R VB states in doped band insulators from Coulomb forces: theory and a case study of superconductivity in BiS\(_2\) layers

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Abstract

Doped band insulators, HfNCl, WO\(_3\), diamond, Bi\(_2\)Se\(_3\), BiS\(_2\) families, STO/LAO interface, gate doped SrTiO\(_3\), MoS\(_2\) and so on are unusual superconductors. With an aim to build a general theory for superconductivity in doped band insulators, we focus on the BiS\(_2\) family which was discovered by Mizuguchi et al in 2012. While maximum T\(_c\) is only \(\sim 11\) K in LaO\(_{1-x}\)F\(_x\)BiS\(_2\), a number of experimental results are puzzling and anomalous in the sense that they resemble high T\(_c\) and unconventional superconductors. Using a two orbital model of Usui, Suzuki and Kuroki, we show that the uniform low density free Fermi sea in LaO\(_{0.5}\)F\(_{0.5}\)BiS\(_2\) is unstable towards formation of the next nearest neighbor Bi-S-Bi diagonal valence bond (charged \(-2e\) Cooper pair) and their Wigner crystallization. Instability to this novel state of matter is caused by unscreened nearest neighbor coulomb repulsions (V \(\sim 1\) eV) and a hopping pattern with sulfur mediated diagonal next nearest neighbor Bi-S-Bi hopping \(t' \sim 0.88\) eV, as well as larger than nearest neighbor Bi-Bi hopping, \(t \sim 0.16\) eV. Wigner crystals of Cooper pairs quantum melt for doping around \(x = 0.5\) and stabilize certain resonating valence bond states and superconductivity. We study a few variational RVB states and suggest that BiS\(_2\) family members are latent high T\(_c\) superconductors, but challenged by competing orders and the fragile nature of many body states sustained by unscreened Coulomb forces. One of our superconducting states has d\(_{xy}\) symmetry and a gap. We also predict a 2d Bose metal or vortex liquid normal state, as charged \(-2e\) valence bonds survive in the normal state.

Keywords: high T\(_c\) superconductivity, strongly correlated electrons, resonating valence bond theory, doped band insulators

(Some figures may appear in colour only in the online journal)

1. Introduction

After the discovery of high T\(_c\) superconductivity in the cuprate family [1] in 1986, efforts to synthesize new superconductors have continued and is gaining momentum. There are notable successes in these efforts, even though T\(_c\) has not surpassed the limit, \(\sim 134\) K, set by a trilayer cuprate at ambient pressure. It is interesting that in most of the newly discovered low and high T\(_c\) superconductors, there are strong signals for electron–electron coulomb interaction based mechanisms for superconductivity. In this background experimental study, observations of superconductivity in doped band insulators HfNCl, WO\(_3\), diamond, Bi\(_2\)Se\(_3\) families, STO/LAO interface, gate doped SrTiO\(_3\), MoS\(_2\) [2–8] and so on have come as a surprise. The BiS\(_2\) family of band insulators with low density doped carriers, discovered in 2012 by Mizuguchi and collaborators [9–13], belongs to this category.

Even at optimal T\(_c\) \(\approx 11\) K, only a low density of carriers, \(\sim 10^{10}/\text{cm}^2\), get added to the two empty conduction bands. Electron–phonon interactions should suffice to explain the observed low T\(_c\). However, various experiments seem to highlight that something different is going on.

With an ultimate aim of providing a general theory of unusual superconductivity in a class of doped band insulators [2–8], we focus on a representative for the BiS\(_2\) family in the
present article. The key result of the present study is that unscreened short range coulomb interactions, among doped carriers in this low career density system, and orbital degeneracy destabilize the free Fermi sea and form charged $-2e$ valence bonds organized as generalized Wigner crystals. We explicitly demonstrate this instability for an interacting Hamiltonian model for LaO$_{0.5}$F$_{0.5}$BiS$_2$, built on a 2 orbital model [13] of Usui, Suzuki and Kuroki (USK model). Furthermore, we show the formation of certain resonating valence bond (RVB) states from the quantum melting of charged $-2e$ Wigner crystal.

Wigner crystals, originally discussed in terms of its Fermi sea in a jellium background [14], contain ordered lattice of spatially localized electrons. This state is possible in low carrier density systems when coulomb forces start to dominate; this occurs as a result of reduced metallic screening. Our generalized Wigner crystal is defined for tight binding band insulators that contain a relatively low density of doped carriers. Depending on the system, they could form (i) ordered lattice of charged $-2e$ valence bonds or (ii) ordered array of doped Mott–Hubbard electron chains or (iii) stacked 2d electron sheets. Notably, it could be electrically insulating or conducting. We illustrate our proposal and theory using the BiS$_2$ layer family as an example. Extensive experimental studies that already exist in BiS$_2$ families gives us interesting phenomenological clues to make theoretical progress.

In what follows, we first discuss the structure of LaOBiS$_2$, quantum chemistry and summarise the USK model [13] for BiS$_2$ layers. Then we discuss in detail the experimental results that seem to be at odds with a simple rigid band filling picture for various properties.

Using insights from these experimental results and analysing the physics of unscreened coulomb interactions for low carrier density systems, we build on the USK model using LaO$_{0.5}$F$_{0.5}$BiS$_2$. We use a case of optimal and commensurate doping as a reference system. We show that a large unscreened nearest neighbor coulomb repulsion $V \sim 1$ eV and a favorable hopping pattern in the conduction band help destabilize the uniform Fermi sea. Hybridization of Bi and S orbitals in the BiS plane is such that the sulfur mediated diagonal, next nearest neighbor Bi-S-Bi hopping $t' \sim 0.9$ eV is larger than the nearest neighbor Bi-Bi hopping $t \sim 0.16$ eV. Therefore, doped electrons in LaO$_{0.5}$F$_{0.5}$BiS$_2$ (i) avoid the nearest neighbor occupancy, hence coulomb repulsion V and (ii) at the same time form a strong next nearest neighbor, diagonal Bi-S-Bi valence bond (figures 3, 4). Through suitable ordered occupancy of 6p, and 6p type Wannier orbitals and quantum fluctuations, the system forms generalized Wigner crystals of valence bonds and prepares the ground for unsuspected resonating valence bond (RVB) states and superconductivity.

