Substitutional doping of Cu in diamond: Mott physics with $p$ orbitals

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Discovery of superconductivity in the impurity band formed by heavy doping of boron into diamond (C:B) as well as doping of boron into silicon (Si:B) has provided a route for the possibility of new families of superconducting materials. Motivated by the special role played by copper atoms in high temperature superconducting materials where essentially Cu $d$ orbitals are responsible for a variety of correlation induced phases, in this paper we investigate the effect of substitutional doping of Cu into diamond. Our extensive first principle calculations averaged over various geometries based on density functional theory, indicates the formation of a mid-gap band, which mainly arises from the $t_{2g}$ and $4p$ states of Cu. For impurity concentrations of more than $\sim 1\%$, the effect of $2p$ bands of neighboring carbon atoms can be ignored. Based on our detailed analysis, we suggest a two band model for the mid-gap states consisting of a quarter-filled hole like $t_{2g}$ band, and a half-filled band of $4p$ states. Increasing the concentration of the Cu impurity beyond $\sim 5\%$, completely closes the spectral gap of the host diamond.

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INTRODUCTION

Diamond is the best thermal conductor [1, 2], and the hardest known material with semiconducting properties. Both pristine form as well as doped films of diamond present unique ground for high-temperature and high-power applications in the industries [3, 4]. Recent discovery of superconductivity in heavily boron doped diamond, has revived the interest in impurity band formation from a fundamental point of view [5, 6]. Similar system of boron doped silicon was also studied [7, 8]. Synthesis of boron doped diamond was first achieved by Ekimov and coworkers [5] and subsequently by Takano et. al. [6]. They used chemical vapor deposition (CVD) for the synthesis of B-doped diamond. At low doping concentrations of typically $10^{17} - 10^{18}$ cm$^{-3}$, boron atoms inject acceptor levels in the electronic energy spectrum of host diamond, hence producing a $p$ type semiconductor [10]. For heavier dopings ($\sim$B)/[	ext{C}] > 5000 ppm in the gas phase, one achieves metallic conductivity in diamond [11]. Eventually increasing the doping beyond $n > 10^{21}$ cm$^{-3}$, i.e. few percents, it superconducts at low temperatures [5, 6]. For higher concentrations, the dopant atoms come closer to each other and start to overlap. Therefore the impurity levels are broadened into authentic impurity bands [12, 13], which are responsible for metallic and superconducting properties [8, 13, 14].

Various forms of defects play crucial role in the physical properties of diamond. For example the fascinating colors of diamond as gem stone, is due to the $\sim$ppm concentration of vacancies [19]. Such vacancies at much higher concentration of the order of few percents, can give rise to an impurity bands inside the diamond gap, which can provide larger number of states than some of the elements from the third and fifth column of the periodic table of elements [20]. Such mid-gap bands of the vacant diamond can be attributed to a localized Wannier wave function composed from the $2p$ states of neighboring carbon atoms. Therefore, previous studies of the possible conductive impurity bands in diamond and/or silicon hosts, have been mainly concerned with the substitution of a $p$-type orbital for the host $p$-states.

In this paper, we are interested in the role of substitution by a $3d$ element. We choose to study the effect of copper substitution in the diamond host. Why is Cu interesting from the impurity band formation point of view? First of all, the same high-temperature, high-pressure techniques employed for the synthesis of boron doped diamond can also be applied to attempt a substitution of Cu atoms into the diamond host [21]. From theoretical point of view, although Cu is a $3d$ transition metal, it does not have magnetic complications, and hence one can avoid possible magnetic ground states at low temperatures which tend to compete against superconducting correlations. Choice of Cu also avoids the possibility of local moment formation. On the other hand $3d^0$ “atomic” configuration of Cu is hoped to provide a hole which plays an important role in the high temperature superconducting (HTSC) materials [22]. The nominal $3d$ hole of atomic Cu in HTSC systems is shared between neighboring oxygen $2p$ and Cu $3d$ states, giving rise to the so called Zhang-Rice singlet state [23] which carries the hole.

