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Phase separation effect in cuprate superconductors

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In terms of the Ginzburg-Landau theory, we investigate the effect of coupling between the paramagnet-antiferromagnet (AF) phase transition, superconducting (SC) phase transition, and phase separation (PS) of doping holes in cuprate superconductors. It is found that in the presence of PS, the hole-rich metallic phase can coexist with the hole-poor insulating AF phase, and there is a metal-insulator transition with increasing doping concentration n beyond a percolation threshold. The occurrence of PS will lead to significant changes in the phase diagram: the SC phase appearing at lower n and the step dependence of T_c on n. These results are qualitatively consistent with experiments of photodoped and oxygen-doped cuprate perovskites.

Recently, phase separation (PS) in high-temperature superconductors[1] as well as in manganese oxides[2] has drawn a considerable amount of attention due to the ubiquity of the stripe phase in doped antiferromagnets.[3] The undoped parent compounds such as $LaCuO_4$ are insulators and exhibit a long-range antiferromagnetic (AF) order, which is rapidly destroyed as holes are doped into the CuO_2 planes. When the concentration of doped holes, n, is in a certain range, the material appears to be of a superconducting (SC) nature below the critical temperature ($T<T_c$). Experimentally, PS is found to appear at intermediate concentrations between the AF and SC regions in the T-n phase diagram.[1,4] For example, in oxygen-doped La_2CuO_{4+y} ($0.01<y<0.05$), a low concentration of holes as well as excess oxygen atoms may drive a macroscopic PS into a hole-rich metallic phase ($y \simeq 0.055$) and a hole-poor insulating AF phase ($y \simeq 0.012$). It was found that at low temperatures, this compound has a stable SC phase with $T_c \simeq 30$ K, independent of y,[5] strongly supporting the existence of the PS. Very recently, ^{63}Cu and ^{139}La NMR/NQR measurements of $La_{1.94}Sr_{0.06}CuO_4$ indicated that the SC phase may coexist with the spin-glass phase at low temperatures.[6] The coexistence of the SC phase with either the AF phase or the spin glass with AF-cluster nature stems from the microsegregation of the mobile holes in cuprates, forming hole-rich and hole-deficient regions. In spite of extensive studies of this PS with the t-J model[7] or the extended Hubbard model,[8] its fundamental mechanism still remains controversial at present.

In the phase diagram of $LaCuO_{4+y}$, there are at least three types of phase transitions: the AF phase transition at the Néel temperature T_N, the SC one at T_c, and the PS one at a critical temperature T_{ps}, below which the segregation of hole-rich and hole-poor regions occurs. In the absence of the PS, the AF and SC phase transitions are two independent ones and they occur at different doping concentrations. The presence of the PS will lead to a coexistence between them, the AF phase appearing in the hole-poor region and the SC phase in the hole-rich region. In present work, we use the phenomenological Ginzburg-Landau theory to investigate the coupling effects among these phase transitions. It is found that owing to the occurrence of the PS there will be a significant change in the phase diagram: the SC phase appearing at lower doping concentrations and step dependence of T_c on n. With increasing y from 0.01, as soon as the PS occurs, the SC droplets begin to appear in the AF matrix and so a small Meissner fraction can be detected at low temperatures. For light doping, however, the proportion of these SC droplets to the AF matrix is too small so that they cannot connect with each other and the sample still exhibits insulating behavior. As y is increased beyond a critical value, the SC regions are interconnected with each other and so the sample enters into superconducting phase with zero resistance. By using numerical simulations, we will show how to evolve from SC droplets separated by AF regions into an interconnected SC sample with increasing doped holes. This behavior is qualitatively consistent with experiment of oxygen-doped $LaCuO_{4+y}$ and photodoped cuprates.[1,9]

First, we consider two independent SC and AF phase transitions. They can be simply described by two local coarse-grained order parameters $\psi_1(\mathbf{x})$ and $\psi_2(\mathbf{x})$, respectively. The free-energy density for the SC phase transition is given by

$$f_{sc}[\{\psi_1(\mathbf{x})\}]=\frac{1}{2}\kappa_1[\nabla\psi_1(\mathbf{x})]^2+\frac{1}{2}(T-T_c)\psi_1^2(\mathbf{x})+\frac{1}{4}\beta_1\psi_1^4(\mathbf{x}). \tag{1}$$

