Phase separation in high-$T_c$ cuprates

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Abstract. We develop a minimal non-BCS model for the CuO$_2$ planes with the on-site Hilbert space reduced to only three effective valence centers CuO$_4$ with different charge, conventional spin, and orbital symmetry, combined in a charge triplet, to describe the low-energy electron structure and the phase states of HTSC cuprates. Using the $S=1$ pseudospin algebra we introduce an effective spin-pseudospin Hamiltonian which takes into account local and nonlocal correlations, one- and two-particle transport, and spin exchange. The $T$-$\eta$ phase diagrams of the complete spin-pseudospin model for the CuO$_2$ planes were reproduced by means of a site-dependent variational approach within effective field approximation typical for spin-magnetic systems. Limiting ourselves to two-sublattice approximation and $nn$-couplings we arrived at several Néel-like phases in CuO$_2$ planes for parent and doped systems with a single nonzero local order parameter: antiferromagnetic insulator, charge order, glueless $d$-wave Bose superfluid phase, and unusual metallic phase. However, the Maxwell’s construction shows the global minimum of free energy is realized for phase separated states which are bounded by the third-order phase transition line $T^*(\eta)$, which is believed to be responsible for the onset of the pseudogap phenomenon.

1. Introduction

Many researchers argue that the main features of the cuprates superconductors phase diagram can be derived considering the disorder and intrinsic mesoscopic static/dynamic phase separation as a key property of these materials (see, e.g. Ref. [1]). However, a correct description of a phase-inhomogeneous state presupposes the use of an adequate physical model. Recent discoveries of anomalous properties of cuprates and nickelates with a $T'$-structure [2, 3] indicate the need to abandon the generally accepted concept of the parent composition as a Mott-Hubbard antiferromagnetic insulator. Instead, we propose to introduce a more universal definition of the "parent” system of CuO$_2$/NiO$_2$ planes with a nominal 3$d^9$ configuration for Cu/Ni sites, or "half-filling”, which, depending on the parameters determined by the "out-of-plane" potential and electron-lattice relaxation, can be found in various states, from an antiferromagnetic or non-magnetic insulator, Fermi metal, to a high-temperature superconductor. Furthermore, from our point of view, the explanation of the cuprate/nickelate puzzle should include some fundamentally new physics, which requires not only going beyond the Bardeen-Cooper-Schrieffer (BCS) paradigm of the superconducting state [4], but also revising a number of other well-established concepts. Following the spin-magnetic analogy proposed by Rice and Sneddon [5] to describe the three charge states (Bi$^{3+}$, Bi$^{4+}$, Bi$^{5+}$) of the bismuth ion in BaBi$_{1-x}$Pb$_x$O$_3$, earlier we started to develop a minimal ”unparticle” model for the CuO$_2$ planes with the ”on-site”
Hilbert space of the CuO$_4$ plaquettes to be a key element of crystal and electron structure of high-T$_c$ cuprates, reduced to states formed by only three effective valence centers [CuO$_4$]$^{7-}$-$6^-$$5-$ (nominally Cu$^{1+}$,$^2+$$^3+$, respectively), forming a “well isolated” charge triplet, or spin-pseudospin quartet (S = 1/2 for “parent” [CuO$_4$]$^{6-}$ center) [6, 7].

2. Effective spin-pseudospin Hamiltonian

As for conventional spin-magnetic systems, we can integrate out the high-energy degrees of freedom, and after projecting onto the Hilbert basis of well isolated charge triplet, or spin-pseudospin quartet, we have chosen, to arrive at the effective spin-pseudospin Hamiltonian obeying the spin and pseudospin kinematic rules with a charge density constraint, $\frac{1}{N} \sum_i \langle \hat{S}_{iz} \rangle = n$, where $n$ is the deviation from a half-filling:

$$\hat{H} = \hat{H}_{pot} + \hat{H}_{kin}^{(1)} + \hat{H}_{kin}^{(2)} + \hat{H}_{ex};$$

$$\hat{H}_{pot} = \sum_i \left( \Delta_i \hat{S}_{iz}^2 - \mu \hat{S}_{iz} \right) + \sum_{i>j} V_{ij} \hat{S}_{iz} \hat{S}_{jz};$$