In this paper, we study the formation of impurity bands in Cu doped diamond in detail and we find that $4p$ states of Cu along with its $t_{2g}$ orbitals are responsible for the formation of impurity band at Cu concentrations $1 - 5\%$. At lower concentrations $2p$ orbitals of neighboring carbon atoms also participate in the formation of mid-gap metallic band. Depending on the experimental conditions, either a combination of most probable geometries is realized, or by slow cooling the system will be given enough time to perform a self-averaging over the phase space of possible geometries. Therefore we undertake
extensive averaging over distinct geometries. The main role of averaging is to restore the symmetries broken by the specific realization, e.g., most probable geometry (MPG). For comparison, we will provide MPG and geometry averaged (GA) results together.

**METHOD OF CALCULATION**

The calculations of electronic structure are performed with the plane-wave pseudopotential [24] of DFT using the PBE functional [25] for exchange and correlation as implemented in the QUANTUM-ESPRESSO package. Ultra-soft pseudopotentials are used with a 30 Ry (230 Ry) cutoff for the expansion of the wave-functions (charge density). We have constructed $2 \times 2 \times 2$ supercell containing 64 atoms with 1, 2 and 3 Cu impurity, leading to doping concentrations of 1.6%, 3.1% and 4.7%, respectively. The sampling of Brillouin zone (BZ) for structural relaxation and DOS calculations are performed on $2 \times 2 \times 2$ and $4 \times 4 \times 4$ grid of $k$-points, respectively. We first minimized the energy of undoped diamond with respect to cell size to calculate the lattice constant. The obtained value was very close to the experimental result. All structures were relaxed by BFGS algorithm [26].

Two types of doping can be considered: substitutional and interstitial. In the case of B-doped diamond, interstitial doping is unstable [27]. Since our study is motivated by B-doped diamond, we only consider substitutional doping of copper. We randomly substituted Cu impurity into the diamond structure. Since there are many different ways of introducing impurity into the host carbon lattice, one needs to average over sufficient number of realizations of randomness. With $m$ impurities in a host of $n$ lattice points, there are $C(n, m) = \frac{n!}{m!(n-m)!}$ different ways of substitution. With $n = 64$ carbon atoms considered here, the most trivial case corresponds to $m = 1$ impurity. By translational symmetry (periodic boundary conditions), it does not matter where we place the single impurity. Therefore the average DOS corresponding to 1 impurity, is identical to any of the random realizations. Next in the case of $m = 2$ impurities, there are in principle $C(64, 2) = 2016$ ways of placing the Cu impurities. However, since the relative distance between the impurities is the physically discriminating factor, many of the above configurations will be essentially identical by translation and rotation symmetries. Therefore the electronic structure calculations must be run for geometrically different configurations. We have used a computer program to count the number of geometrically independent configurations which in the case of $m = 2$ impurities gives 23. Therefore one has to perform the electronic structure for all 23 distinct geometries, taking into account the multiplicity $w_g$ of each geometry $g$. In the case of $m = 3$ impurities, we have $C(64, 3) = 41664$ nominally different configurations. Again our counting algorithm gives 430 distinct geometries, where each geometry is meant to represents a distinct set of 3 mutual distances between the impurity atoms. We used 60 most probable geometries to calculate the averages. Note that the above 60 geometries cover more than half of the total 41664 choices. We have checked that, the average DOS obtained for 60 most probable geometries can be more or less achieved even with 10 most likely geometries. The geometry averaged values of various quantities $X$ such as $\rho(\omega)$, $E_F$ can be calculated as follows:

$$X_{GA} = \sum_g w_g X_g,$$

where $g$ runs over geometries, and $w_g$ is its relative weight.

**METALIZATION OF DIAMOND**

In Fig. 1 we have plotted the DOS of doped diamond lattice with (left) and without (right) averaging over geometries. The doping rates in the figure correspond to 1, 2, 3 Cu impurities in a host of 64 carbon atoms, from bottom to top, respectively. The presence of Cu impurities, affects the entire spectrum (not shown here). In this figure we have focused on the region of spectrum corresponding to gap in the pristine diamond. By increasing the doping rate from 1.6 to 4.7 percent, the deviation in the DOS of Cu-substituted diamond from the DOS of perfect diamond becomes more and more significant.

