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RVB Contribution to Superconductivity in MgB_2

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We view MgB_2 as electronically equivalent to (non-staggered) graphite (B^- layer) that has undergone a zero gap semiconductor to a superconductor phase transition by a large c-axis (chemical) pressure due to Mg^{++} layers. Further, like the $p\pi$ bonded planar organic molecules, graphite is an old resonating valence bond (RVB) system. The RVB's are the 'preexisting cooper pairs' in the 'parental' zero gap semiconducting B^- (graphite) sheets that manifests themselves as a superconducting ground state of the transformed metal. Some consequences are pointed out.

Nature has once again surprised us through a high temperature superconductivity in MgB_2 , discovered by Akimitsu and collaborators [1]. This has resulted in a spurt of activity both in the experimental [2–9] and theory [10–12] front. The aim of the present letter is to search for possible electronic contribution to the mechanism of superconductivity in MgB_2 . Our theory uses the well recognized connection of electronic structure of boron sheets to graphite sheets [1,10]. In particular we view MgB_2 as a (non-staggered) graphite that has undergone a semi-metal to superconductor transformation because of a c-axis chemical pressure.

The following are some of the phenomenological reasons for looking for an electronic contribution to superconductivity in MgB_2 : i) similarity to $p\pi$ bonded planar systems like graphite, organic molecules and carbon nano-tubes where correlations play varying roles ii) absence of Hebel- Slichter peak in NMR relaxation [3] iii) a temperature dependent peak around 17 meV in energy resolved neutron scattering [6] iv) first order metal to metal transition on Al or C substitution [7] v) possible anomalous temperature dependence of R_H [9] and also London penetration depth [8] and vi) need to use an anomalously small μ^* in phonon based theories [13] to get a reasonable T_c .

MgB_2 is very similar to graphite both crystallographically and electronically. While the carbon hexagonal lattices are staggered in graphite, the boron hexagonal layers are on top of each other in MgB_2 . The boron layers alternate with a triangular lattice of Mg layers. There is nearly complete 2e charge transfer from Mg to the boron sub system: $MgB_2 \equiv Mg^{++}(B^-)_2$. Each boron acquires one electron and acquires the electron configuration of a carbon atom:

$$B^-(2s^2 2p^2) \equiv C(2s^2 2p^2)$$

Thus the B^- sheets are electronically like graphite sheets. The Mg^{++} ion with its strong positive charge pulls the charged boron sheets closer and reduces the c-axis separation. The ratio of B-B distance along the ab plane to that along the c-axis is ≈ 2.0 as opposed to the corresponding C-C distance ratio ≈ 2.4 in graphite. *This 15 % shortening of c-axis distance and removal of staggering converts a semi conducting 'graphite' into a high Tc superconductor !*

Graphite, like the $p\pi$ bonded planar organic molecules, has been the testing ground for the ideas of resonating valence bonds (RVB) from early times. While Pauling [14] and others emphasized the idea of valence bond resonance and delocalization in the calculation of ground state (cohesive) energy and to some extent a quantitative understanding of anomalous diamagnetism [15], non trivial consequences of RVB ideas for graphite have not been seriously discussed. The aim of the present letter is to argue that RVB's, the preexisting enhanced singlet (cooper pair) correlations in graphite, a zero gap semiconductor should reveal itself as a superconducting ground state after an application of sufficient c-axis pressure (when no structural modification intervenes). Nature seems to realize this through a chemical pressure in MgB_2 , a system isoelectronic to graphite.

In order to understand MgB_2 we should understand an isolated graphite layer. The relevant valence orbital is the p_z orbitals of carbon with a mean occupancy of one electron. In the honeycomb structure there are two equivalent carbon atoms and two valence electrons per unit cell. According to band theory, in view of two orbitals per unit cell, we get an empty and a filled band. Symmetry forces either a zero or a positive overlap between the two bands. That is we either have a zero gap semiconductor or a semi metal. For a $p\pi$ bonded system like graphite a well known model is the Hubbard model (simplified PPP model) on a honeycomb lattice with nearest neighbor hopping:

$$H = -t \sum_{\langle ij \rangle} C^\dagger_{i\sigma} C_{j\sigma} + h.c. + U \sum n_{i\uparrow} n_{i\downarrow} \qquad (1)$$

The kinetic energy term gives us a zero gap semiconductor with a valence and conduction band dispersion

$$\epsilon_\pm(k) = \pm\, 2t \left[\frac{3}{4} + \frac{1}{2} \cos k_x + \cos \frac{k_x}{2} \cos \frac{\sqrt{3} k_y}{2} \right]^{\frac{1}{2}} \qquad (2)$$

of the C layers with $t \approx 2.5eV$. The zero gap is not due to electron correlation; it is symmetry dictated. It

disappears and produces small electron and hole fermi pockets if we introduce next nearest neighbor hopping term in the planes or finite c-axis hopping term $t_\perp$. Experimentally, in pure graphite the electron and hole concentrations are rather small $\sim 10^{-4}$electron or hole per site; pure graphite sheets cleave and the binding between layers is van der Waals and not metallic.