Here κ_1 and β_1 are positive constants, and T_c is the transition temperature corresponding to the optimally doped superconductor. Similarly, the free-energy density of the paramagnetic (PM)-AF phase transition is given by

$$f_{af}[\{\psi_2(\mathbf{x})\}]=\frac{1}{2}\kappa_2[\nabla\psi_2(\mathbf{x})]^2+\frac{1}{2}(T-T_N)\psi_2^2(\mathbf{x})+\frac{1}{4}\beta_2\psi_2^4(\mathbf{x}). \tag{2}$$

Here κ_2 and β_2 are also positive constants, and T_N is the Néel temperature of the undoped parent compound. At this

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stage, both T_N and T_c in Eqs. (1) and (2) are taken to be their maximal values and their dependence on the doping concentration n has not been taken into account.

Second, we consider the PS of the doped holes. Under an AF background, lightly doped holes always favor to clump together in order to break fewer AF bonds.[10] Its mechanism can be thought of as a strong attractive interaction between holes, or an ejection of holes from the antiferromagnet.[1,11] To describe the PS, we introduce the position-dependent and coarse-grained order parameter: $C(\mathbf{x})=\alpha[2n(\mathbf{x})-n_1-n_2]$, where $n(\mathbf{x})$ is the average fraction of the doped holes per Cu atom around $\mathbf{x}$, n_1 and n_2 represent those in the hole-poor and hole-rich regions, respectively, and α is a constant. According to this definition, the order parameter is always equal to zero in the absence of PS ($n=n_1=n_2$); while as the PS occurs, $C(\mathbf{x})=\alpha(n_2-n_1)$ for $\mathbf{x}$ at the hole-rich region and $C(\mathbf{x})=-\alpha(n_2-n_1)$ at the hole-poor region. We apply the Ginzburg-Landau functional for the PS free-energy density as[12]

$$f_{ps}[\{C(\mathbf{x})\}]=\frac{1}{2}\kappa_3[\nabla C(\mathbf{x})]^2+f_1\left[\frac{1}{2}(T-T_{ps})C^2(\mathbf{x})+\frac{1}{4}\beta_3 C^4(\mathbf{x})\right]. \tag{3}$$

Here κ_3, β_3, and f_1 are positive constants, too. T_{ps} is the critical temperature at which the two-phase segregation begins to appear. It was reported that $T_{ps}\simeq 260$ K in La_2CuO_{4+x}.[13] In the absence of the gradient term, two minima of f_{ps} in Eq. (3) are given by $C(\mathbf{x})$ $C(\mathbf{x})=\pm\sqrt{(T_{ps}-T)/\beta_3}$ for $T<T_{ps}$ where the plus and minus signs correspond to hole-rich and hole-poor phases, respectively. Such a PS consisting of the hole-rich and hole-poor phases is very similar to that of a simple binary alloy consisting of two atomic species A and B. For the latter, the form of the free-energy functional f_{ps} has strictly been deduced by Cahn and Hilliard.[14] It is worth pointing out that Eq. (3) can describe not only a continuous phase transition at T_{ps} above which there is no PS, but also the PS of two-phase coexistence for $T<T_{ps}$.

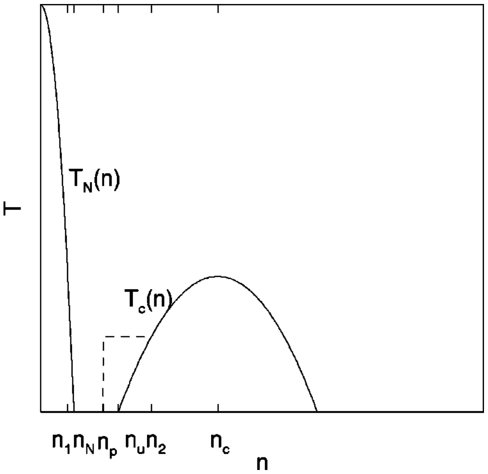

FIG. 1. Doping dependence of T_c and T_N in the absence of PS (solid lines). The change of $T_c(n)$ due to PS is shown by the dashed lines.