The most spectacular effect of substituting Cu in the insulating host of diamond, is the formation of mid-gap impurity band. In the right panel of Fig. 1 DOS corresponding to
FIG. 2: (Color online) LDOS for $s$, $p$ and $d$ orbitals of Cu corresponding to three concentrations considered. Fermi level $E_F$ is indicated by vertical dashed line. MPG values on the right panel are given for comparison. As can be seen the contribution of $4s$ orbitals to the impurity band is negligible.

MPG is shown. By averaging over different geometries, the corresponding geometry averaged DOS in the left panel will be obtained. As can be seen in the figure, for both GA and MPG, the width of the impurity band increases with increasing the Cu concentration. At 4.7% Cu substitution, the gap completely disappears. The averaged Fermi energy, $E_F$ is indicated with vertical dashed line. As it is evident, although the most probable geometry in the case of $2/64$ impurity concentration gives a little gap in the spectrum, other geometries with high probability will fill in that small gap and the resulting GA density of states will be a metallic band. This indicates that the best known insulator, namely diamond, can be metalized by few percent Cu substitution. The important result from Fig. 3 is that in all three considered concentrations, and for both MPG and GA situations, only $t_{2g}$ sub-band of the $d$-orbitals contribute to the impurity band, while the $e_g$ sub-band will give energy levels inside the valence band.

Role of Cu atoms

To consider this question, we first examine the occupation of various orbitals. We find that unlike the atomic configuration $4s^23d^9$ of Cu, in the presence of carbon neighbors, the occupancy of $4s$ orbitals is changed as $4s^2 \rightarrow 4s^{0.5}$. The missing 1.5 electron changes the $3d^9 \rightarrow 3d^{0.5}$, $4p^0 \rightarrow 4p^1$. Hence $4p$ orbitals are pushed down to acquire occupancy of $\sim 1$. We find that the above Lowdin charges are more or less independent of the geometry, as well as concentration of Cu impurities. This can be qualitatively seen in Fig. 2 where local density of states (LDOS) for $s$, $p$ and $d$ orbitals of Cu are plotted. Therefore the relevant orbitals of Cu are both $4p$, as well as a subspace of $3d$ states.

To further identify which subspace of Cu $d$—orbitals contribute to impurity band, in Fig. 3 we resolve the contribution of $t_{2g}$ and $e_g$ sub-bands. In the case of one Cu atom, the impurity atom feels a perfect diamond environment; thereby giving three-fold degenerate $t_{2g}$ band and two-fold $e_g$ bands. Note that $e_g$ bands are located at lower energies with respect to $t_{2g}$ bands. By increasing the number of Cu atoms, the above crystalline degeneracies start to be lifted, as the crystalline environment at higher Cu concentrations will deviate from perfect diamond symmetry. At the same time the average distance between Cu atoms decreases. Especially in the case of three Cu atoms, diamond crystalline environment is totally lost in the DOS of MPG. Even after averaging over geometries, substantial degeneracy lifting in each $t_{2g}$ and $e_g$ sub-bands can be observed. The important result from Fig. 3 is that in all three considered concentrations, and for both MPG and GA situations, only $t_{2g}$ sub-band of the $d$-orbitals contribute to the impurity band, while the $e_g$ sub-band will give energy levels inside the valence band.
Role of neighboring carbon atoms

Now let us concentrate on the effect of neighboring carbon atoms on the formation of the impurity band. In Fig. 4, we plot DOS corresponding to three concentrations for MPG and GA. In terms of the relative weights of neighbors, both MPG and GA give similar results. Note that for one Cu impurity, MPG and GA quantities must always be the same. By moving from bottom to top (increasing the concentration) in Fig. 4 one notices that only at low concentration nearest neighbor (NN) carbon atoms contribute significantly. By increasing the concentration, contribution of NN carbon atoms compared to the Cu atoms is reduced and becomes as low as the next nearest neighbor (NNN) contributions. This can be attributed to the fact that at higher Cu concentration, average Cu-Cu distance is reduced and the Cu-Cu hopping matrix elements become dominant. At lower concentrations in addition to Cu-Cu hoppings, there is also substantial hopping amplitude between the dangling orbitals of neighboring carbon atoms. This can be thought of hopping between appropriate Wannier orbitals localized around Cu atoms which is composed of the dangling $2p$ orbitals of neighboring carbon atoms.