We simplify the model Hamiltonian of USK and present detailed three lower energy states in the neighborhood of doping $x = 0.5$: (I) Wigner crystal of charged $-2e$ Cooper
For a range of doping around \( x = 0.5 \), the energy of the state II using perturbative arguments.

In state II delocalization is two dimensional and along the Bi planes. This will be an isotropic 2d Kosterlitz–Thouless superconductor within the ab-plane. We also show that valence bond resonance within a plaquette favor an order parameter with \( d_{xy} \) symmetry. It is gapful as the nodal lines pass between disconnected Fermi surfaces.

In state III electrons delocalize along X or Y chains and form weakly coupled doped Mott–Hubbard chains. This occurs by using the large Bi-S-Bi hopping matrix element. For a range of doping around \( x = 0.5 \) we have doped Mott insulating chains containing RVB superconductivity correlations [16–18]. Anisotropic 2d superconductivity gets stabilized by interchain pair tunneling [19–21]. In this case, superconductivity will be an anisotropic 2d Kosterlitz–Thouless superconductor within the ab-plane.

Presently, we are unable to distinguish between the 2d isotropic and anisotropic superconducting states within the accuracy of our microscopic theory. We suspect that both types of superconductivity occur in different family members and at different parts of the phase diagram, or they could even coexist. There is also some experimental evidence for this, as we will later discuss.

Our phases, sustained by unscreened short ranged coulomb interactions, are fragile. There are underlying spontaneous breaking of rotational and translational symmetry in the square lattice. Superconductivity and other orders owe their existence to an organized orbital order. In the Hubbard chain scenario, state III, the normal state is a highly anisotropic metal even within the ab-plane; however, this is dependent on the orientation of Mott chain arrays. Corresponding local superconductivity is also anisotropic within the 2d plane. Doped 1d Mott insulating chains, belonging to a class of Luttinger liquids, have several intrinsic instabilities: CDW, SDW and superconductivity. For a range of interaction parameters, even p-wave superconductivity is possible. It will be interesting to see if such a possibility is present for some ranges of physical parameters. Available experimental results [22–25] have been interpreted as providing evidence for gapped s-wave superconducting states. In scenario II, the normal state is likely to be a 2d Cooper pair metal, Bose metal [26], or a vortex liquid [27].

Several theoretical research [29–33] provide electronic–phonon interaction based BCS mechanism and phenomenological attraction models [34] for superconductivity. Other work [35–38], including the original work of USK [13], emphasize the importance of coulomb interactions based on spin fluctuation mediated superconductivity and possibility of unconventional superconducting order parameters. However, they work with rigid band filling (an uniform state with no orbital order/polarization) as a starting point and study superconducting instabilities arising from coulomb interactions. Our work, on the other hand, reorganizes a rigid band filled Fermi sea into generalized Wigner crystals at the very start by using orbital degeneracy, and avoids a strong nearest neighbor repulsion. We utilise a basic building block, namely the Bi-S-Bi diagonal spin singlet or valence bond. Our correlated many body state contain an optimal gain in delocalization and correlation energy. Effects of spin–orbit coupling [39], known to be important in the heavy Bi atom based systems, will be discussed in a later publication.

The present paper, which is based on phenomenology, microscopic, quantum chemical and physical arguments, is an attempt to show new possibilities in doped band insulators. We suggest a novel mechanism for superconductivity and certain unusual orders. Our estimates of superconducting Tc’s are very crude. However, they point toward a possibility of higher Tc’s. The message is that using suitable materials in engineering the BiS2 family, we can avoid competing charge ordered phases as well as reaching higher superconducting Tc’s. Our mechanism of a strong charged –2e pairing also suggests anomalous normal state describable as Bose metal or vortex liquid [26, 27].

2. Crystal and electronic structure

LaOBiS2 is a representative member of the parent compound of the undoped band insulating BiS2 family. LaO layers and BiS2 layers are alternately stacked along the c-axis [9]. Electron hopping between layers along the c-axis is weak. A LaO layer consists of square lattice oxygen layers sandwiched by two La square lattice layers, such that we get a 2D network of edge sharing LaO octahedra. This insulating charged reservoir layer has a nominal valency La\(^{3+}\)O\(^{2-}\).

The BiS2 layer consists of two layers of edge sharing square pyramids made of 5 sulfur atoms. At the base center of
each pyramid is a Bi atom. Bases of edge shared pyramids form a BiS square lattice with Bi and S atoms forming two square sublattices. Sulfur atoms at the apex of the pyramid are bonded directly to the Bi atom at the base center. Bases of the pyramids of the two layers face each other and form two in-plane staggering BiS square planes. The two BiS planes are weakly coupled electronically [40].

Nominal valency of BiS2 layer is Bi$^{3+}$($S^{2-}$)$_2$. The $S^{2-}$ ion has a filled shell and the Bi$^{3+}$ ion has an electronic configuration [Xe]4f$^{14}$5d$^{16}$6s$^2$. The two lowest degenerate 6$p_x$ and 6$p_y$ empty orbitals of Bi, after suitable hybridization with orbitals of the bridging sulfur atom, form the two lowest empty conduction bands in the BiS square lattices of the BiS2 layer. These two degenerate Wannier orbitals, with 6$p_x$ and 6$p_y$ symmetry, form the basis for the 2 orbital tight binding model of USK [13]. Because of strong hybridization through the S atom at the middle of elementary plaquettes of Bi atoms, the degenerate Wannier orbitals orient and hybridize maximally along the two diagonal direction of the square lattice (figure 1). Two oriented orbitals with positive and negative slopes will be referred to as X and Y orbitals, respectively (figure 2).