It is known [15] that in $p\pi$ bonded planar organic molecules the screened on site coulomb interaction in carbon (and also boron) p_z orbitals is $U \sim 6\ eV$ (the bare atomic $U \sim 12\ eV$), making the ratio $\frac{U}{t} \sim 2.5$. According to early studies of Sorella and Tosatti [16] and a very recent study of Furukawa [12] a Mott insulating behavior is obtained for a honeycomb lattice only when $\frac{U}{t} \geq 3.5$. Below this critical value of $\frac{U}{t}$ the zero gap character of the one electron states should make the many body effects at low energies less pronounced even though one is in 2 dimensions. However, some studies [17,18], indicate anomalous life time for the quasi particles close to the fermi level in graphite.

The intermediate coupling character of the Hubbard model for graphite makes it very difficult to approach it either as a weak coupling or a strong coupling problem analytically. To circumvent this problem, and also inspired by early RVB ideas on graphite, we propose an effective Hamiltonian for graphite/MgB_2 on semi phenomenological grounds, and later sketch a possible microscopic derivation of this from the Hubbard model.

In the early treatment of graphite and $p\pi$ bonded planar organic molecules, such as the discussion due to Pauling [14], the resonating valence bond (RVB) and enhanced valence bond amplitude is emphasized. Configurations with nearest neighbor singlet bonds (VB) are encouraged in comparison to the polar (double and single occupancy in the p_z orbitals) configurations. This concept gave good estimate for cohesive energy, C-C bond distance and even some excited state properties, such as the singlet triplet exciton energy differences. From the theoretical study [19–21] of cuprates in the last one dozen years we have also realized that RVB's are also preformed cooper pairs. They may have profound consequences such as high temperature superconductivity under appropriate conditions.

Our primary aim now is to incorporate the well recognized RVB character of graphite in our effective Hamiltonian for MgB_2 . With this in mind we propose the following model Hamiltonian for MgB_2 :

$$H_{eff} \approx -t \sum_{\langle ij \rangle,\sigma} C^\dagger_{i,n\sigma} C_{j,n\sigma} - t_\perp \sum_{i,n,\sigma} C^\dagger_{i,n\sigma} C_{i,n+1\sigma} + h.c. - J \sum_{\langle ij \rangle,n} b^\dagger_{in,jn} b_{in,jn} + -J_\perp \sum_{i,n} b^\dagger_{in,in+1} b_{in,in+1} \quad (3)$$

Here i or j denotes a lattice point on the 2d honeycomb lattice and 'n' is the layer index. The singlet operator $b_{ij} \equiv \frac{1}{\sqrt{2}}(C_{i\uparrow}C_{j\downarrow} - C_{i\downarrow}C_{j\uparrow})$. The two body term with $J_{ij} > 0$ represents an energy gain when two electrons in neighboring sites i and j form a singlet (valence bond), as $b^\dagger_{ij} b_{ij}$ is a number operator for bond singlets. That is, this term stabilizes covalent configurations relative to ionic configurations between any two neighboring sites. Tight binding fit of the states close to the fermi level as obtained from ab-initio band structure calculation for MgB_2 give the values of the parameter $t \approx 1.6eV, t_\perp \approx 1.25eV$.

Now we outline an approximate microscopic derivation of the interaction term of our Model Hamiltonian (equation 3) and also estimate the phenomenological parameters J and $J_\perp$. In spirit it is similar to superexchange theory, but it is also designed to handle the weak and intermediate coupling regions approximately.

In graphite as well as MgB_2 we are exactly at half filling in the sense of having one electron per p_z orbital. It is here we expect maximum effects of two body interactions (Hubbard U) in the ground state. In a free fermi gas in tight binding system, the spin state of two electrons in neighboring sites can be a singlet or a triplet. The local singlet character in k-space, as enforced by Pauli principle, does not enforce any type of singlet correlations in real space. However, two body collisions arising from the Hubbard U term, encourages singlet amplitude between two electrons of neighboring sites. This is the origin of the kinetic or superexchange term in a Mott insulator at and close to half filling.

