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TOPICAL REVIEW

Impurity band Mott insulators: a new route to high T_c superconductivity

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Online at stacks.iop.org/STAM/9/044104**Abstract**

Last century witnessed the birth of semiconductor electronics and nanotechnology. The physics behind these revolutionary developments is certain quantum mechanical behaviour of ‘impurity state electrons’ in crystalline ‘band insulators’, such as Si, Ge, GaAs and GaN, arising from intentionally added (doped) impurities. The present article proposes that certain collective quantum behaviour of these impurity state electrons, arising from Coulomb repulsions, could lead to superconductivity in a parent band insulator, in a way not suspected before. Impurity band resonating valence bond theory of superconductivity in boron doped diamond, recently proposed by us, suggests possibility of superconductivity emerging from impurity band Mott insulators. We use certain key ideas and insights from the field of high-temperature superconductivity in cuprates and organics. Our suggestion also offers new possibilities in the field of semiconductor electronics and nanotechnology. The current level of sophistication in solid state technology and combinatorial materials science is very well capable of realizing our proposal and discover new superconductors.

Keywords: superconductivity, Mott insulators, resonating valence bond, cuprates, diamond

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Semiconductor electronics is a matured field and is at the heart of modern technology and science. It has had an intimate and symbiotic relation with the field of condensed matter science—both have grown together. This field has used and also generated key notions and phenomena over decades: idea of electrons and holes in a band, collective quantum states such as electron–hole droplets produced by intense laser beams, fractional quantum Hall effect and fractional charges in two-dimensional electron gas in semiconductor interfaces, dilute magnetic semiconductors, quantum dots, novel spin transport and qubits. At a microscopic level, laws of quantum mechanics play an inevitable role in solid state electronics, leading to unimaginable consequence the modern world is enjoying. The possibility of any new collective behaviour

among the electrons in semiconductors and ‘band’ insulators, that has been so well studied, is likely to have important consequences both in basic science and technology.

The aim of the present article is to suggest that another well-known collective phenomena in solids, namely superconductivity, could be realized in crystalline insulators such as GaN, ZnO, SiC and a host of other insulators, by making use of Coulomb repulsion among the (impurity state) electrons that we introduce intentionally by specially chosen dopants. In making the above proposal we are influenced partly (i) by the significant developments in the last 22 years or so in the field of high-temperature superconductivity in cuprates [1], (ii) the phenomena of ferromagnetism in dilute magnetic semiconductors, (iii) a very recent discovery of superconductivity in heavily doped diamond [2–4], (iv) and some recent theoretical developments, such as our theory

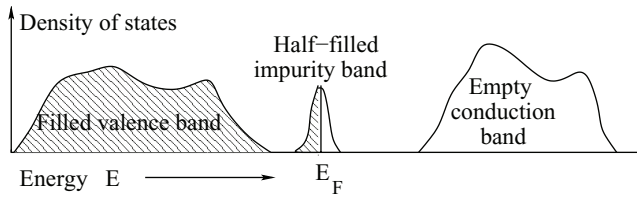


Figure 1. A dopant-induced impurity band. Unlike the broad valence or conduction band, the impurity band is a narrow and half-filled, strongly correlated system. It can be either on the conducting or insulating side of the Anderson–Mott transition.

of impurity band superconductivity [5–7]. The logic of our arguments is compelling. In the present paper, we do not present any detailed theoretical analysis but focus on the physics and principles involved with simple order of magnitude estimates, where necessary, in order to substantiate our suggestion.

The discovery of superconductivity in $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ by Bednorz and Muller [1] opened a new field of high-temperature superconductivity and led to an electron correlation based mechanism of superconductivity and theoretical ideas [8], such as *doped Mott insulator is a seat of high-temperature superconductivity*. Quantitative calculations are hard in the strong coupling many body theory, needed to solve the cuprate problem. But a significant progress has been made by the resonating valence bond (RVB) theory by identifying a correct model, key notions, mechanism [8], a solid mean-field theory foundation [9], and a way to go beyond the mean-field theory [10].

