A resolution to doping asymmetry puzzle in high Tc cuprates

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We present a microscopic model for 'electron doped' Nd$_{2-x}$Ce$_x$CuO$_4$ family and offer a resolution to a long standing doping asymmetry puzzle. Here, i) Ce atoms do not dope free electrons, instead a Ce atom effectively quenches a Cu$^{2+}$ spin moment at an adjacent site, at an energy scale > superexchange J of CuO$_2$ plane and 'site dilutes' the Mott insulator, ii) effective chemical pressure, caused by increased Ce substitution, induces a first order Mott insulator to superconductor transition in the CuO$_2$ plane. We predict, i) equal number of +e and -e carriers in metallic state and ii) a line of first order transition ending at a critical point in normal state. Phenomenology gets organized.

Following the seminal discovery of superconductivity in La$_{2-x}$Ba$_x$CuO$_2$ [1], the idea of resonating valence bond mechanism of superconductivity in 'hole doped Mott insulator' was born [2]. In this theory [3], based on a single band model, electron doping of Mott insulator should equally well lead to superconductivity and one expects some kind of symmetry between electron and hole doping. When a so called 'electron doped' superconductor Nd$_{2-x}$Ce$_x$CuO$_4$ was discovered [4] there was a surprise. At the level of phase diagram (figure 1a) there was a striking asymmetry and significant differences. A large body of experiments [4-23] devoted to a study of this asymmetry exists now. In spite of several theoretical [24] attempts, our understanding of this asymmetry is not satisfactory.

Antiferromagnetism in Nd$_{2-x}$Ce$_x$CuO$_4$ family extends to a doping of nearly 12 %, in contrast to a 2% doping in LSCO (figure 1). Superconductivity appears abruptly at a first order transition with a maximum Tc, which decreases on further Ce doping [4-6]. Hall and other transport measurements show anomalies [7,8], different from that shown by hole doped cases.

The large asymmetry naturally points to some missing features in the current modeling of superconductivity in Nd$_{2-x}$Ce$_x$CuO$_4$ family. In the present article we identify these features and propose a new model, where strong electron correlations continue to play major role. The missing features follow from some known experimental results and some physical arguments. Our model is consistent with the large body of existing phenomenology. It also makes some predictions.

We argue that root cause of doping asymmetry lies in the T'-structure of Nd$_{2-x}$Ce$_x$CuO$_4$ family and ambivalent (sic) character of Ce valence. T' differs from T, the structure of La$_2$CuO$_4$: apical oxygen of CuO$_4$ octahedra (T-structure) are displaced in the ab-plane and fall in line with the oxygens of CuO$_2$ layers along the c-axis. A remarkable consequence of missing apical oxygen in T'-structure seems to be a nearly 1 eV reduction in Mott-Hubbard gap in Nd$_{2-x}$Ce$_x$CuO$_4$ (compared to La$_2$CuO$_4$ ), as seen in recent x-ray scattering experiment [10]. This makes Nd$_2$CuO$_4$ a fragile Mott insulator, close to a Mott insulator to superconductor transition point. The unstable tetra valent state of Ce is likely to play a key role in quenching a Cu$^{2+}$ spin moment, and also generate required chemical pressure for a Mott insulator to superconductor transition, that we propose below.

In what follows, we define our microscopic model and discuss its solution. We also indicate how existing quantitative theoretical understanding on the hole doped case can be transferred to the Nd$_{2-x}$Ce$_x$CuO$_4$ family, because of some special feature of our model.

Hypothesis leading to our model are: A) CuO$_2$ planes are not electron doped by Ce reservoir, instead every Ce effectively quenches a Cu$^{2+}$ spin moment of an adjacent site, over an energy scale > superexchange J of CuO$_2$ plane and 'site dilutes' the Mott insulator. B) chemical pressure arising from increased Ce substitution, induces a first order Mott insulator to superconductor transition in the CuO$_2$ plane, resulting in a 'self doping' of Mott insulator with equal number of +e and -e carriers.

Our model is 'a site diluted Heisenberg model' for the insulating phase, which exists in the experimental up to a value of $x_c \approx 0.12$. For $x > x_c$, we have a conductor, described by a 'site diluted 2-species t-J model', which we elaborated later. In both cases, number of 'missing Cu sites' or 'diluted sites' is $Nx$, where N is the number of sites and x is the Ce density.
It should be mentioned that effective ‘site dilution’ as an experimental consequence of Ce doping (in the insulating antiferromagnetic order regime) is known in the literature\(^1\), including a recent theoretical fit of their neutron scattering result to the site diluted Heisenberg model by Mang et al.\(^2\). Results, which is behind the site dilution hypothesis are: i) the Neel temperature \(T_N\) has a slope which is the same as the slope for a well established site dilution situation namely La\(_2\)Cu\(_{1-x}\)Zn\(_x\)O\(_2\), and ii) the long range antiferromagnetic order continues to be a commensurate \((\pi, \pi)\) order. These two results are qualitatively different from the hole doped case, where \(T_N\) is suppressed completely by about 2 % doping and any magnetic quasi long range order is incommensurate and not at \((\pi, \pi)\).