Based on a naive $sp^3$ picture of bonding in perfect diamond, one expects $2s$ and $2p$ orbitals of neighboring carbon atoms to have comparable contribution to the formation of impurity bands. However, Cu substitution drastically changes this picture. As can be seen in Fig. 5, in both MPG and GA situations $s$ orbitals are irrelevant and the contribution of NN and NNN carbon atoms comes from their $2p$ states. These contributions become comparable to local DOS arising from Cu atoms only in low Cu concentration limit. When comparing Figs. 4, 5 one has to note the scales. Note that 1/64 concentration can also be reproduced in the simulation with two Cu atoms in host supercell of 128 carbon sites. Therefore the growth in the relative weight of neighboring $p$ orbitals can be partly due to finite size artifacts of the simulation, which of course is expected to be minimal with the periodic boundary conditions employed in the calculations. Therefore we expect the neighboring atoms to have significant $2p$ orbital contributions for concentrations well below $\sim 1\%$. At higher concentrations, the contribution of neighboring atoms becomes less and less significant. A comparison of MPG and GA density of states in Fig. 5 indicates that the role of averaging is to slightly increase the contribution of $p$-orbitals which is essentially a statistical effect.
DISCUSSION AND CONCLUSION

Examining the bond lengths show that Cu-C bond is elongated by approximately 0.2 relative to C-C bonds in undoped structure which has been almost compensated by a similar decrease in the surrounding C-C bond lengths. C-C bonds far away from Cu undergo negligible changes of the order 0.01 Å. Therefore in terms of structural changes, Cu substitution will give rise to local effects. In terms of electronic properties, in the regime of \( t_{pd} \) being large, one would have a quarter-filled band of 3d holes, along with a half-filled 4p band constituting the impurity band. In this limit for large enough Coulomb correlations among the Wannier orbitals derived from parent 4p states, the electron-like band undergoes a Mott transition, while the 1/4-filled hole bands derived from \( t_{eq} \) states can be subject to various forms of density waves [28]. Theoretically speaking, in the opposite limit when \( t_{pd} \) is large, the original half-filled electron band and the quarter filled hole band, get mixed giving rise to an effective quarter filled band whose electrons have a mixed character,

\[
\epsilon_{i\sigma} = \frac{d_{i\sigma}^\dagger + p_{i\sigma}^\dagger}{\sqrt{2}}.
\]

This can be thought of as analogue of Zhang-Rice singlet state [23]. Although this limit seems to be hard to realize in the experiment, but from theoretical point of view it may prove useful in studying transition from two-band situation to effective one-band model. In the intermediate regime where \( |t_{pd}| \sim t_{pp}, t_{dd} \), copper doped diamond will offer an opportunity to study both theoretically and experimentally the competition between the instabilities of a half-filled electronic band [22] with that of a quarter-filled hole band [23]. Our model Hamiltonian [2] defines the competition between instabilities of two bands in the 3D. The randomness in the matrix elements can not be avoided, as there is no control over the location of Cu impurities. Robustness of Lowdin charges in various geometries imposed the restriction \( t_{dd}, t_{pp} > 0 \) for studying Anderson localization effects in such 3D bands. The fact that in \( t_{pd} \ll t_{pp}, t_{dd} \) limit electronic bands of 4p orbitals are half-filled, suggests the possibility of Mott-Anderson physics in 4p orbitals.

To summarize, from both experimental and theoretical point of view, impurity band formation in Cu/C system provides interesting ground to study the orbital selective phenomena and novel forms of Anderson localization properties in a combination of electron and hole like bands with different fillings in 3D.

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