We suggest that for certain choice of dopants, relatively ‘deep level’ impurity states can be made to overlap by changing the dopant concentration and cause a transition from impurity band Mott insulator to superconductor (figure 1). The spin singlet correlations, that are unavoidable in the impurity band Mott insulators, are the pre-existing neutral singlets. As we approach transition point, the impurity wave functions overlap more and become ‘dense’; consequently, the neutral singlets (valence bonds) resonate and a quantum spin liquid phase is formed. Across the Mott insulator to conductor transition, a small density of delocalized holes and electrons are spontaneously generated (required for a self-consistent screening of long-range Coulomb interaction, as suggested by Mott). These carriers delocalize, or equivalently a fraction of neutral singlet pairs get charged and delocalize, leading to a superconducting state (figure 2).

In our RVB mechanism of Mott insulator to superconductor transition, the following is a minimal requirement for superconductivity: (i) a spin 1/2 Mott insulating reference state and (ii) antiferromagnetic superexchange leading to spin singlet correlations and valence bond resonance. The resonating singlets are the pre-existing Cooper (neutral) pairs. Absence or minimal orbital degeneracy is important least (a) Hund rule intervenes and stabilizes metallic magnetic states or (b) Jahn–Teller effect intervenes and traps doped carriers or stabilizes charge/orbital orders. Whereas lower dimensionality is helpful, it is not absolutely important in the RVB theory.

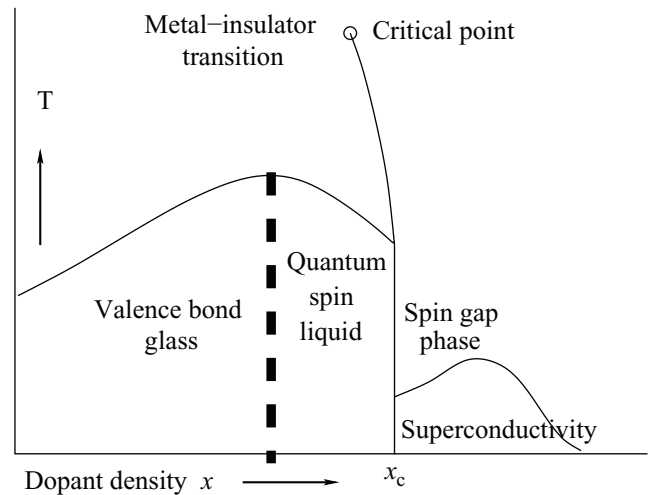


Figure 2. The schematic phase diagram for insulator to metal transition as a function of the dopant density x . For small x we have a valence bond glass, followed by a quantum spin (valence bond) liquid state and a superconducting state. In general, the first-order insulator to metal transition will end in a critical point, whose nature will be strongly influenced by disorder. A spin gap normal state will mark the region near the insulator to metal transition point x_c .

While the above requirements may favour superconductivity, they may also encourage certain competition from charge orders and spin orders in the conducting state; but in the known few cases, superconductivity is the winner. Organic ET-salts [11, 12], which are quasi-two-dimensional spin 1/2 Mott insulators, provide an excellent example for Mott insulator to superconductor transition. The key difference from our impurity band Mott insulators is that the singly occupied molecular orbital plays the role of the singly occupied impurity orbital. Unlike the ET salts, the impurity orbitals do not form a periodic lattice. Another, less known example [13] is the pair of compounds GaNb_4Se_8 and GaTa_4Se_8 , where under pressure there is a Mott insulator to superconductor transition with a $T_c \approx 3$ and 6 K, respectively.

When we look at currently available Mott insulators from superconductivity point of view, majority of them have a spin larger than half and orbital degeneracies. However, there are some Mott insulators in nature which satisfy our conditions to varying degrees. Often inability to realize superconductivity in them seems to be chemical in origin, such as not being able to dope the system or irreducible oxygen vacancies. A good example is tenorite, CuO , an excellent Mott insulator, the parent compound of the cuprate superconductors. No one seems to have succeeded in doping this system. It has been suggested [22] that this and other systems might undergo a Mott insulator to superconductor transition under pressure. There are also families of spin 1/2 paramagnetic salts where, even if one succeeds in doping the band, its width is too narrow to have any reasonable T_c .

In the present paper, we suggest that nature offers us a new possibility through impurity band Mott insulators or Anderson–Mott insulators. While the intrinsic randomness in the impurity band systems in general is a great hindrance for metallization from single electron delocalization point of view, electron correlation based superexchange or

pairing of electron into spin singlet states can lead to delocalization of charged singlets resulting in an inhomogeneous superconducting state. Since the number of possibilities is at least as large as the number of available band insulators in nature, the Mott insulating impurity band route we are proposing is worth pursuing!

