Materials and mechanisms of hole superconductivity

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The theory of hole superconductivity proposes that there is a single mechanism of superconductivity that applies to all superconducting materials. This paper discusses several material families where superconductivity occurs and how they can be understood within this theory. Materials discussed include the elements, transition metal alloys, high $T_c$ cuprates both hole-doped and electron-doped, $MgB_2$, iron pnictides and iron chalcogenides, doped semiconductors, and elements under high pressure.

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I. ‘CONVENTIONAL’ SUPERCONDUCTORS

We denote by ‘conventional’ superconductors those that are generally believed to be described by conventional BCS-Eliashberg theory.

Almost all superconducting elements have positive Hall coefficient in the normal state, indicating that hole carriers dominate the transport. Examples are $Pb$, $Al$, $Sn$, $Nb$, $V$, $Hg$. Instead, most elements with negative Hall coefficient are non-superconductors at ambient pressure down to the lowest temperatures checked so far, for example $Ca$, $Sc$, $K$, $Mg$, $Ag$, $Au$. This was noted by several workers in the early days of superconductivity [6]. The sign of the Hall coefficient is the strongest normal-state indicator of superconductivity among thirteen normal state properties considered in ref. [7]. This is not accounted for by BCS theory, and normal state properties expected to be related to superconductivity within BCS theory (like ionic mass, Debye temperature, specific heat and resistivity) show substantially weaker correlation with superconductivity [7].

The behavior of the transition temperature of alloys of transition metals in different columns of the periodic table versus composition shows characteristic behavior that can be understood by a ‘universal’ curve in terms of electrons per atom ratio ($e/a$). This is known as ‘Matthias’ rules [8], and is shown in the top panel of Fig. 2 for a large number of transition metal alloys with $e/a$ ratio between 4 and 6 (from ref. [9]). It can be simply understood from the carrier density dependence of $T_c$, in a simple one-band model for hole superconductivity [10].

The pairing interaction is given by

$$ V_{kk'} = U + V(k - k') - \alpha(\epsilon_k + \epsilon_{k'}) $$  \hspace{1cm} (1)

where $\epsilon_k$ is the band energy measured from the center of the band, $U$ and $V$ are on-site and more extended Coulomb repulsions and $\alpha > 0$ arises from ‘correlated hopping’ [11], an electron-electron interaction term that is proportional to the hopping amplitude [12]. The interaction Eq. (1) becomes progressively less repulsive as the Fermi level goes up in the band (as $\epsilon_k$, $\epsilon_{k'}$ for $k$ and $k'$ at or near the Fermi surface increase). Superconductivity arises as the Fermi level approaches the top of the band, $T_c$ increases as the pairing interaction gets stronger with
FIG. 2: $T_c$ versus $e/a$ ratio (from ref. [9] (top panel)) and Hall coefficient versus $e/a$ ratio (from ref. [13]) (bottom panel. Note that $T_c$ goes to zero at the point where the Hall coefficient shows a pronounced kink, for $e/a \sim 5.6$.

FIG. 3: Band structures of elements Ti, V, Cr with $e/a = 4, 5, 6$ in the fourth row of the periodic table, from ref. [14]. The horizontal line denotes the position of the Fermi level.

increasing band filling, reaches a maximum, starts decreasing as the number of carriers (holes) becomes small, and reaches zero when the Fermi level crosses the top of the band. This is indicated in the anomaly in the Hall coefficient shown in the bottom panel of Figure 2 (from ref. [13]). Figure 3 shows the calculated band structure for elements Ti, V and Cr, corresponding to $e/a = 4, 5$ and 6 respectively (from Ref. [14]). $T_c$ goes to zero as the Fermi level crosses the top of the band at the Γ point and the hole pocket disappears. A calculation using a realistic band structure and interactions of the form Eq. (1) reproduces this behavior closely [10].

FIG. 4: The left panel shows schematically the boron $p_{xy}$ orbitals in the $B^-$ planes, where conduction occurs through holes in the pocket near the Γ point indicated by the red arrow on the right panel, that shows the band structure of $MgB_2$ from Ref. [16]. The blue arrow shows a three-dimensional band where the carriers are electron-like.