In the tight binding parametrization of USK (figure 1), four important matrix elements are: $t' = 0.88$ eV, $t'_1 = 0.094$, $t = -0.167$ and $t_1 = 0.107$. Matrix elements $t'$ and $t_1$ are between two next nearest neighbor Bi atoms bridged by a S atom; $t'$ is between Wannier orbitals directed along the diagonal direction Bi-S-Bi; $t'_1$ is between Wannier orbitals directed perpendicular to the diagonal direction Bi-S-Bi. Matrix elements $t$ and $t_1$ are between two nearest neighbor Bi atoms with orbitals parallel or mutually perpendicular to each other.

As discussed in detail in [13], if we only keep the largest diagonal hopping term, $t' \approx 0.88$, and ignore the rest, the rigid band filling scenario becomes simple. The free part of the Hamiltonian in this case describes a collection of disconnected tight binding electronic chains running along the two diagonal direction [13, 41], we call them the X and Y chains (figures 1, 2). In the X-chain, electrons hop between next nearest neighbor 6$p_x$ orbitals with a matrix element $t'$; this mechanism occurs similarly for the Y-chains. Enery dispersion relation for X and Y chains are:

$$e_X(k_x, k_y) = 2t' \cos(k_x + k_y)$$

$$e_Y(k_x, k_y) = 2t' \cos(k_x - k_y)$$

Band filling in this limit is simple and featureless. However, incorporation of $t$, $t_1$ and $t'_1$, the interchain hopping parameters, modify dispersion relations, resulting in a well discussed topological change in Fermi surface shape as one goes through a van Hove singularity as $x$ is increased from 0.0 to 0.5. It should be pointed out that topological phase transitions generated by the weak interchain hopping, only occur at small Fermi energies where a significant modification of the Fermi sea, from the strong unscreened coulomb interactions, is expected.

Coulomb interactions, also considered by other authors [13, 35–38], will play important role in our theory. We consider onsite Hubbard $U$ and nearest neighbor repulsion $V$. We approximate the inter and intra orbital two electron repulsion at a given site by a single $U \sim 2eV$. Similarly, we assume a single $V \sim 1eV$, for two electron repulsion between nearest neighbor sites, independent of the orbitals they occupy.

Another important off-diagonal two body Coulomb term represented by $J_p \approx \frac{1}{\sqrt{8}} \sim 0.25$ eV (according to our estimate), rotates a diagonal spin singlet pair (figure 5) in an elementary Bi plaquette, by an angle $\frac{\pi}{2}$.

An inter orbital Hund coupling at a given Bi site can be ignored, as probability of such occupancies are very low in our low carrier density systems.

Larger values of $U$ and $V$ have been suggested in the literature. We find that even with our conservative values of $U$ and $V$, rich physics emerge.

Having gotten an idea about the electronic structure, we will move on to a summary of the puzzling phenomenology. It guides us to build a model and suggest physics beyond rigid band filling.

3. Puzzling experimental results

In this section we briefly summarise experimental results and point out certain puzzling aspects, we begin with ARPES [42–46]. For low doping, one observes small Fermi pockets, as predicted by the theory. However the pockets do not close and resemble Fermi arcs seen in underdoped high Tc superconductors. Further experiments find that the volume of the Fermi pockets do not agree with doping density $x$; this indicates a possible failure of the Luttinger theorem. A careful estimation of Bi deficiency is necessary, as this could also change the carrier density [12]. The Quasi particle width, as
given by ARPES, are very broad and have widths comparable to underdoped cuprates.

A recent ARPES study [45] highlights orbital polarization content in different parts of the BZ. This has been interpreted to mean that underlying Bloch states of the Fermi sea differ in orbital content, due to a strong ld character of the band. We suggest that this data is not inconsistent in real space domains containing ordered doped Mott–Hubbard electronic chains (domains of generalized Wigner crystal). This interpretation has some support from STM results which we will shortly discuss.

ARPES also shows, as doping is changed [44] an indication for change in the Fermi surface topology, as in a rigid band filling scenario. However, spectral functions are very broad. We interpret the observed topology change as an interesting, but residual feature of a strongly affected non-interacting Fermi surface. Fermi liquid, as we know in metals for example, has a sharp feature in the quasi particle width vanishing as \( T^2 \) reaches low temperatures. Electron–phonon interactions, important in low carrier density materials, could explain the broad spectral features through polaronic effects. However, it is difficult to explain other features, as in the case of cuprates.

In a soft x-ray photo emission study [47], a strong suppression of the Fermi edge is seen in a BiS\(_2\) family member. The authors bring out an interesting similarity of this suppression to that seen in strongly correlated systems such as cuprates.

STM studies [48–50] for different family members exist. A recent observation [48] of strong local orbital ordering and checker board pattern of such local orders is very interesting. Though, we are cautious that this could be a surface effect, rather than a bulk phenomenon. It is likely that what is seen is a surface modification of our generalized Wigner crystallization supported array of doped Mott–Hubbard chains and/or ordered plaquette valence bond resonances in the bulk.

Giant superconducting fluctuations, resembling pseudo gap of cuprates have been also reported. In one of the STM studies [49], what is believed to be a superconducting gap does not efficiently close above \( T_c \), reminiscent of underdoped cuprates. A large variation in the superconducting gaps seen in one experiment is also reminiscent of underdoped cuprates [50]. It is also noteworthy that a large value \( \frac{\Delta}{k_B T_c} \approx 16 \) seen in some experiments [49] is significantly different from weak coupling BCS expectations.

Tunneling asymmetry has been argued to be an important consequence of an underlying Mott character in doped Mott insulating systems [51]. The work reported in [48], clearly shows a marked tunneling asymmetry. We interpret this as a signal for the presence of self-organized doped Mott insulator character.

Neutron scattering results [53, 54] show the presence of strong local structural (pyramid) distortions. The results indicate one of the large octahedral rotations and local distortions in \( \text{CuO}_2 \) planes seen in single layer cuprate materials such as LSCO or 2201 BISCO, where the superconducting \( T_c \) is considerably low. These local distortions or rotations help charge localization and favor competing orders such as charged stripes, spin stripes and so on at the expense of the superconducting order [55, 56].

In one of the BiS\(_2\) family members, a signal for CDW transition [52] around 250 K is reported. It will be interesting to see if this is connected to our proposal of generalized Wigner crystallization that supports superconducting RVB states at low temperatures.