The next step is to model the coupling between the PS and the PM-AF phase transition as well as the SC one. There is no direct coupling between the AF and SC phase transitions, they are coupled via the PS, leading to their coexistence. With symmetry requirements, the free-energy density of the simplest coupling is given by

$$f_{cp}[\{C(\mathbf{x})\},\{\psi_1(\mathbf{x})\},\{\psi_2(\mathbf{x})\}]=\lambda_1\psi_1^2(\mathbf{x})[C(\mathbf{x})+C_{01}]^2+\lambda_2\psi_2^2(\mathbf{x})[C(\mathbf{x})+C_{02}]^2, \tag{4}$$

where λ_1 and λ_2 are the coupling coefficients, C_{01} and C_{02} will be discussed later. The total free-energy density is the sum of f_{sc}, f_{af}, f_{ps}, and f_{cp}. If renormalizing the prefactors of $\psi_1^2(\mathbf{x})$ and $\psi_2^2(\mathbf{x})$ in the total free-energy density, we obtain doping-dependent critical temperatures $T_c(n)$ and $T_N(n)$, having the following parabolic forms:

$$T_c(n)/T_c=1-[n_c-n(\mathbf{x})]^2/(n_c-n_u)^2, \tag{5}$$

for $n_u<n(\mathbf{x})<2n_c-n_u$, and

$$T_N(n)/T_N=1-n^2(\mathbf{x})/n_N^2, \tag{6}$$

for $n(\mathbf{x})<n_N$. Here n_c is the hole concentration of the optimally doped SC sample, n_N is the hole concentration where $T_N(n)$ reaches the vanishing point, and n_u is the minimal hole concentration of appearing the SC phase. In obtaining Eqs. (5) and (6), we have taken $C_{01}=\alpha(n_1+n_2-2n_c)$, $C_{02}=\alpha(n_1+n_2)$, $\lambda_1=T_c/[8\alpha^2(n_u-n_c)^2]$, and $\lambda_2=T_N/(8\alpha^2 n_N^2)$. In the absence of PS, $n(\mathbf{x})$ is independent of position and equal to the average hole concentration n. With the replacement of $n(\mathbf{x})$ by n in Eqs. (5) and (6), the doping dependence of T_c and T_N is shown by solid lines in Fig. 1. They are very similar to those in the T-n phase diagram of the high-T_c cuprates.[15] With the doped holes increasing from zero, the Néel temperature $T_N(n)$ decreases rapidly to zero followed by a so-called spin-glass region; as n is increased beyond n_u, the sample enters the SC region. We wish to point out here that both n_N and n_u are defined in the absence of PS, and n is the constant hole concentration independent of $\mathbf{x}$. In this case, $C(\mathbf{x})=0$ and $n_1=n_2=n$, so that $C_{01}=2\alpha(n-n_c)$ and $C_{02}=2\alpha n$. Both of them are coupled with the two order parameters $\psi_1(\mathbf{x})$ and $\psi_2(\mathbf{x})$ via Eq. (4) to make T_c and T_N have the correct doping dependence given by Eqs. (5) and (6). If PS occurs for $n_N<n<n_u$ and $T<T_{ps}$, the hole concentration is no longer homogeneous in the system and the resulting change in the T-n phase diagram will be discussed below. In this case, the order parameter $C(\mathbf{x})=\pm\alpha(n_2-n_1)$, so that $C(\mathbf{x})+C_{01}=2\alpha(n_2-n_c)$ and $C(\mathbf{x})+C_{02}=2\alpha n_2$ in the hole-rich region, $C(\mathbf{x})+C_{01}=2\alpha(n_1-n_c)$ and $C(\mathbf{x})+C_{02}=2\alpha n_1$ in the hole-poor region. It follows that the above choice of C_{01} and C_{02} guarantees the validity of Eqs. (5) and (6) in the PS case. In the presence of PS, the average hole concentration, $n=n_2\delta+n_1(1-\delta)$, where δ is the fraction of the hole-rich regions in the CuO_2 sheet. n_1 for the hole-poor phase must be smaller than n_N and n_2 for the hole-rich phase greater than n_u, so that a coexistence of SC and AF phases can be realized. As the same as n_N, n_u, and n_c, which can be found in

the real T-n phase diagram, n_1 and n_2 are also the intrinsic parameters of the material and have been determined in Ref. 5.