As in superexchange perturbation theory, we concentrate on two sites involving two electrons, but solve the two site problem exactly. The two electron ground state is a singlet with an energy $E_g = -\frac{1}{2}\left[U^2 + 16t^2\right]^{\frac{1}{2}} + \frac{U}{2}$. The energy of the triplet state is at $E_T = 0$. Two excited singlet states are at positive higher energies. In our effective Hamiltonian (equation 3) the energy gain of a nearest neighbor singlet (valence or covalent) bond is represented by the term

$$-Jb^\dagger_{ij} b_{ij}, \qquad \text{where } J = \frac{1}{2}\left[U^2 + 16t^2\right]^{\frac{1}{2}} - \frac{U}{2} \quad (4)$$

In the large $t >> U$ limit the singlet stabilization energy $J \approx \frac{4t^2}{U}$, agreeing with the superexchange perturbation theory.

For MgB_2 using equation (4) we estimate $J \approx 1.3eV$ and $J_\perp \approx 0.4eV$. Ideally, in the conducting metallic state it is more meaningful to talk about residual coupling among excitations in momentum space. From this point of view the above estimates of singlet stabilization terms in real space should be treated with caution.

The valence bond stabilizing term is an attraction in the two body BCS singlet channel, near the fermi surface for our half filled case:

$$-J \sum_{\langle ij \rangle} b^\dagger_{ij} b_{ij} \rightarrow -J \sum C^\dagger_{k\uparrow} C^\dagger_{-k\downarrow} C_{-k'\downarrow} C_{k'\uparrow} \quad (5)$$

This attraction, under normal conditions, will lead to a superconducting ground state. However, graphite is unusual in the sense the density of states vanishes at the fermi level. A simple cooper pair analysis shows us that the above attraction is incapable of converting the zero gap semiconducting state into a superconducting state unless the attraction J exceeds a critical value $J_c \approx 3t$. Thus graphite does not have a superconducting ground state, in spite of its RVB character !

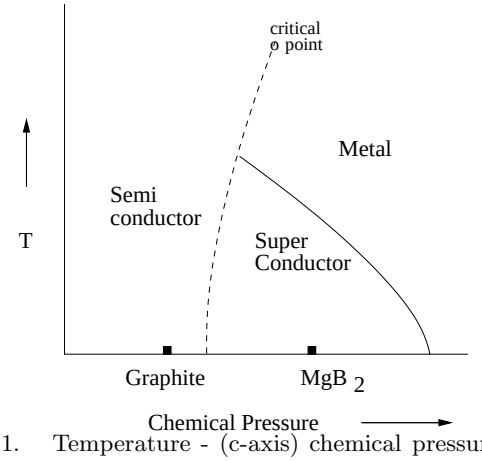

FIG. 1. Temperature - (c-axis) chemical pressure phase diagram. Dashed line is the first order phase transition line that ends in a critical point

Now we qualitatively discuss the zero gap semiconductor to superconductor transition when we go from graphite to MgB_2 . As mentioned earlier, the ratio of the B-B distance along the c-axis to that in the plane gets reduced from 2.4 to 2.0, when we go from graphite to MgB_2 . The coupling along the c-axis is van der Waals like in graphite. Early band structure calculations and transport studies have suggested a c-axis hopping matrix element $t_\perp \leq 0.25eV$ for graphite. The band structure results for MgB_2 show a large value of $t_\perp \sim 1.2eV$ resulting in two large $p\pi$ fermi surfaces and an addition of a small hole density to the the 2 dimensional σ bands of the honeycomb lattice.

Thus the major difference between graphite and MgB_2 is the c-axis metallization resulting from the chemical pressure. This has given rise to a finite density of states at the chemical potential for MgB_2 . Further, the local electronic structure and lattice structure has not undergone any qualitative modification between graphite and MgB_2 . Thus MgB_2 , in view of its finite density of states at the fermi level is capable of utilizing the local RVB correlations and go into a superconducting state.

The vanishing density of states due to the zero gap character in MgB_2 makes the valence bond stabilization term 'irrelevant', as long as $J < J_c \approx 3t$. That is, as a function of J there is a quantum phase transition from a zero gap semiconductor to a superconductor. The value we have estimated for graphite $J << 3t$, is consistent with the experimental observation that graphite is not a superconductor.

A simple BCS mean field theory of our model Hamiltonian (equation 3) gives the approximate formula for T_c

$$k_B T_c \approx W e^{-\frac{1}{J\rho_0}}, \tag{6}$$

Where W is the bandwidth of the $p\pi$ band and ρ_0 is the density of state at the fermi level. From the band structure calculations, there are two $p\pi$ bands of width 18 and 13 eV. We can take the mean bandwidth to be $W \approx 15eV$. The mean density of states arising from the two bands is $\rho_0 \approx \frac{2}{15}$ states per eV. If we assume a value of $J \approx 0.9eV$ we get a $T_c \approx 40K$. This suggests that our renormalized $J \approx 1.3$, as obtained from our microscopic derivation is in the right ball park.