A controlled study [57, 58] has been performed in \( \text{Sr}_{1-x}\text{La}_x\text{PBiS}_2\) as a function of doping \( x \). There is a good indication of a first order insulator to superconductor, as a function of \( x \). In our opinion, this points out that charges in the insulating phase (below the critical \( x \)) are organized in special ways (Cooper pair Wigner crystals or self trapped valence bonds from a strong electron–phonon interactions) that enable a first order transition to a superconducting state. However, detailed STM and ARPES studies in these systems are required.

Hydrostatic pressure and uniaxial pressure experiments [59–63] also show first order phase transition, between two superconducting states having different \( T_c \)’s. We suggest that they represent transition between two different self organized RVB phases supported by different patterns of generalized Wigner crystallization.

Optical conductivity [64] in one of the BiS\(_2\) systems exhibit an upper Hubbard band like maxima centered around 1.5 eV. This interesting feature, according to our interpretation which will be discussed later, provides evidence for the presence of strong Bi–S–Bi valence bonds in the ground state.

With this background in mind we will discuss our model and show that coulomb interactions can organize conduction electrons in special ways and give rise to an electron correlation based superconductivity.

4. Instability of the uniform Fermi sea towards cooper pair wigner crystal formation

In this section, we start with the 2 band model of USK and show that even a conservative value of coulomb interaction parameters encourage orbital order and modifies physics in an interesting way. The commensurate doping \( x = \frac{3}{5} \), in \( \text{LaO}_x\text{Fe}_y\text{BiS}_2 \) offers us a convenient place to illustrate the importance of coulomb interactions and our generalization Wigner crystallization of charged –2e valence bonds. First, we estimate the total energy per site in the rigid band filled scenario. Then we construct a few RVB states with lower energies.

We consider the many chain Hamiltonian \( H \) for a single Bi square lattice. It contains two parts: X and Y chain hopping terms and onsite, nearest and neighboring coulomb interactions U and V. To begin with, we ignore the interchain hopping terms \( t_\perp \), \( t \), and \( t_\perp \), as they are small compared to the largest \( t \). Their important effects will be studied later. The
many chain model Hamiltonian is:

\[
H_c = -t' \sum_{\langle j,k \rangle} c_{j,\sigma}^\dagger c_{k,\sigma} - t' \sum_{\langle j,k \rangle} c_{j,\sigma}^\dagger c_{j,\sigma} + \frac{U}{2} \sum_{ij} n_i n_j - V \sum_{\langle i,j \rangle \neq \langle i,j \rangle} n_i n_j,
\]

where \( n_i \equiv \sum_{\sigma} (n_{i,\sigma} + n_{i,\sigma}^\dagger) \) is the total number of electrons at site \( i \). The summation ‘nn’ ‘nnn’ stands for nearest neighbor and next nearest neighbor (diagonal) hopping, respectively. We will construct a few variational wave functions and compute their energy exactly for the many chain model Hamiltonian \( H_c \) (equation (3)). This will help us demonstrate an instability of the uniform free Fermi sea. At the filling \( x = 0.5 \) under consideration, mean number of electron added per site is \( \frac{1}{3} \). So every X and Y chain is \( \frac{1}{8} \) th filled for each spin species (figure 2). This uniform state has full orbital and lattice symmetry.

Band width of the 1d chains is 4t’. Kinetic energy per site, counting contributions from two types of chains and two spin species is:

\[
KE_0 = -2 \times 2 \times \frac{2t'}{2\pi} \int_0^{2\pi} \cos k dk \approx -t'.
\]

Hartree energy of this uncorrelated state can be estimated in the presence of coulomb repulsions \( U \) and \( V \). A given Bi site, containing two orbitals can have a total 16 many electron states = 1 (empty) + 4 (one electron) + 6 (two electron) + 4 (three electron) + 1 (completely filled 4 electron) states. Probability of finding a 2 electrons at a given site for the filling \( x = 0.5 \) is \( \left( \frac{1}{8} \right)^2 \times 6 \). Here, the first term is the probability of finding two electrons in a single site and the second term is the number of two electron states. We ignore three and four electron states, which occur with lower probabilities, \( \left( \frac{1}{8} \right)^3 \) and \( \left( \frac{1}{8} \right)^4 \). So energy cost from onsite repulsion is \( \approx \frac{U}{2} \). Similarly, energy cost (Hartree energy) per site from the nearest neighbor coulomb repulsion from four neighbors is \( \left( \frac{1}{8} \right)^2 \times 4^2 \times \frac{4}{2} \times V = \frac{V}{2} \). In the decoupled chain limit under consideration, Hartree–Fock contribution from \( V \) term is zero.

Thus kinetic plus interaction energy per Bi site for the Fermi sea, with complete orbital symmetry, for \( x = 0.5 \) is

\[
E_{0.5} \approx -t' + \left( \frac{6}{64} U + \frac{1}{2} V \right) \approx -0.2 \text{ eV}
\]

Inclusion of interchain and other hopping matrix elements do not produce appreciable correction to the variational energy. We observe that major energy increase in this low density system comes from the nearest neighbor repulsion \( V \).

Let us consider a classical electron crystal state, which avoids coulomb repulsion \( U \) and \( V \) completely (for \( x = 0.5 \)), through single electron occupancy of one of the sublattices of Bi square lattice and zero occupancy in the other (figure 3). This crystalline state of electrons is highly degenerate in which the \( 4^2 \) fold degeneracy arises from the two fold orbital and two fold spin degeneracy.

We will remove degeneracy of the above classical ground state step by step, to see the emergence and importance of the diagonal Bi–S–Bi valence bond. In the first step, we form charged –2e Cooper pairs or valence bonds as shown in figure 4. It is a Wigner lattice of ordered and frozen diagonal valence bonds, where no two electrons are nearest neighbors.