We also argue that the intrinsic randomness has certain advantage in the sense of reducing the orbital degeneracy of the donor or acceptor impurity states that arises from point group symmetries and valley degeneracy. The degeneracy of the donor or acceptor impurity states is lifted by random strain, electric field and covalency effects. This phenomena of lifting the orbital degeneracy increases the chance for finding Anderson–Mott insulator to superconductor transition in nature, in comparison to crystalline materials.

Another advantage is the scale of superexchange that nature offers us through our mechanism. It can be as large as the superexchange that exists between copper spins in the cuprates! We will see how this scale of superexchange interaction depends on the band gap and the impurity binding energy of our impurity acceptor or donor states.

The route we are suggesting is likely to be trodden with experimental difficulties (imagine heavily doping a diamond, keeping it still a diamond), hindrances and surprises. One can say with some confidence that it is going to be interesting and rewarding.

2. Impurity state Mott insulators and neutral singlet pairs

When a dopant atom replaces a host atom in a band insulator, in general, localized impurity electronic states are formed. Impurity atom and its interaction with the host determine the nature of the impurity states. In a case like boron-doped diamond, the substitutional boron gets nicely accommodated in the sp^3 bonding with the four carbon neighbours; an extra hole of boron gets loosely bound to the parent boron atom. The impurity eigenfunction is well described by suitable linear combination of sp^3 band of states. This is at the heart of the well known effective mass theory of impurity states in semiconductors. The impurity state has a ‘hydrogenic envelope’, and one defines an effective Bohr radius $a^* \equiv e^2/(2\epsilon_0 E_B)$, where E_B is the binding energy of the dopant’s electron or hole and ϵ_0 is the low-frequency dielectric constant of the parent insulator.

In all our discussion, for convenience, we use boron impurity in diamond for illustrating our proposal. Our discussion goes through equally well for donor impurities, such as nitrogen or phosphorus doped in diamond. Let us assume for simplicity that the ground state of the impurity state is non-degenerate and also ignore effects of low-lying excited impurity states and the conduction band. When we have a finite dopant density $x = N_d/N$, where N_d is the total number of substitutional dopant atoms in N atom lattice, statistically, the neutral dopant (D^0) atoms are well separated with mean separation large compared to the effective Bohr radius a^* . In this situation, we have one dangling electron

per D^0 -atom, which is practically bound to the respective impurity atoms. This is an impurity state Mott insulator or an Anderson–Mott insulator. What is preventing it from becoming a half-filled impurity band metal is (i) Anderson localization phenomena and (ii) the Mott localization; i.e., energy gain by delocalization of an electron among the impurity states (band width, $\sim W$) is small compared to the energy U (sum of ionization and electron affinity) required to remove an electron from one D^0 -atom and put it on another D^0 -atom in the impurity state; i.e. to create a real charge fluctuation D^+D^- out of a D^0D^0 pair.

In the Mott insulating state, there is virtual charge fluctuation leading to the well known super/kinetic exchange. That is, virtual transition of a neighbouring neutral dopant atom pair to a higher energy (U) polar state

$$D^0(\downarrow)D^0(\uparrow) \rightarrow D^-(\uparrow\downarrow)D^+(0) \quad (1)$$

leads to an effective Heisenberg coupling between the two dangling spins (figure 1). In the dilute limit, the impurity spin coupling is well represented by the following Heisenberg Hamiltonian:

$$H_s \approx \sum J_{ij} \left(\mathbf{S}_i \cdot \mathbf{S}_j - \frac{1}{4} \right) \quad (2)$$

where \mathbf{S}_i is the spin operator of an electron in the i th impurity atom, $J_{ij} \approx 4t_{ij}^2/U$ is the superexchange between the moments and t_{ij} is the hopping matrix element. As the hopping matrix element t_{ij} falls off exponentially with DD separation $|\mathbf{R}_{ij}|$, the superexchange J_{ij} has a large variation. It should be pointed out that in some special circumstances the superexchange may become ferromagnetic. We focus on situations involving antiferromagnetic coupling. When ferromagnetic coupling dominates impurity band ferromagnetism may be formed.