$$\hat{H}_{kin}^{(1)} = - \sum_{i>j} \sum_{\nu} \left[ t^p_{ij} \hat{P}_{i-}^{\nu} \hat{P}_{j+}^{\nu} + t^n_{ij} \hat{P}_{i-}^{\nu} \hat{N}_{j+}^{\nu} + \frac{1}{2} t^m_{ij} \left( \hat{P}_{i+}^{\nu} \hat{N}_{j-}^{\nu} + \hat{P}_{i-}^{\nu} \hat{N}_{j+}^{\nu} \right) + h.c. \right];$$

$$\hat{H}_{kin}^{(2)} = - \sum_{i>j} \sum_{\nu} \left[ t^b_{ij} \left( \hat{S}_{i+}^{\nu} \hat{S}_{j-}^{\nu} + \hat{S}_{i-}^{\nu} \hat{S}_{j+}^{\nu} \right), \right], \hat{H}_{ex} = \sum_{i>j} J_{ij} (\hat{s}_i \cdot \hat{s}_j) = s^2 \sum_{i>j} J_{ij} (\sigma_i \cdot \sigma_j).$$

For the properties of the pseudospin ($\hat{S}_{iz}^{2}$) and spin-pseudospin ($\hat{P}_i^{\nu}, \hat{N}_i^{\nu}$) operators, see, for example, Refs.[7, 8]. The first on-site term in $\hat{H}_{pot}$ relates with the on-site density-density interactions, $\Delta = U/2$, $U$ being the local correlation parameter, or pair binding energy for composite boson, $\mu$ in the second term is the hole chemical potential, the third one describes the nonlocal correlations. Kinetic energies $\hat{H}_{kin}^{(1)}$ and $\hat{H}_{kin}^{(2)}$ describe a single- and two-particle transport, respectively, where $t^p, t^n, t^m$ and $t^b$ are integrals for the correlated single-particle and the composite on-site boson hopping, respectively. Operator $\sigma = 2\hat{s}^3$ in $\hat{H}_{ex}$ takes into account the on-site spin density $\hat{\rho}^{\nu} = (1 - \hat{S}_{iz}^{2})$. Depending on the values of the effective Hamiltonian parameters, the model predicts the possibility of realizing even for parent cuprates/nickelates both a typical antiferromagnetic insulating state (AFMI), charge order (CO), unusual Fermi liquid (FL) phase with electron-hole interplay and a bosonic superconductor (BS) phase with effective on-site hole bosons.

The atomic limit of the spin-pseudospin model, which assumes a complete neglect for kinetic energy, was considered within the mean-field approximation (MFA), Bethe cluster approach, and classical Monte-Carlo (MC) technique with a clear manifestation of the CO-AFMI phase separation (PS) (see, e.g., Ref.[9]). In the large ”negative-U” approximation, which assumes complete neglect for local correlations, single-particle kinetic energy, and spin exchange, the CuO$_2$ plane becomes equivalent to hard-core (hc) boson system. In addition to the conventional CO and Bose superfluid BS phases the MFA predicts the appearance of an unconventional uniform supersolid phase (SS) with the “on-site” coexistence of the insulating and superconducting properties[11]. However, detailed analysis of the hc boson model shows that the SS phase is a MFA artefact, de facto this homogeneous phase is intrinsically unstable[12]. For nn-interactions and finite temperatures the ”post-MFA” Maxwell’s construction shows that the phase-separated CO-BS phase has a lower energy than the uniform SS phase, though at $T=0$ the both phases have the same energy. This result is confirmed within Bethe cluster approximation[10]. Under doping away from half-filling, the CO phase undergoes PS: the superfluid BS and solid CO phases coexist but not as a single thermodynamic SS phase as predicted in the MFA[11]. Thus, the both limits of the complete spin-pseudospin system exhibit the PS effect typical of systems with competing order parameters.
Figure 1. (Color online) Model $T$-$n$ phase diagrams of the hole-doped CuO$_2$ plane calculated in the EF approximation ($n = p$ for the hole doping) with constant values of the Hamiltonian parameters (see inset); (a) phase diagram assuming main homogeneous phases with no allowance made for the possible coexistence of two adjacent phases; (b) phase diagram with the PS taken into account via the Maxwell’s construction. Dashed curves in (b) point to fifty-fifty volume fraction for two adjacent phases, yellow curves in present the third-order phase transition lines, these limit areas with 100% volume fraction.