We calculate energy of a Bi–S–Bi diagonal valence bond (charged –2e state) using the ground state energy of a two site Hubbard model (Hubbard dimer)

\[
E_{vb} = -\frac{1}{2} \left( U^2 - 16t'^2 \right) + \frac{U}{2}.
\]

This expression is very instructive. Since the ratio of \( U \) to band width \( 4t' \) is small, we expand \( E_{vb} \) in powers of \( \frac{U}{4t'} \) and get \( E_{vb} = -2t' + U - \frac{U^2}{16t'} \). The first term denotes the kinetic energy of two electrons occupying a bonding state. The second term is the Hartree term, coming from onsite repulsion \( U \). Third term represents the important correlation energy gain, that arises through a suppression of double occupancy in the exact solution of the Hubbard dimer. This bonding between next nearest neighbor Bi sites (along diagonal Bi–S–Si direction) avoids the nearest neighbor repulsion \( V \).

Thus, energy per Bi site of the frozen charged –2e Wigner crystal state is given by

\[
E_{vbc} = \frac{1}{4} E_{vb} \approx -0.3 \text{ eV}
\]

This energy is lower than the energy of the uniform shallow Fermi sea state (equation (5)), for our model Hamiltonian (equation (3)). Within the limitations of our simple model, this completes our proof for the instability of uniform Fermi sea towards charged –2e Cooper pair formation and Wigner crystalization.

In proving an instability we have used a key nearest neighbour repulsion energy parameter \( V \sim 1 \text{ eV} \). An accurate and microscopic evaluation of this parameter, relevant for low energy physics in BiS2 layers, as a function of doping \( x \), in itself is a challenging many body problem. Our parameter \( V \), in some senses encodes all (non on-site) short distance unscreened electron–electron coulomb repulsions.

The effective value of \( V \) for a given family member will depend on crystal and electronic structures, nature and dielectric properties of the reservoir layer and so on. For a large value of \( V \), we have assured that it is reasonable in an insulating state, such as the Wigner crystal we previously discussed. Once the system gets metallized, effective \( V \) will be modified. We believe that modifications at short distances are not significant enough to alter our picture.

Our main message is that in a low carrier density Fermi sea, unscreened short range repulsions can not be ignored; this is an insight that Wigner provided us back in 1934. In tight binding models with orbital degeneracies, unscreened coulomb interactions appear to be even more important and have a potential to provide rich physics, through self organization of generalized Wigner crystal, RVB states and so on.
5. Quantum melting of cooper pair wigner crystal and superconductivity

Having demonstrated an instability of the uniform Fermi sea to Wigner crystal formation, we study quantum fluctuations in the Cooper pair Wigner crystal. A given valence bond can undergo different quantum fluctuations, by electron hopping to available empty degenerate orbitals. Using the diagonal hopping ′ a given X or Y-valence bond can (i) expand its size by one diagonal unit in the diagonal (forward or backward) direction and (ii) (pair) hop in the diagonal (forward or backward) direction by one unit. Our estimate of energy gain from these processes is \(-\nu' \cdot \frac{1}{8}\). Furthermore, an X valence bond can quantum tunnel to become a Y valence bond (a \(\frac{\pi}{2}\) rotation) using an off diagonal two body coulomb matrix element \(J_p\), and taking advantage of non-zero overlap charges between X and Y \(\sigma\) bonding orbitals. Energy gain from this plaquette resonance (with \(d_{X\bar{Y}}\) orbital symmetry, figure 5) per site is \(-\frac{\nu}{4}\). Since overlap charges are localized to the neighborhood of sulfur atoms, our estimate of \(J_p\) is \(\sim \frac{\nu}{4}\).

In the above processes we also create virtual nearest neighbor occupancies. An estimate of coulomb energy cost per site from the above is \(\frac{\nu}{8}\). Thus total energy gain from quantum fluctuations in the Cooper pair Wigner crystal state per Bi site is

\[
\frac{-\nu'}{8} - \frac{J_p}{4} + \frac{\nu}{8} \sim 0.06 \text{ eV.}
\]

According to this estimate, a stable phase for the commensurate doping \(x = 0.5\) is a Wigner crystal of plaquette resonance bonds, or a Wigner crystal of charged \(-2\text{e}\) Cooper pairs, shown in figure 5. It is also interesting to note the sign difference between the X and Y valence bonds. A positive \(J_p\) (pair hopping between X and Y chains) indicates a \(d_{X\bar{Y}}\) type of order parameter symmetry for superconductivity in this scenario.

Additional quantum fluctuations might melt the charged \(-2\text{e}\) Cooper pair Wigner crystal even at the commensurate filling \(x = 0.5\). In existing experimental results for Tc as a function of \(x\), there is no dip seen around \(x = 0.5\). This could indicate that the Cooper pair Wigner crystal has quantum melted and become a superconductor, even at \(x = 0.5\).

As we move away from \(x = 0.5\) we loose commensurability and Wigner crystal will quantum melt. Cooper pairs will also delocalize and expand their sizes, to take advantage of single particle delocalization. However, we expect the nature of valence bond correlations to survive at short distances even after quantum melting. That is, quantum melted Cooper pair fluid is a strongly correlated charged \(-2\text{e}\) fluid that avoids nearest neighbor coulomb repulsions. This as an interacting charged \(-2\text{e}\) bose fluid, known as a Kosterlitz-Thouless superconductor. Scale of superconducting Tc is determined by the effective band width of the delocalized charged \(-2\text{e}\) valence bond. An unscreened near neighbor coulomb repulsion, a two fold orbital degeneracy and geometry of chemical bonding in the BiS lattice has stabilized this phase.

In view of the positive matrix element for the hopping of valence bond between X and Y chains, we expect \(d_{X\bar{Y}}\) symmetry for the spin singlet Cooper pair order parameter. This is likely to be a gapful \(d_{X\bar{Y}}\) state as Fermi surfaces are fragmented, as seen in ARPES experiments [42–46]. Specifically, nodal lines pass between Fermi surfaces.