We take site dilution as a phenomenological input to our modeling and do not discuss mechanism and theory behind it. As far the theory of site diluted 2D Heisenberg model, we refer to existing work in the literature.

Two sceneries are possible in metallic state \((x > x_c)\) of Nd\(_{2-x}\)Ce\(_x\)CuO\(_4\): i) Ce does not quench a Cu\(^{2+}\) moment (i.e., no site dilution), instead becomes Ce\(^{4+}\) and electron dopes the CuO\(_2\) layer, and ii) spin quenching (site dilution) continues and we reach metallic state through a Mott transition, induced by chemical pressure. Recent observation of Kondo like effect\(^12\) in Pr\(_{2-x}\)Ce\(_x\)CuO\(_4\), according to us, indicates that Ce continues to be involved in spin quenching in the metallic state. Further there is a strong indication of first order insulator to metal transition\(^13\), reminiscent of of ET-salts (organic superconductor), where pressure drives a Mott insulator to superconductor phase transition\(^25\). Thus we hypothesize that, based on the above and overall phenomenological grounds, our system undergoes a transition from a (site diluted) Mott insulator to (site diluted) superconductor. The pressure in the present case is an effective chemical pressure, arising from reorganization of electron wave functions and hopping parameters, arising from a strong electronic coupling to the cerium subsystem.

What do we know about pressure driven Mott insulator to superconductor transition? The present author recently predicted\(^27\) such a possibility in cuprates and other systems; Zhang\(^24\) has an independent and some what different approach. In our mechanism long range coulomb interaction, originally invoked by Mott plays a key role in establishing a strong first order transition. Our key new input is to view the metallic state close to the Mott transition as a ‘projected metal’, a ‘self doped’ Mott insulator, where superexchange survives in the conducting state. Within a simple tight binding model, the transition is viewed as a spontaneous creation of a small but finite and \emph{equal density} of -e (doubly occupied orbital or ‘doublon’) and +e (empty orbital or ‘holon’) charge carriers, whose individual number is approximately conserved at low energies. What is important is that the superexchange survives in this conducting state - this is a memory of the Mott insulator. The concentration of self doped carriers \(2y (= y + y)\) for e\(^-\) and e\(^+\) carriers) is decided by long range coulomb interaction, local dielectric constant and band parameters. A projected metal is meaningful as long as \(2y < < 0.5\) (fig.3b). Here 0.5 is density of doubly occupied and empty orbitals in one orbital tight binding model of free electrons at half filling.

In our work\(^27\), proposing a mechanism for Mott insulator to superconductor transition under pressure, we introduced a 2-species t-J model, to take care of the projected character of the self-doped state, and discussed superconductivity. While the insulating phase of Nd\(_{2-x}\)Ce\(_x\)CuO\(_4\) is described by a Heisenberg model on a diluted lattice, the conducting state is described by our 2-species t-J model on a diluted lattice:

\[
H_{2tJ} = \sum_{ij\sigma} -t_{ij}s_i^{\sigma}s_j^{\sigma}(e_i^{\dagger}e_j^\sigma - d_j^{\dagger}d_i^\sigma) + \text{h.c.}
\]

\[
- \sum_{ij} J_{ij}(S_i \cdot S_j - \frac{1}{4} n_i n_j)
\]

including local constraint \(d_i^{\dagger}d_i + e_i^{\dagger}e_i + \sum_{\sigma}s_i^{\sigma}s_i^{\sigma} = 1\). Summation over sites excludes ‘diluted’ sites. Here we have used the slave boson representation for an electron \(e_i^{\sigma} = e_i^{\dagger}s_i^{\sigma} + \sigma d_i^{\dagger}d_i^\sigma\), with e’s, d’s and s’s representing zero occupancy (+e), double occupancy (-e) and single occupancy (neutral). The first term of equation 1, represents holon hopping and doublon hopping, the second term the superexchange among neutral sites. The conserved number of singly occupied sites is fixed through a global constraint, \(\sum_{\sigma}s_i^{\sigma}s_i^{\sigma} = (1 - 2y)N\); this in turn also fixes the holon and doublon numbers to be \(yN\). As mentioned earlier, \(y\) is a self consistent parameter that depends on the chemical pressure, in our case on Ce concentration \(x\). The physics of long range coulomb interaction that caused a first order Mott transition is contained in our 2-species t-J model, parametrically through the self doping density \(y\).