3. Valence bond glass to quantum spin liquid crossover with increased doping

Dopant atoms form a random lattice with some short-range correlations, leading to a distribution of superexchange coupling among neighbouring spins. A wide distribution of antiferromagnetic exchange constant J_{ij} in a random lattice should normally lead to a spin glass order among impurity spins because of *frustration* and inability to form a spin arrangement in which every neighbouring pairs of spins are antiparallel. However, as it has been well established for impurity spins in phosphorus-doped Si, quantum fluctuations, arising from spin 1/2 character of the dangling spins, destabilize spin glass order and lead to a so called valence bond glass state, depicted schematically in figure 3. This state has neutral singlets dominating the ground state. The random character makes less resonance among the neutral singlets, except in places where there is clustering of the impurity atoms. Further we also get some lone spins, which are weakly coupled to their neighbours. As has been shown both experimentally [16–19] and theoretically [20, 21], the

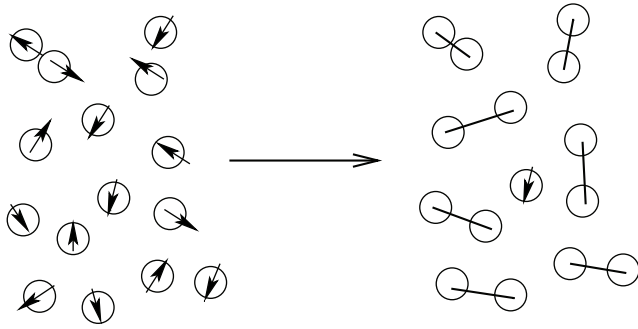


Figure 3. In view of the strong quantum fluctuations, the spin 1/2 moments form a valence bond glass or frozen spin singlet bond phase rather than a frozen spin glass order.

hierarchical fashion in which spins get singlet-coupled as temperature T is reduced, leads to a non-Curie form for the spin susceptibility $\chi_{\text{spin}} \sim \frac{1}{T^{1-\alpha}}$, where $\alpha > 0$.

As we approach the metal-insulator transition, with increase in dopant concentration, at least three phenomena take place simultaneously: (i) the impurity state wave functions overlap more and electrons try to overcome Anderson localization to form extended one-particle states and (ii) the mean value of neighbouring superexchange constant J grows and its distribution becomes narrower and (iii) because of the reduction of the mean charge gap, multi-spin exchange processes start contributing. We hypothesise that the net effect is a valence bond delocalization and formation of a percolating region of quantum spin liquid (figure 4). The above two processes are connected. A quantitative analysis of them is out of the scope of the present paper. However, it should be pointed out that the above becomes very plausible, once we recognize that the impurity wave functions are dense and overlapping (figure 4) in the sense that at the Mott transition point, the mean inter-impurity distance and the effective Bohr radius become comparable—their spatial pattern is like a frozen configuration of a dense fluid of hard spheres, rather than a dilute gas.

In view of the above, there is enhanced valence bond resonance, and a valence bond glass crosses over continuously to a valence bond liquid in the region just prior to the Mott transition point. In other words, our hypothesis states that *for low energy scales, we may view the many-body insulating spin state just close to the Mott transition point as a non-random homogeneous quantum spin liquid state*, in a first approximation. If the dopants were to form a regular three-dimensional lattice, the spin liquid state will be unstable towards long-range antiferromagnetic order.

In the above sense, we have a system, which has resonating neutral singlets, or *performed Cooper pairs*, that is ripe for superconductivity. We can introduce delocalized charges into the systems and get superconductivity in two ways: (i) by external doping, through partial compensation and (ii) self-doping, by increasing the dopant concentration beyond the insulator to metal critical point.