We estimate the effective band width of the valence bond pair using the perturbation theory argument. An elementary valence bond pair motion involves two single electron hopping events. In the intermediate state, valence bonds are broken. The perturbation theory estimates that the valence bond pair hopping is \(t_{\phi} \approx \frac{\nu^2}{4(U^2 - 16\nu^2)^2 + \nu} \sim 0.7\text{ eV.}\) This is indeed a large energy scale. However, short range coulomb repulsion in this dense fluid of valence bonds will renormalize the hopping matrix element significantly downwards and make Cooper pairs heavy. Additionally, fusion and regrouping of valence bonds through collisions will make the simple Bose fluid picture less and less relevant as we move away from the doping \(x = 0.5\). This brings in exponential suppression factors, similar to BCS and RVB mean field theories [17], giving us the following expression for Tc:

\[
K_B T_c \sim \frac{t_{\phi} e^{-\frac{\rho A_{\text{eff}}}{T_c}}}{\rho A_{\text{eff}}}
\]

Here, \(\rho_{\text{eff}}\) is a mean energy required to break spin singlet pair and create two electrons at the Fermi level, for a short time scale. The exponential factor indicates a BCS like condensation of spin singlet spinon pairs, which is similar to the situation in the RVB mean field theory for cuprates [17], \(\rho_{\text{eff}} = \rho(\epsilon_F)\) is the density of states at the reference uniform Fermi sea. When \(\nu/\nu'\) is large, \(\rho_{\text{eff}}\) is approximated by the superexchange \(J \approx \frac{\nu^2}{U} \). However, for the present case of intermediate \(\nu/\nu'\), the energy difference between the singlet ground state and excited triplet state of a Hubbard dimer is a good measure of \(\rho_{\text{eff}}\),

\[
\frac{1}{2} (U^2 + 16\nu^2) - \frac{\nu'}{2} \sim 1\text{ eV.}
\]

This rough estimate gives us a maximum scale of Tc in the range 20 to 100 K.

A good way to study ground state properties of superconductivity quantitatively is to use the following variational RVB wave function for the plaquette bond resonance (PBR) state:

\[
|\text{PBR}\rangle_{\text{SC}} = P_{\phi} \left( \sum_j \phi_j b_j^\dagger \right)^{\frac{\nu}{2}} |0\rangle.
\]

Here, \(b_j^\dagger \equiv \frac{1}{\sqrt{2}} (c_i^\dagger c_j^\dagger - c_j^\dagger c_i^\dagger)\) is the bond singlet operator. The function \(\phi_j\) represents Cooper pair functions for a singlet valence bond electron pair at sites i and j. In terms of relative coordinates, amplitude \(\phi_j\) is large within a plaquette for diagonal singlets. A coherent superposition of diagonal singlets, within a plaquette represents the plaquette valence bond resonance with \(d_{X\bar{Y}}\) symmetry. The projection \(P_{\phi}\) prevents overlap or touching of resonating plaquettes. This takes care of the short range coulomb repulsion and internuclear overlap of valence bonds.
We defer the study of the above variational wave function to a future publication and instead just highlight that the short range repulsions in the BiS lattice, orbital degeneracy and a favorable hopping pathway has given us an opportunity to have stable charged $-2e$ Cooper pairs and a means to achieve superconductivity.

In the next section we will see another nearly degenerate superconducting state that can be obtained by creating quantum fluctuations in a charged $-2e$ Wigner crystal.

### 6. Transformation of 2d cooper pair wigner crystal into 1d array of doped mott-hubbard chains

The superconducting and normal state that we are going to construct is interesting in its own right and has some phenomenological support as we will soon discuss. To realize this variational state we allow electrons to delocalize only along X chains, using hopping $t'$, as shown in figure 6. This results in decoupled 1d chains, whose effective Hamiltonian within this manifold of X-orbital occupancy are decoupled 1d Hubbard X-chains. We start with a variational state denoted as $(\ldots, \frac{1}{2}, 0, \frac{1}{2}, 0, \ldots)$ to indicate a collection of parallel chains in their ground state with a staggered occupancy of $\frac{1}{2}$ and 0. As nearest neighbor occupations are absent in this variational state, inspite of delocalization along the chains, nearest neighbor repulsion V term drops out in the energy estimate.

Energy of the above state at half filling is obtained using exact solutions of Lieb and Wu [15]:

$$E_{ih}(U) = -2t' \int_0^{\infty} \frac{J_0(\omega)J_1(\omega)}{\omega \left(1 + \exp \frac{-\omega}{2\epsilon}\right)} d\omega,$$  \hspace{0.5cm} (11)

where $J_0(\omega)$ and $J_1(\omega)$ are Bessel functions. This expression explicitly shows band narrowing effects or renormalization of the hopping matrix element, as a function of $U$. For $U \approx 2$, which is relevant for our problem, band narrowing is about 40 percent. Thus, our interesting many body ground state has an energy per site:

$$E_c \approx -\frac{2t'}{\pi} \times \frac{3}{5} \approx 0.42t' \approx -0.3 \text{ eV}. \hspace{0.5cm} (12)$$

Compared to the energy $\sim -0.2 \text{ eV}$ of free fermi gas with a full orbital and square lattice symmetry for the same value of $x = 0.5$, our correlated many body state has a lower energy of $\sim -0.1 \text{ eV}$ per site.

We also find that we can reduce the energy of the above state further (figure 5), by a staggered chain occupancy $(\ldots, \frac{1}{2} - \epsilon, \epsilon, \frac{1}{2} - \epsilon, \ldots)$, where the variational parameter is $\epsilon \leq 0.25$. This state is a self doped state where Mott insulating chains have transferred a fraction $\epsilon$ of electrons to empty chains. We will discuss the optimal value of $\epsilon$ in a future publication; however, we would like to point out that for $\epsilon = 0.25$, we have a series of weakly coupled quarter filled bands where only rotational symmetry is broken and lattice translation symmetry is preserved.

The above intrinsically anisotropic reference variational state allows us to construction anomalous normal and superconducting states by making use of interchain hopping events that we have ignored so far.

Mott insulating subsystems that are commonly encountered, for example in CuO or LaMnO$_3$, are robust Mott insulators. Mott insulating 3d electrons are robust organizations through strong chemical bonding of various atoms and after removal of orbital degeneracies. They are supported by the underlying lattice and a set of atoms.