How superconductivity arises in 2-species t-J model? We have shown earlier\(^27\) that for the case of bipartite lattice a 2-species t-J model can be exactly mapped onto the regular (single species) t-J model. This mapping follows once we recognize that d’s and e’s are hard core bosons and they also commute at different sites. The transformation \(d_i \rightarrow e_i^{\dagger}e_i\) implements the exact mapping. Here \(e_i^{\pm}\) on the A and B sublattices of the square lattice. As site dilution preserves the bipartite character of the square lattice, the mapping survives and we get a regular t-J model on the same diluted lattice.

Presence of (a small) next nearest neighbor hopping \(t’\) makes the transformation inexact. However, in such a case one can study the 2 species t-J model directly using various known approximate methods.

What is the effect of site dilution on the symmetry of superconducting order parameter. Site dilution is a
strong perturbation. One would expect, based on Anderson’s theorem on dirty superconductors, that Tc of d-wave superconductivity will be very sensitive to the site dilution disorder. Here, something remarkable happens and makes site dilution disorder less effective in suppressing d-wave superconductivity. We will not go into the details, except to point out that this happens within our RVB mean field analysis for the following reason. A general scatterer will cause phase randomization as cooper pairs scatter in k-space, because of the change in sign (arising from d_x-y^2 symmetry). However, our scatterer is a site dilution and phase randomization does not occur, as two sublattice character is preserved by site dilution. That is, in real space, the d-wave order parameter fits into a site diluted 2D square lattice without any frustration.

The above is consistent with what is experimentally known about symmetry of the superconducting order parameter and also the scale of superconducting Tc for the Nd_{2−x}Ce_{x}CuO_4 family. It should be pointed out that a d_x-y^2 to extended-S transition suspected in some experiments is allowed by our theory, as site dilution will have different quantitative effects on an extended-S solution and d_x-y^2 solution and might stabilise s-wave at higher dopings.

In the light of our model the following experimental results get organized and are less puzzling, and also some predictions follow. We summarize them below:

i) In a recent work, Tsukada et al. [16] found superconductivity in La_2CuO_4 in T'-structure, for trivalent rare earth substitution, La_{2−x}R_{x}^{3+}CuO_4; R = Lu and Y, among others. This is an unexpected and remarkable finding. A well known stable trivalent state of Lu and Y makes doping of CuO_2 plane unlikely. We suggest that La_{2}CuO_4 in T'-structure has an inherent enhanced chemical pressure, which is further increased by Lu or Y substitution leading to Mott insulator superconductor transition without external doping, via our mechanism.

A recent inelastic X-ray scattering study[17] gives a Mott Hubbard gap of Nd_{2−x}Ce_{x}CuO_4 smaller than LSCO by about 1 eV. This is an experimental evidence for different quantum chemistry in T and T' structure and that Nd_{2−x}Ce_{x}CuO_4 is under higher chemical pressure and close to a Mott transition point compared to La_{2}CuO_4 (figure 3a). It will be important to measure the Mott Hubbard gap in La_{2}CuO_4 in T'-structure, which according our suggestion will also be close to the Mott transition point.

ii) The shape of the superconductor-antiferromagnetic phase boundary and various experiments indicate a strong first order character of the transition and phase separation. Our hypothesis B not only explains it in a most natural fashion but also makes the following important prediction. On very general thermodynamic grounds, the first order transition (as it is driven by coulomb interaction among charges) will continue beyond the antiferromagnetic phase boundary into the paramagnetic normal state and end at a critical point, as shown in figure 2. This is experimentally established in organic superconductors, where pressure drives a Mott insulator to superconductor transition.

When the critical concentration x_c is small, disorder will have less effect on the first order line and the end critical point. As smaller critical x_c is realized in annealed Pr_{2−x}Ce_{x}CuO_4 and La_{2}CuO_4 systems, it may be easier to confirm our prediction of first order transition line and critical point in the normal state. Nuclear and muon spin resonance will be good local probes to study the above. Further, as the first order phase transition is charge driven, there will be a volume change across the phase boundary, due to coupling of the charges with the lattice. This can be detected by sound velocity, elastic
constant studies.

iii) In a recent paper, Anderson and Ong [19] have suggested that tunneling conductance should be intrinsically asymmetric, in either electron or hole doped Mott insulators. We have applied their analysis to our 2-species t-J model and find a symmetric tunneling conductance, as expected on symmetry grounds. There is some asymmetry to the extent of particle-hole asymmetry (arising from t' etc.). Recent results show [20] a high symmetry in the tunnelling conductance. In figure 4, the high symmetry in Nd$_{2-x}$Ce$_x$CuO$_4$ compared to the case of YBCO of reference [20] is exhibited; it is consistent with our proposal. To substantiate our model further, it will be interesting to perform more study on symmetry aspect of tunneling in Nd$_{2-x}$Ce$_x$CuO$_4$, as well as other systems with T' structure.

iv) Earlier electrical transport studies have invoked [7] the presence of two species of charges to explain certain anomalous results. It will be interesting to look for our effective carrier density $2\gamma$; and $2\gamma$ is determined by band parameters, dielectric constant and coulomb interaction physics.

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