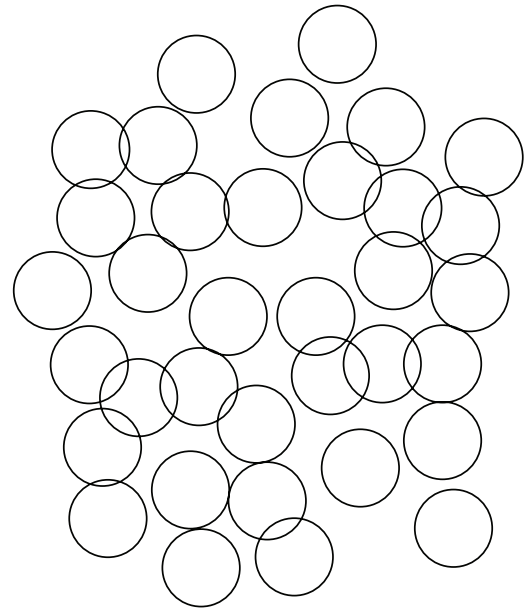


Figure 4. The impurity wave functions overlap and become *dense* and the distribution of nearest neighbour superexchange becomes narrower, leading to a quantum spin liquid or valence bond liquid.

The intrinsic randomness will introduce an inhomogeneous superconducting state.

4. Mott insulating quantum spin liquid to a superconductor transition

Once we have made a hypothesis of homogeneous quantum spin liquid state, the issue of Mott insulator in a quantum spin liquid to metal transition becomes similar to the analysis of Mott insulator to superconductor transition in crystalline organics and other systems [22, 23]. We will also argue that an intrinsic randomness in our case is not a serious hindrance for Mott insulator-superconductor transition; on the contrary, it has certain advantages! Our theory of Mott insulator to superconductor transition closely followed Mott's argument for insulator to metal transition, but with two new and important ingredients: (i) unlike Mott, who focussed on charge delocalization, we also consider spin physics and singlet correlations on the conducting side and (ii) unlike Brinkman and Rice and other authors, we view the conducting side as a Mott insulator with a small density of 'self-doped' carriers, rather than a half-filled band of a Fermi liquid with a very large effective mass. That is, a small but equal densities of 'self-doped' carriers, doublons (D^-) and holons (D^+) delocalize in the background of the resonating singlets. In the conducting state, superexchange survives because the upper and lower Hubbard band features persist even after metallization, as suggested by frequency dependent conductivity experiments in the organics [22, 23], for example. Survival of upper and lower Hubbard band means presence of local moments in the metallic state with superexchange interactions. Schematically, the *neutral dopant* of the impurity state Mott insulator N_d gets separated, across

the Mott insulator to metal transition as follows:

$$\begin{aligned}
 N_d &\rightarrow (1-x)N_d + \frac{x}{2}N_d + \frac{x}{2}N_d, \\
 [D^0] &\rightarrow (1-x)[D^0] + \frac{x}{2}[D^+] + \frac{x}{2}[D^+].
 \end{aligned}
 \tag{3}$$

Creation of a self-doped Mott insulating state (that is, a metallic state with surviving superexchange) crucially depends on the first-order character of the Mott transition, which in turns depends on the long-range nature of the Coulomb interaction. That is, a finite global charge gap that exists on the insulating side survives as a local charge gap on the metallic side, in the presence of a small density of self-doped carriers. The value of the charge gap at the insulating side at the insulator to metal transition determines the magnitude of the superexchange on the metallic side. Further, self-consistency demands that the larger the charge gap at the transition point the lesser is the self-dopant charge density. A Hubbard model, which generically produces a continuously vanishing charge gap at the insulator to metal transition, is thus not capable of describing a self-doped Mott insulating state.

The dynamics of spins and charges in the above situation is summarized by the following effective Hamiltonian, which we called a two-species t - J model; adapted to our present situation the Hamiltonian is

$$\begin{aligned}
 H_{2U} = & - \sum_{ij} t_{ij} P_d c_{i\sigma}^\dagger c_{j\sigma} P_d - \sum_{ij} t_{ij} P_e c_{i\sigma}^\dagger c_{j\sigma} P_e + \text{h.c.} \\
 & - \sum_{ij} J_{ij} (\mathbf{S}_i \cdot \mathbf{S}_j - \frac{1}{4} n_i n_j) + \sum_i \epsilon_i c_{i\sigma}^\dagger c_{i\sigma}.
 \end{aligned}
 \tag{4}$$

Here P_d and P_e keep hopping, involving doubly occupied and empty sites only. The presence of a special form of kinetic energy and superexchange term tells us that the system is a Mott insulator that is self doped. The conventional kinetic energy gets modified and we get doublon and holon hopping terms. A part of the kinetic energy term that represents annihilation of a doublon and a holon into two spinons (equation 1) does not appear in the above effective Hamiltonian, as its effect has already been taken into account in generating the superexchange terms.