Magnesium diboride ($MgB_2$) is a textbook example of the mechanism of hole superconductivity at work [16]. The system consists of negative ions $B^-$ forming planes, separated by arrays of positive $Mg^{++}$ ions. The charge transfer is however not complete, and as a result a small density of hole carriers exist in the $B^-$ planes, some of which reside in planar $p_{xy}$ orbitals and propagate through direct overlap of these orbitals shown schematically in the left panel of Fig. 4. The right panel of Fig. 4 shows the resulting small hole pocket at the Γ point that gives rise to a cylindrical Fermi surface describing hole conduction in the $B^-$ planes [16]. There is also electron conduction in this system in three-dimensional bands involving boron $p_z$ orbitals and $Mg^{++}$ orbitals.

Tunneling experiments show the existence of two superconducting gaps, as shown in the left panel of Fig. 5 [17]. The larger gap is associated with hole carriers propagating through the $B^-$ planes, and the smaller gap is associated with a three-dimensional band with electron carriers. Several years earlier Marsiglio and the author calculated the superconducting properties of a two-band model with holes in one band and electrons in the other band within the model of hole superconductivity [18], and found a behavior for the gaps similar to the one seen in $MgB_2$, as shown on the right panel of Fig. 5.

In the model of hole superconductivity, the transition temperature is higher when hole conduction occurs through negatively charged ions [2, 19]. Thus, the fact that $T_c$ is so high in $MgB_2$ compared to other $s-p$ superconductors derives from this feature together with the hole conduction.

II. ‘UNCONVENTIONAL’ SUPERCONDUCTORS

By ‘unconventional’ superconductors we denote those that are generally believed to be not described by conventional BCS-Eliashberg theory. The high $T_c$ cuprates (both hole- and electron-doped), iron pnictides and iron selenium/tellurium show features clearly consistent with
FIG. 5: Left panel: two gaps versus temperature for MgB$_2$ obtained from NIS tunneling\cite{17}. The large and small gap correspond to the band structure states indicated by the red and blue arrows respectively in the left panel of Fig. 4. The right panel of this figure shows results of a two-band model calculation within the theory of hole superconductivity obtained 10 years before the discovery of MgB$_2$\cite{18}.

the mechanism of hole superconductivity. Other superconductors generally agreed to be `unconventional' are heavy fermion materials and strontium ruthenate. Because their $T_c$ is so low, it is difficult to find clear signatures in favor of our mechanism for those materials.

We will skip here a discussion of the cuprates, which we have discussed in detail in several papers\cite{4, 5, 11, 18, 20, 21}. Let us just mention that our model\cite{20} predicted\cite{20} that in electron-doped cuprates hole carriers exist and are responsible for superconductivity well before this prediction was supported by detailed transport measurements\cite{21}. For iron pnictides, we have discussed the mechanism by which hole carriers are expected to be generated both through electron- or hole-doping\cite{28}. For electron doping, the mechanism is similar to the one proposed for the electron-doped cuprates\cite{20}. The negatively charged anion $\text{As}^{5-}$ is the key element in these superconductors to give rise to the high transition temperatures.

The iron-selenium system (FeSe) is another textbook example of the applicability of our model\cite{20}. Under pressure, this system increases its critical temperature from 8K to 37K for pressures in the range 6-9 GPa\cite{30, 31}. The main effect of pressure is to decrease the distance between Se atoms in neighboring planes as shown schematically in Fig. 6, from 3.68Å to 3.16Å\cite{29, 32}. The Pauling radius of the $\text{Se}^{2-}$ ion is 1.98Å, so the ions increase their overlap substantially under pressure, which should lead to a large increase in $T_c$ according to the model of hole superconductivity. Indeed, in discussing the large positive pressure dependence of $T_c$ in the cuprates over 20 years ago we proposed that it arises from increase of the overlap of the $\text{O}^{2-}$ ions in the $\text{Cu} - \text{O}$ planes according to the model of hole superconductivity\cite{20}.