3. Effective-field approximation for the complete spin-pseudospin model

Making use of the effective field (EF) theory which combines the MFA with the exact accounting of local correlations, the variational approach (VA) based on the Bogolyubov inequality for the grand potential, and the Caron-Pratt model for the on-site description of the FL phase [13], we were able to numerically calculate the phase diagrams of the complete spin-pseudospin CuO$_2$ system within the framework of a simplified model (two sublattices, nn-coupling,...) [8]. The left hand side of the Figure 1 shows an example of the phase diagram calculated given quite arbitrarily chosen parameters of the model Hamiltonian and assuming main homogeneous single-order parameter, or “monophases” with no allowance made for the possible coexistence of two adjacent phases. However, the numerical implementation of the Maxwell’s construction shows that the minimum of free energy corresponds to PS realized in the region of coexistence of phases separated by the first-order phase transition lines. This works for phases AFMI-FL, AFMI-BS, CO-BS, CO-FL, and BS-FL, but not for AFMI-CO (see Figure 1, the right hand side panel). We can immediately note that the mysterious pseudogap phase is nothing more than the AFMI-FL-CO-BS PS state with the third-order phase transition line $T^*(n)$, which separates the gapless 100% FL phase from the gapped phases, to be the highest pseudogap temperature. The PS model does predict several temperatures of the “third order” PS transitions limiting the PS phases, that is delineating areas with 100% volume fraction, and the temperatures of the percolation transitions, which can manifest itself in the peculiarities of the temperature behavior for different physical quantities. Obviously, the ground state and $T-n$ phase diagrams of the system described by the effective spin-pseudospin Hamiltonian are determined by the relationship between the values of the parameters, a relatively small change in the parameters can radically affect the phase diagram. Thus, a small increase in the local correlation parameter $\Delta$ and the transfer integral of composite bosons $t_b$ can lead to suppression of the both AFMI and CO phases in favor of BS and FL phases. It is this situation is shown in the phase diagram in the Figure 2a-b, calculated numerically with the parameters shown in the inset to the Figure 2a, which presents the results of conventional EF approach, while the phase diagram in the Figure 2b does illustrate the BS-FL interplay with the PS taken into account via the Maxwell’s construction. Such phase diagrams with no signatures of the long-range AFMI and CO orderings turn out to be typical of cuprates with an ideal, or almost ideal, $T'$-structure [2].
Figure 2. (Color online) Model $T$ - $n$ phase diagrams of the CuO$_2$/NiO$_2$ plane in the hole-doped cuprate/nickelate calculated in the EF approximation under constant values of the Hamiltonian parameters (see inset), which illustrate an AFMI-BS-FL and BS-FL interplay with (b,d) and without (a,c) PS taken into account. Solid yellow curves in (b,d) present the third-order phase transition lines, black solid curves point to fifty-fifty volume fraction for two adjacent phases.

as well as nickelates, the structure of which also lacks apex oxygen [3].

For the chosen values of the Hamiltonian parameters, the AFMI phase is energetically unfavorable, but its energy differs little from the energy of the BS and FL phases, so that the slightest 1% increase in the value of the exchange integral, or a corresponding decrease in the remaining parameters, is sufficient to restore the AFMI phase, albeit in a small region of the phase diagram (see Figures 2c,d). Interestingly, a similar effect of suppression/restoring of the AFMI phase is observed in $T'$-cuprates at the slightest change in the concentration of nonstoichiometric apical oxygen [2], accompanied by corresponding change of the external potential for CuO$_2$-planes.

4. Conclusion

Effective field theory for the model spin-pseudospin Hamiltonian points to the phase-separated coexistence of main phases AFMI, CO, BS, and FL to be the typical one for the CuO$_2$/NiO$_2$ planes in cuprates/nickelates. Despite the many simplifications our model approach is believed to be a reliable starting point for description of the 3D phase diagrams in cuprates/nickelates with experimentally observed $T_N$, $T_c$, and $T^*$ as the critical temperatures for the 3D phase transitions.

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