After years of theoretical and experimental efforts, there is a good consensus [24, 25] for the validity of one-band t - J model in describing the low-energy physics such as superconductivity and magnetism. In spite theoretical efforts, no rigorous proof exists for superconductivity in the t - J model. As t - J model is proved right by the experiment, in a sense experiments provide strong support for the existence of superconductivity in a 2D t - J model. However, it is fair to say that the RVB mean-field theory has been very successful in describing qualitatively the overall phase diagram and even the symmetry of the order parameter. Years of efforts on variational wave functions have also given a very good support for the RVB mean-field scenario and existence of superconductivity. Our current proposal of impurity band Mott insulator route to high- T_c superconductivity brings in an additional feature namely randomness. Here we can also invoke some kind of Anderson's theorem

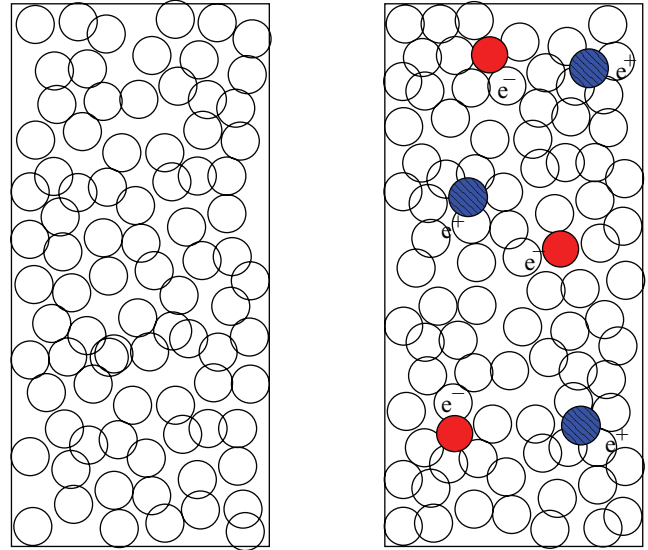


Figure 5. The nominal charge states of the dopant atoms on the insulating and metallic side in the vicinity of the insulator to metal transition. On the insulating side we have no real charge fluctuations; superexchange leads to a neutral spin liquid. On the metallic side long-range interaction manages to self-dope a small and equal density of negative (red, doublon) and positive (blue, holon), even while maintaining the local Mott insulating and spin singlet character everywhere.

and suggest that randomness gets renormalized to small values when we consider pairing among time-reversed states rather than Bloch states. The scanning tunnelling microscopy in superconducting boron doped diamond [26, 27] does show strong spatial inhomogeneity in the order parameter, and at the same time, the system exhibits a robust bulk superconductivity. It has been suggested that the (singlet) valence bond maximization [28] holds the key to superconductivity. It is unlikely that the randomness will completely eliminate superconductivity.

5. Estimation of impurity band width W , critical doping x_c and superexchange J

Effective mass theories have been successful to find the insulator to metal transition for various shallow dopants [30]. For deep-level impurities the problem is hard. However one can use various quantum chemical insights and quantum chemical calculations and estimates. With the availability of powerful computers, it is possible to infer the bandwidth and superexchange J among impurity states, for the specific system under consideration, using local density approximation method and supercell analysis. The values will be system specific and we can choose systems that gives satisfactory W and J . What is satisfactory will be discussed in what follows. As emphasized in [29], the difference in spatial extent of the impurity state wave function in D^- and D^+ will modify the superexchange constant and also introduce asymmetry between doublon and holon hopping matrix elements.

Using available data on impurity states of substitutional nitrogen impurity in diamond, we estimate that close to the

critical point, the deep-level nitrogen impurity states offer a substantial antiferromagnetic superexchange ~ 0.5 eV.