Note also that if the Fe ion would play a substantial role in the superconductivity, as expected within other theories, it would be difficult to explain the very large effect of pressure in increasing the critical temperature since the change in distance within a $\text{Fe} - \text{Se}$ plane (e.g. the $\text{Fe} - \text{Fe}$ distance decreases from 2.67Å to 2.60Å, $\sim 2\%$) is much smaller than the distance decrease between $\text{Se}$ atoms in adjacent planes (3.69Å to 3.17Å, $\sim 16\%$).

At higher pressures, the system undergoes a structural transition and is no longer superconducting. Figure 7 shows the structures before and after the transition. It can be seen that the high pressure phase (right panel in Fig. 7) does not allow for direct overlap of anion orbitals, therefore it is expected within the theory of hole superconductivity that it will not be a high $T_c$ superconductor.

Finally, note that the compound SnO, with no traces of magnetism, has the same structure and similar band structure as FeSe and is a superconductor\cite{33}. This is consistent with our model and inconsistent with theories that assume magnetic fluctuations play an important role in the superconductivity of these materials\cite{34}.

III. ‘UNDETERMINED’ SUPERCONDUCTORS

For several classes of materials there is no consensus in the community whether they are 'conventional' or 'unconventional'. Among the members of this class we will discuss the recently discovered hole-doped semiconductors and simple metals under high pressure.

It has been found in recent years that doping diamond, Si and Ge with holes gives rise to superconductivity\cite{35}.
This is consistent with the theory of hole superconductivity, as is the fact that superconductivity is not found when these semiconductors are doped with electrons. BCS-Eliashberg theory did not predict the existence of superconductivity in these materials upon hole doping, nor does it explain why electron doping does not give rise to superconductivity. The $T_c$ is quite low (maximum is $11.4K$) consistent with the prediction of the theory that requires negatively charged ions in addition to hole carriers to give rise to high temperature superconductivity, as well as with the fact that the coordination number in these materials is quite small which disfavors a high $T_c$ within our model.[11]

The rather high $T_c$'s recently found in simple and early transition metals under high pressure are claimed to be explained by conventional theory but were not predicted by it. Examples are Li ($T_c = 20K$), Ca ($T_c = 25K$), Sc ($T_c = 19.6K$) and Y ($T_c = 19.5K$). Within our theory superconductivity occurs in these materials[36] because under application of pressure new Bragg planes develop that convert electron carriers into hole carriers[37]. We predict that the Hall coefficient (not yet measured) of these materials under pressure will change sign from negative to positive in the range of pressures where they become superconducting[38], or at least that there will be clear evidence in magnetotransport studies for two-band conduction, with one of the carrier types being hole-like. If this is not observed it would cast serious doubt on the validity of the theory.

IV. DISCUSSION

The theory of hole superconductivity is qualitatively different from BCS-Eliashberg theory. Thus for many materials the predictions of both theories will disagree. For example, contrary to BCS-Eliashberg theory[39] we predict no high $T_c$ superconductivity in hole-doped LiBC because there is no conduction through overlapping orbitals of negatively charged ions. We also predict no superconductivity in metallic hydrogen unless the structure distorts to accommodate an even number of atoms per unit cell, in contrast to conventional BCS theory that predicts high $T_c$ with no lattice distortion[39]. However for some materials both theories could agree on their predictions. For example, BCS theory predicts that superconductivity is favored when there is a soft phonon mode[40]. A soft phonon mode is often a precursor to a lattice instability and is likely to occur when there are antibonding electrons that disfavor the stability of the solid because they give rise to low charge density in the region between the atoms. At the same time, antibonding electrons reside in the high states in the band, hence give rise to hole carriers. We argue that superconductivity appears to be favored by soft phonon modes because it is the antibonding electrons that are responsible for both the (hole) superconductivity and the existence of soft phonon modes.

Within the theory of hole superconductivity all superconductors should be explainable by the same mechanism. A single superconductor that demonstrably does not fit the requirements of the theory, for example a superconductor that does not have any hole-like carriers in the normal state, would prove the theory wrong. We have seen in this paper that a wide variety of materials appear to be in agreement with this theory. No other single theory can explain such widely different material classes. If the theory is correct, realistic calculation of electronic structure looking at the right quantities should be predictive as far as whether the material will or will not be a superconductor, and give at least a semiquantitative estimate of $T_c$.

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