We employ the coupled time-dependent Ginzburg-Landau equations to calculate equilibrium distributions of order parameters $\psi_1(\mathbf{x})$, $\psi_2(\mathbf{x})$, and $C(\mathbf{x})$. Since $C(\mathbf{x})$ is conserved while $\psi_1(\mathbf{x})$ and $\psi_2(\mathbf{x})$ are nonconserved, the equations for them are given by[16,17]

$$\frac{\partial C}{\partial t}=D\nabla^2\frac{\delta F(\{C\},\{\psi_1\},\{\psi_2\})}{\delta C}, \tag{7}$$

$$\frac{\partial \psi_1}{\partial t}=-\tau_1\frac{\delta F(\{C\},\{\psi_1\},\{\psi_2\})}{\delta \psi_1}, \tag{8}$$

and

$$\frac{\partial \psi_2}{\partial t}=-\tau_2\frac{\delta F(\{C\},\{\psi_1\},\{\psi_2\})}{\delta \psi_2}, \tag{9}$$

where $F=\int(f_{sc}+f_{af}+f_{ps}+f_{cp})d\mathbf{x}$ is the total free energy, D, τ_1 and τ_2 are the kinetic coefficients. By considering a two-dimensional lattice of 128×128 sites in size with periodic boundary conditions, we solve numerically Eqs. (7)–(9) with a finite-difference scheme in both time and space to simulate spatial equilibrium distributions of these order parameters. Starting from an initial condition of homogeneous distribution of doped holes, a segregation of the hole-rich and hole-poor phases can be obtained at $T<T_{ps}$.

In what follows we focus attention on the PS effect. For a given doping density ($n_N<n<n_u$) and temperature ($T<T_{ps}$), where the PS has appeared, taking $\alpha=1/(n_2-n_1)$, we have $C(\mathbf{x})=1$ for $\mathbf{x}$ in the hole-rich region and -1 for $\mathbf{x}$ in the hole-poor region, the average order parameter given by $\overline{C}=2\delta-1$ where $\delta=(n-n_1)/(n_2-n_1)$. We select three sets of doping densities: $\delta=0.1$, 0.5, and 0.9, corresponding to $\overline{C}=-0.8$, 0, and 0.8, respectively. Here we take La_2CuO_{4+y} as an example by using $T_N=300$ K at $n=0$, $T_c=45$ K at $n_c=0.16$, $n_N=0.025$. In the hole-poor AF phase of La_2CuO_{4+y}, $y\simeq0.012$ and the doping efficiency is 2 holes per excess oxygen atom,[5] so that $n_1=0.024$ and $T_N(n_1)=24$ K from Eq. (6); while in the hole-rich phase, $n_2=0.10$ and so $T_c(n_2)=15$ K. We wish to point out here that the preset Ginzberg-Landau approach is mostly suitable for the case where both order parameter $\psi_1(\mathbf{x})$ and $\psi_2(\mathbf{x})$ are small. This condition can be well satisfied when (T,n_1) is very close to the transition line of $T_N(n)$ from the left in Fig. 1 and (T,n_2) very close to that of $T_c(n)$ from the right. As either of them departs from the corresponding transition line, the present approach may be only aproximately suitable by neglecting high-order terms in the Ginzberg-Landau formalism. However, it is expected that the qualitative results remain valid as long as the departure is not very large. Other coefficients are taken: $f_1=5$, $\beta_1=\beta_2=\beta_3=250$, $\kappa_1=\kappa_2=\kappa_3=1$, and $\tau_1=\tau_2=D=1$. Figure 2 shows calculated results for the spatial distribution of $\psi_1(\mathbf{x})$, $\psi_2(\mathbf{x})$, and $C(\mathbf{x})$ with $T=10$ K. The black parts represent the hole-rich SC regions where $C(\mathbf{x})=1$, $\psi_1(\mathbf{x})\neq0$, and $\psi_2(\mathbf{x})=0$; while the white parts indicate the hole-poor regions where $C(\mathbf{x})=-1$, $\psi_1(\mathbf{x})=0$, and $\psi_2(\mathbf{x})\neq0$, exhibiting a coexistence of the AF and SC phases at $T<T_c(n_2)$. If $T_c(n_2)<T<T_{ps}$, the AF phase will coexist with a normal metallic phase.[18] Evidently, such an AF and SC (or metallic) phase separation arises from the aggregation of the doped holes.