6. Estimation of superconducting T_c

In the RVB mechanism, superconductivity is a robust phenomenon and estimation of T_c should be relatively easy, provided our analysis captures the robust character correctly. Historically two approaches are available for estimating T_c : (i) Bose condensation of a fraction x of charged singlet bonds in an RVB state (x is the self or external doping fraction) and (ii) estimating T_c directly by various approximate analyses of the large- U Hubbard model. The Bose condensation approach gives the famous dome phase diagram for T_c in the x - T plane. That is superconductivity is basically a Bose–Einstein condensation phenomenon of a dilute liquid of charged valence bonds. The charged valence bonds have a short range repulsion. Consequently, for two dimensions we have a Kosterlitz–Thouless transition with a T_c given by

$$k_B T_c \approx \frac{2\pi \hbar^2 n_d}{m_d^*}. \quad (5)$$

In three dimensions, the expression for the Bose–Einstein condensation temperature of non-interacting Bose gas gives an estimate of T_c :

$$k_B T_c \approx \frac{2\pi}{(2.612)^{2/3}} \frac{\hbar^2 n_d^{2/3}}{m_d^*}. \quad (6)$$

Here m_d^* and n_d are the effective mass and density of the self-doped or externally doped carriers. For a given x , the background singlet pairing among spins continues till the so-called *spin gap* temperature T^* . That is, the above formulae are good at small dopings, when T_c is small compared to the temperature scale above which RVB singlets are unstable. Earlier RVB mean-field theory and later developments provide an estimate of T^* as follows:

$$k_B T^* \sim J_{\text{eff}} e^{-1/(\rho_0 J_{\text{eff}})} \sim J(1 - \alpha x), \quad (7)$$

where the density of states at the Fermi energy of the spinon Fermi surface $\rho_0 \approx 1/(J_{\text{eff}})$ and the effective interaction among spinons is $J_{\text{eff}} \approx J(1 - \alpha x)$, where $\alpha \approx W/J$. The spin gap temperature provides a natural cutoff for Bose condensation of charged singlet bonds. As a result, we have the *dome*-like behaviour [32]¹ of the superconducting T_c in the x - T plane with maximum T_c at an optimal doping.

In the second approach, one directly analyses the large- U Hubbard model for superconductivity using various approximate methods. We will not go into the details of the result. However, what one finds is that the superconducting T_c at optimal doping is in the range $W/100$ to $W/50$. For example, for cuprates the band width $W \approx 1$ eV leads to a $T_c \sim 100$ K. The value of T_c is also relatively insensitive to the value of U , provided $U > W$. From the above discussions we conclude that the impurity band width W provides an

important scale for superconducting T_c in the insulator-metal transition region, provided the Mott insulating character survives (that is $U > W$) in the metallic state in the presence of a small density x of self-doping. When the self-doping or external doping reaches the optimal value ($x \approx 0.15$ for cuprates) we will get maximum superconducting T_c .

Keeping in mind the randomness in our impurity band Mott insulators, we will get a rough estimate of T_c for boron-doped diamond. For the impurity band to retain its identity, the band width should be less than the binding energy $\epsilon_0 \approx 0.36$ eV. Considering the tail in the density of states arising from randomness, we can take an effective band width, $W \approx 0.18$ eV, which is about half the above value. This gives us a maximum possible value of T_c in the range 10–30 K.

This is indeed interesting. In boron-doped diamond, experimentally we still do not have a good control over homogeneous substitutional doping. There is also difficulty in characterizing the real doping density, as a fraction of boron's does not provide carriers [33]. *It is likely that we have not reached the maximum possible T_c in boron-doped diamond.* Further increase in T_c may be possible, according to our estimates. When we apply the above estimation to phosphorus-doped Si, we get a superconducting T_c , which is at least a factor of 5 lower compared to boron-doped diamond. It follows from the fact that phosphorus is a shallow donor with a binding energy of about 50 meV. Correspondingly, the impurity band width in the vicinity of the insulator to metal transition is considerably low compared to boron impurity band in diamond. Recent experiments in heavily boron doped Si and SiC have yielded low- T_c (<1.5 K) superconductivity [14, 15]. The low value of T_c is consistent with the small impurity state binding energy. Further, in these experiments one is far away from the insulator to metal transition, as the doping level is high. So it is likely that the impurity bands have disappeared. In such a situation, the doped Mott insulator picture that we are advocating is clearly not applicable and an electron-phonon mechanism might suffice. On the other hand, if one does find superconductivity at the metal-insulator transition (like in boron-doped diamond), the strong correlation mechanism we are suggesting is inescapable in that neighbourhood.