In our model, as we increase $t_\perp$ continuously from zero, the T_c increases continuously; in reality, with the increase of c-axis pressure we expect a first order phase transition. The zero gap semiconducting state has a screening which is fundamentally different from the metallic screening of a semi metal with a finite band overlap. On general grounds, using arguments similar to Mott, the metalization along the c-axis arising from an uniaxial pressure will be a first order phase transition. The c-axis lattice parameter collapse arising from the c-axis metalization will add to this and make it a stronger first order transition like some of the known metal insulator transition.

We have sketched our general view on the zero gap semiconductor to superconductor transition schematically in figure 1 and 2. In figure 1, there is a first order zero gap (or very small gap) semiconductor to superconductor phase transition as a function of pressure in the ground state.

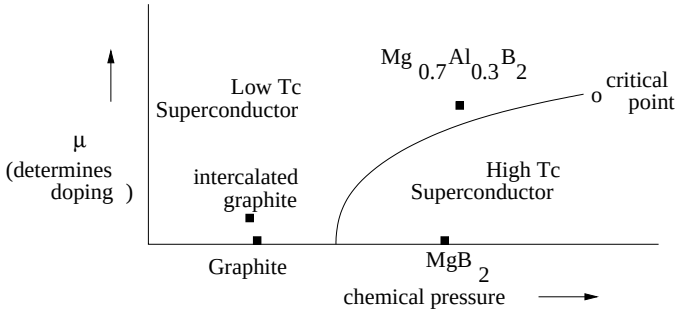

FIG. 2. Chemical potential (μ) - (c-axis) chemical pressure phase diagram. The line separating graphite and MgB_2 is a first order phase boundary and it ends at a critical point

With a small addition of carriers (through Al substitution at Mg site for example) we expect the first order phase transition to survive as a function of chemical pressure. In figure 2, we have extended the phase diagram to the chemical potential (related to doping) vs chemical

pressure (related to the c-axis lattice parameter) phase diagram. The first order line ends in a critical point.

Experiments [7] on $Mg_{1-x}Al_xB_2$ and $MgB_{2-x}C_x$ have been performed for a range of x. In the case of Al substitution, T_c decreases gradually until x $\approx$ 0.1 and for $0.1 < x < 0.25$ we have a two phase region. Superconductivity disappears across the two phase region and the c-axis lattice parameter jumps down by about 10 %. Al being trivalent adds an additional electron to the Boron subsystem. We believe that with Al or C substitution one crosses the first order phase boundary.

It is also known that intercalated graphites show low temperature superconductivity. According to our picture intercalated graphites never get a large fermi surface (and hence low T_c); as the average c-axis separation increases on intercalation, the c-axis metalization does not occur.

There are several issues that need to be understood both qualitatively and quantitatively from our stand point. Further our theory has certain consequences which can be tested experimentally.

Symmetry of the order parameter is an important issue. Even in cuprates, from the numerical analysis it is clear that the d-wave and extended-s wave state are nearly degenerate. In the present situation, where double occupancy is not be completely projected in the low energy subspace, both s-wave and d-wave solutions are possible. The absence of Hebel-Slichter peak in the NMR does indicate some similarity to the cuprates and organic superconductors. The penetration depth study Panagopoulos and collaborators [8] also points to some gapless region. Further studies are necessary to settle this issue.

There has been an intriguing neutron scattering result [6], where one sees two unexpected peaks at 17 meV and 30 meV in the phonon density of states. The 17 meV peak in particular has a temperature dependence that peaks around the T_c . As the authors have mentioned, is there a connection of this with the 41 meV peak of YBCO materials ? We suggest that this peak is magnetic in origin and expresses an underlying RVB character, and polarized neutron scattering experiment can prove its spin 1 character. It is also interesting that this peak starts building up around 150 K, indicating some kind of preformed pairing activity. It is also possible that the intrinsic T_c of MgB_2 is larger $\approx 200K$ and that the small carrier concentration in the 2d σ bond is acting like a source of dissipation for superconductivity in the $p\pi$ system, through interband scattering thereby reducing T_c considerably. For us the lightly doped 2d σ band, that is predicted by band theory and used by electron and phonon based theories, does not play a crucial role in establishing high temperature superconductivity. As mentioned earlier, it might interferes with superconductivity in the $p\pi$ band.

It is also interesting that the Hall resistivity R_H has a temperature dependence [9] below about 150 K. The strong temperature dependence of R_H in cuprates are known to arise from the built up of RVB singlet correlations, suggesting a built up of RVB correlations in MgB_2 .

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