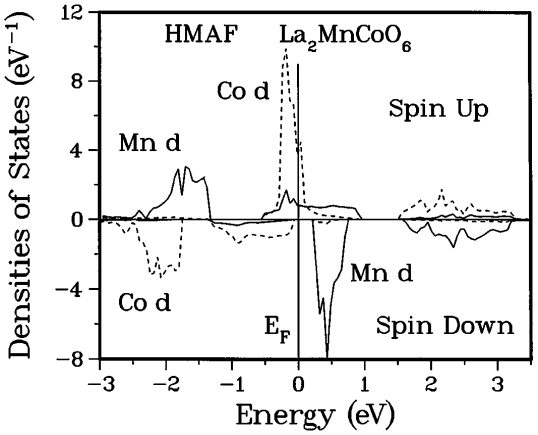

FIG. 2. d densities of states of La_2MnCoO_6, illustrating the HMAF character. Solid (dashed) lines denote Mn (Co) character, and ↑ spin (↓ spin) is plotted upward (downward). Note the gap at E_F in (only) the ↓ spin channel. The conduction states lie in a band formed by Mn majority e_g states and Co minority t_{2g} states.

The possibility of single spin channel, triplet superconductivity in a spin-compensated compound with ferromagnetic symmetry has been raised in this Letter. Crystal structures other than the perovskite structure discussed here may be promising. We suggest to experimenters that metallic "nonmagnetic" samples involving magnetic ions should be checked for superconductivity whenever possible. Two caveats should be noted. The requirement of zero net spin magnetization appears to limit this phenomenon to stoichiometric compounds (or compensated alloys with an integer number of electrons per unit cell). Finally, triplet superconductivity is more sensitive to defect scattering than is conventional superconductivity, but if the coupling is moderately strong this should not preclude SSS [17].

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