In our case of generalized Wigner crystals, orbital selection and orbital order self organizes and supports doped Mott insulating chains with reduced symmetries. Doped Mott–Hubbard chain arrays breaks rotational and translational symmetry of the square lattice. There are $2 \times 2 = 4$ possible chain orders: they are obtained by globally (i) replacing X chains by Y chains and (ii) interchanging empty band chains and half filled band chains.

This leads to four different types of domain formation and accompanying phase boundaries, which are topological defects and under suitable conditions these domains could form an order. Domain formation can be encouraged by disorder, for example arising from positional disorder of F atoms in LaO$_{0.5}$F$_{0.5}$BiS$_2$.

Energy gain in our low carrier density system by formation of doped Mott insulating state is small $\sim 0.1 \text{ eV}$. The self organized Mott chains can also disappear as a function of temperature, for entropic reasons. This will be a thermal melting of a generalized Wigner crystalline state.
7. Interchain pair tunneling and anisotropic 2d RVB superconductivity

We will sketch the mechanism of superconductivity in the weakly coupled doped Mott insulating chain scenario and make an estimate of superconducting $T_c$. As we move away from half filling, Mott insulating chains develop strong local spin singlet pairing correlations. This is known in theory, from the Lieb-Wu solution and numerical studies. Using the RVB theory for cuprates [16–18], we suggest that neutral spin singlet pairs in Mott–Hubbard chains pre-exist Cooper pairs. In view of a finite Mott–Hubbard gap, singlet spinon pairs present in the ground state are not capable of transporting charges and remain neutral. Doping makes room for a fraction of electron singlets to coherently delocalize and transport charged $-2e$. A fraction of charges that are capable of transporting charged $-2e$ is the superfluid fraction, and is proportional to the variational parameter $\epsilon$ (amount of self doping) or doping, $\delta \equiv 0.5 - x$.

A doped Mott-Hubbard chain can not support true long range superconducting orders, due to divergent 1d fluctuations. Notably, the interchain hopping can help in establishing a 2d Kosterlitz Thouless state. This is closely related to the interlayer pair tunneling [19] and interchain pair tunneling [20] mechanism of superconductivity, which we briefly describe below.

A doped Mott–Hubbard chain, at low energies has spin-charge decoupling and is described by the Luttinger liquid theory. Coherent electron quasi particles are absent at the Fermi surface. Consequently, interchain hopping matrix elements get renormalized to zero at low energies [21]. This means that two conducting chains are effectively insulated and single electrons are confined within the chains. This is a many body effect that was discussed in detail in the context of interlayer pair tunneling mechanism in cuprates [19–21]. However, if we consider a second order process involving the tunneling of electron pairs, there can be coherent transport of a spin singlet charge 2e pair using strong pairing correlations present in the individual chains.

This coherent transport of charged 2e spin singlet pairs from chain to chain acts like a local Josephson tunneling. What is important is that energy gain from Josephson tunneling can (i) increase local superconducting correlation and (ii) establish Kosterlitz–Thouless superconductivity in two dimensions. In establishing 2d superconductivity, RVB superconducting correlations in doped Mott chains play a fundamental role.

Expression for $T_c$ for 2d superconductivity in interchain pair tunneling mechanisms involve the pair tunneling matrix element $t^{2d}$:

$$K_B T_c \sim \frac{t^{2d}}{J_{\text{eff}}} e^{\frac{1}{\Delta_{\text{pair}}}}$$

(13)

Here, $J_{\text{eff}}$ is the mean energy required to break spin singlet pairs and create two electrons at the Fermi level during a short time scale; this allows for pair tunnelling via a second order process involving the interchain hopping matrix element $t^{2d}$ among others. The meaning of the BCS like dependence is similar to the one we discussed in section 5 (following equation (13)), for isotropic 2d superconductivity. By substituting suitable numbers, we get an estimate for the maximum scale of $T_c$ in the range $\sim 2$ to 20 K. This scale of $T_c$ is much lower than the isotropic 2d state that we discussed in section 5.

A well known place, where interchain pair tunneling seems to be at work, is in quasi 1d organic conductors [65]. The scale of interchain tunneling is typically 10 to 20 times lower. Interchain pair tunnelling has also been suggested [20] to be a mechanism for pairing, when weakly coupled charge stripes are present in underdoped cuprates.

8. Tunneling asymmetry, optical conductivity, Bose metal and vortex liquid

Asymmetry in the tunneling conductance feature has been suggested to be an important signal of an underlying Mott character in doped Mott insulating systems [51]. Physically this asymmetry arises from differences in many electron reorganization, for example, this can occur while adding or removing an electron in an STM experiment. The experimental work reported in [48], clearly shows a marked tunneling asymmetry. In our theory, in Mott–Hubbard chain and valence bond Wigner crystal scenarios, we have strongly correlated Mott chains or Hubbard dimers which could produce the required asymmetry [66] in tunneling conductance.

Ideally, it would be nice to repeat the tunneling measurement for various doping levels and study the asymmetry. Our expectation is that the asymmetry will be stronger at lower doping levels.

A very neat upper Hubbard band like feature is seen in optical conductivity around the energy 1.5 $eV$ reported in [64]. We suggest that this is a signal for the presence of Bi-S-Bi singlet pairs in the ground state. Energy required to break a valence bond pair in our theory (equation (6)) is $E_{\text{pair}} \approx 1.2$ eV. Inclusion of residual coulomb interactions within our scenario could account for the peak seen at an energy of 1.5 eV in optical conductivity. However, more experiments are needed to verify this result.

In the pseudo gap phase of cuprates, pairing correlations or pre-existing RVB singlet pairs survive well above $T_c$. In such a situation, electrical transport, magnetic field dependence and properties such as the Nernst effect are dominated by Cooper pairs present at the Fermi level and in populations of thermal vortices in the 2d CuO$_2$ planes. Anderson calls this phase a vortex liquid [27]. In another context, namely superconductor to insulator transition in 2D, induced by disorder, an intermediate metallic state dominated by Cooper pairs like Bose correlations have been suggested. This is called Bose metal [26] by Das and Doniach. In our opinion there is a close connection between Bose metals and vortex liquids [28].