7. Advantages of disorder for superconductivity

While randomness inherent in our impurity band approach can decrease superconducting correlations, it has the following advantage. It is known from the two decades of experimental and theoretical work in cuprates that in doped Mott insulators there are competing orders such as valence bond localization, spin or charge order or chiral orders. Any encouragement of these competing orders from the lattice, such as a strong electron-lattice coupling and valence bond localization, will decrease superconducting T_c resulting from a reduced valence bond resonance. In general, a random lattice frustrates real-space spin or charge orders. It also frustrates d-wave superconducting order, for example. However, it does not frustrate the extended-S superconducting order, one of the stable solution of the RVB mean-field theory [9].

¹ Superconducting ‘dome’ was theoretically predicted first in the paper [31].

8. Search for systems with a larger T_c

In the last section, we have seen that the maximum value of superconducting T_c in our strong correlation based impurity band mechanism is primarily measured by the impurity band width. The maximum allowed impurity band width, in turn, is limited by the impurity state binding energy. So any search for higher T_c should also focus on impurity binding energy. First we will discuss optimization of T_c in the case of diamond. Heavy doping of any foreign atom into diamond is notoriously hard. Boron continues to be the dopant with the highest density. Doping with nitrogen is interesting but experimentally difficult. We have estimated parameters such as critical nitrogen concentration for insulator to metal transition and maximum possible transition temperature for nitrogen-doped diamond. Experimentally it is known that substitutional nitrogen is a donor with a high binding energy of about 1.7 eV, about four times larger than that of boron in diamond. Correspondingly we estimate a large T_c of about 50–120 K.

However, there are quantum chemical constraints and lattice instabilities which prevent attaining the required heavy doping regime for nitrogen. The critical doping concentration $x_c > 0.2$ necessarily for insulator to metal transition is too large to be experimentally achieved at present. That is, a stable solid solution $C_{1-x}N_x$ that also maintains a diamond lattice structure doesn't seem to exist for the range of x of interest to us. The nitrogen dopants form pairs, or generate nitrogen-vacancy pairs or create a large Jahn–Teller distortion.

In addition to stabilization of the valence bonds through electron correlation that we have outlined, it has been suggested that the high-frequency C–C bond vibration in boron-doped diamond will help in stabilizing and delocalizing the valence bonds [34] and hence increasing T_c .

Other authors have argued that electron-phonon interaction is the major contributor to pairing and superconductivity. As an evidence, observation of isotope effect [36, 37] is presented. It is important to note that isotope effects of similar magnitude could appear through modification of the hopping matrix element of the impurity band by change in zero-point oscillations. This is known in the case of cuprates [38]. We find that similar arguments can be offered for the observed isotope effect [39].

Nature offers us a wealth of band insulators with large band gaps. It will be very interesting to explore possibility of creating impurity band Mott insulators with a larger band width. There has been one theoretical suggestion by Alaeia *et al* [35], that a high density of vacancies in diamond can form an impurity band and that our superconductivity mechanism might work. On the experimental side, inspired by our mechanism, there has been a collective effort, 'super hydrogenic state' project headed by Venky Venkatesan (NUS, Singapore) to create impurity band Mott insulator and search for superconductivity.

The choice of dopants is also very important. Inspired by boron-doped diamond, we have been talking about traditional dopants such as boron and nitrogen. The transition metals or rare earths can easily form deep-level impurity states.

However, because of electron–electron interaction effects in the partially filled impurity d or f shell, Hund coupling stabilized high-spin states, and ferromagnetic or spin glass state will be the ground state. The multiple charge states associated with transition metal deep impurity states also brings in features, which are hard to comprehend at present from superconductivity point of view. Transition metals on the border of the row, such as Sc, Ti and Cu are good candidates for dopants, as well as monovalent alkali metals and noble metals Au and Ag. While it may be difficult to accommodate the above dopants in diamond, various oxides and other insulators might offer opportunities for heavy doping and creation of impurity band Mott insulators. So one should try a variety of large band gap band insulators.

9. Conclusions

Superconductivity in new systems have always led to new high- T_c superconductors. Good examples are the *copper route* ($La_{2-x}Ba_xCuO_4$), *organic route* (Bechgaard salt), *fullerene route* (K_3C_{60}) and more recently *iron route* (LaOFeAs). We believe that boron-doped diamond is also the beginning of a new route, *diamond route* to high- T_c superconductivity; it is worth exploring.

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