The theory we have developed in this paper for Bi$_2$S$_3$ offers a new playground to achieve the physics of Bose
metals and vortex liquids. In our model, pairing correlations arising from avoidance of next nearest neighbor repulsions, favors strong valence bond correlations with a large energy scale. This bosonic charged \( -2e \) correlation should survive in the normal state. Our suggestion is that the normal state of BiS\(_2\) family of superconductors should be studied carefully from the view of Bose metal and anomalous Nernst effects.

In general, the pseudogap features seen so far in various experiments should be investigated further to get a deeper insight into the fascinating BiS\(_2\) family.

9. Discussion and some predictions

What is novel in our research is the organization of a dilute Fermi sea in a band insulator into states containing certain diagonal valence bonds (charged \( -2e \) Cooper pairs). These states range from Cooper pair Wigner crystals to weakly coupled arrays of 1d Mott–Hubbard chains. The family of states we have suggested could support isotropic as well as anisotropic 2d Kosterlitz–Thouless superconductivity. It is likely that both occur in different members of the BiS\(_2\) family for different range of parameters.

We have suggested that self organization makes onsite Coulomb repulsion important, while trying to avoid near neighbor Coulomb repulsions. It is a delicate interplay between onsite interaction and residual long range Coulomb interactions, that leads to doped Mott physics and superconductivity.

In the Cooper pair Wigner crystal phase we have proposed, a disorder free \( \text{LaO}_x\text{F}_{1-x}\text{BiS}_2 \) is likely to be an insulator. In an ideal situation, deviation away from \( x = 0.5 \) will act like a doping parameter. Disorder could quantum melt and create superconductivity even for \( x = 0.5 \). It will be interesting to see if the superconducting dome, currently observed around \( x = 0.5 \), develops a dip around \( x = 0.5 \) in superconducting \( T_c \) as a function of \( x \), with a decrease in disorder.

Diagonal valence bond singlets, Bi-S-Bi, play a fundamental role in our theory. Topological defects in generalized Wigner crystals may contain a finite density of unpaired spins (spinons) through broken diagonal valence bonds. This may lead to low temperature Curie contributions to spin susceptibility.

In the present paper, we have only focussed on certain simple energy minimizing generalized Wigner crystal states. A closer look suggests that a variety of ordering of diagonal singlets, with nearby energies are possible. One also expects glass like organization of the diagonal singlets for some range of parameters, leading to interesting electron pair glass or valence bond glass phases. As we indicated earlier, in the Mott–Hubbard chain scenario p-wave instability nematic metallic state are interesting possibilities.

The self organized states could be easily affected by disorder and temperature. So we expect interesting phase transitions as a function of temperature and disorder. As there is a spontaneous translation and orientational symmetry breaking associated with the self organization interesting topological defects, induced charges are possible. To test our theory, it will be interesting to look for signals for enhanced antiferromagnetic (spin singlet) correlations in neutron and NMR experiments.

Electronic coupling between two Bi-S layers in the BiS\(_2\) bilayers [40], in our theory, could play an important role in stabilizing different generalized Wigner crystals and their quantum melting properties. This needs to be investigated.

Instability towards the two phases can also be justified by using a weak coupling approach and a proper use of Umklapp electron pair scattering. These help build Mott localized spin singlet pairs [66].

Our self organized Wigner crystals that support doped Mott–Hubbard chains or sheets is different from the stripes we see in underdoped cuprates and other Mott insulator based systems [67]. We organize strongly correlated systems starting from a Fermi sea in a doped band insulator. Whereas stripe states in cuprates are reorganizations of an underlying Mott insulator after doping.

Electron–phonon interactions play a very important role for small values of \( x \). It is likely to stabilize isolated or islands, or even ordered arrays of Bi-S-Bi diagonal valence bonds. In the superconducting state, where valence bonds are delocalized, it is likely to play a less important role.

We hope to present, in a future publication, a general theory of RVB states in doped band insulators from Coulomb forces and apply it to other systems [2–8], such as HINCl, WO\(_3\), diamond, Bi\(_2\)Se\(_3\) families, STO/LAO interface, gate doped SrTiO\(_3\) and MoS\(_2\), which we alluded to earlier.

10. Summary

In this article we discussed the puzzling phenomenology of the BiS\(_2\) layered family of superconductors and have suggested that they point towards a mechanism of superconductivity that is based on electron–electron repulsion. Our main point is that by utilizing the two fold orbital degeneracy at the Fermi level and unscreened nearest neighbor Coulomb repulsion, doped electrons self organize into arrays of doped Mott chains or a quantum liquid or isotropic 2d RVB states.

We have called them Wigner crystal supported RVB states. Superconductivity, within our theory, can be either isotropic 2d or anisotropic 2d Kosterlitz–Thouless states. In the isotropic (melted Wigner crystal) scenario, order parameter symmetry is a gapful \( d_{xy} \) symmetry; in the anisotropic (doped Mott–Hubbard chain array) scenario we have a gapful extended-S symmetry.

We made an accurate estimate of energy of the variational state, using known exact results from Lieb and Wu for the 1d repulsive Hubbard model. We can conclude that a possible second phase containing plaquette bond resonances logically follow from this starting point. Currently, our work is semi quantitative and suggestive and it needs to be addressed more quantitatively in the future.

The novel scenario and the theory we have presented, emphasizes the importance of unscreened Coulomb interactions in doped band insulators, and is encouraging from the point of reaching higher superconducting \( T_c \)’s in this s-p, non
transition metal based systems. We hope it will raise debates, initiate further work and be of assistance to experimentalists to synthesize new members of the family which have reduced competing orders and higher superconducting Tc.

Thanks to a referee, we became aware of a very recent work from the group of S Mazumdar and RT Clay [68] on enhanced singlet pairing correlations, induced by short range coulomb repulsions and lattice frustration, in the quarter filled 2d single orbital Hubbard model. Their mechanism bears some similarity to ours. However, in our mechanism a novel orbital frustration, rather than lattice frustration, in a 2 orbital Hubbard model induces enhanced singlet pair correlations.

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