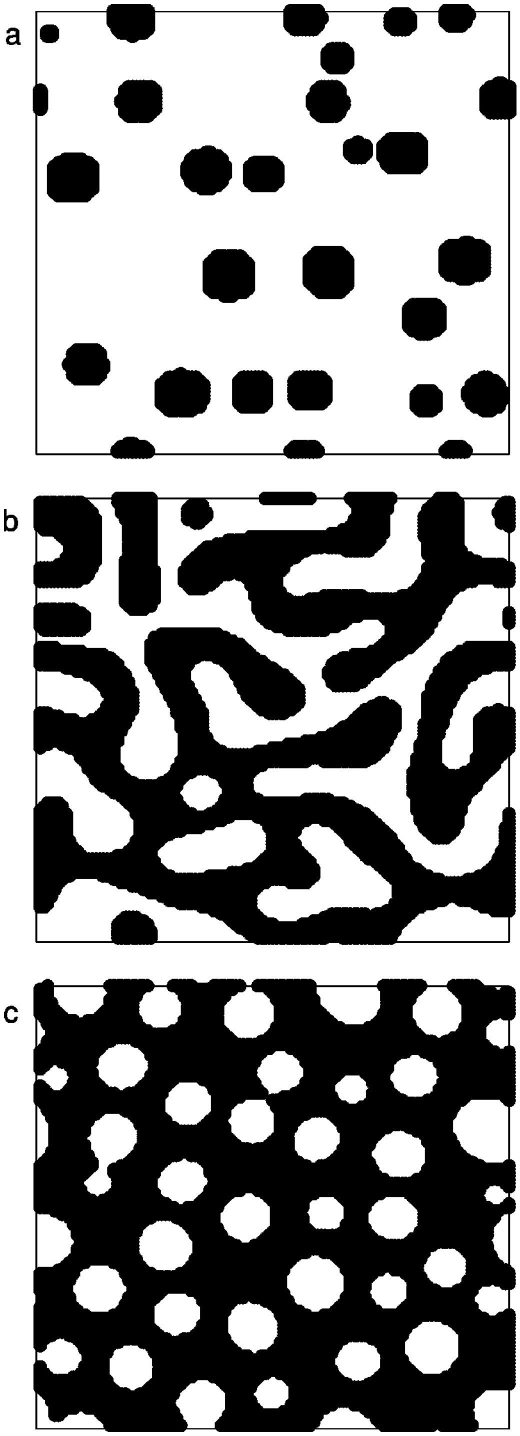

FIG. 2. Growth of the SC phase in AF regions with increasing doping concentration: (a) $C(n)=-0.8$, (b) $C(n)=0$, and (c) $C(n)=0.8$. Black and white regions represent SC and AF phases, respectively.

It is shown in Fig. 2 that the SC phase grows gradually in the AF region as the concentration of doped holes increases. At low hole concentrations (n slightly greater than n_1), only some SC droplets appear and they are separated by the insulating AF region, as shown in Fig. 2(a). In this case, even though the Meissner effect may be detected, zero-resistance

SC behavior can not be realized. As the hole concentration is increased to a percolation threshold, $n_p \simeq (n_1 + n_2)/2$, these SC droplets connect with one another to form connected channels of zero resistance. At this moment, the insulating sample suddenly becomes a superconductor and thus there is a discontinuous jump in T_c from zero to $T_c(n_2)$. With further increasing n, the SC regions continue to enlarge but the hole concentration of the SC regions remain unchanged. As a result, T_c exhibits a plateau of $T_c = T_c(n_2)$ for $n_p < n < n_2$. Such a jump in T_c at n_p and a plateau of T_c are plotted as dashed lines in Fig. 1, which are the main changes in the phase diagram resulted from PS. In Fig. 2(c), where n is smaller than and close to n_2, AF regions become disconnected and are encircled by the SC region. The picture above agrees basically with the experiment of the photodoped crystals of $YBa_2Cu_3O_{6.3}$. Photons with high energy can stimulate electron-hole pairs; while the electrons are rapidly captured by oxygens, the holes keep staying on CuO_2 planes and clump together to form metallic SC droplets separated by the AF region. This scenario is derived from the experimental result that the photoinduced conductivity of the sample increases rapidly below T_c, but does not go to infinity because the SC clusters have not been macroscopically connected to each other (below the percolation threshold). With increasing time and intensity of illumination, the SC regions in the sample continuously enlarge, and so a photogenerated metal (SC)-insulator tranistion may occur due to PS.

The present approach is readily extended to describing the PS of two SC phases with different T_c's. If there still appears a PS for $n > n_2$ at low temperatures, a lower-T_c SC phase and a higher-T_c one could coexist, so that there would be another jump of T_c and another higher-T_c step in the T_c-n phase diagram. As a result, the single-step dependence of T_c on n shown in Fig. 1 would become two-T_c-step ladderlike. Such a picture can account for the coexistence of two SC phases with $T_c \simeq 15$ K and 32 K observed experimentally in $LaCuO_{4+y}$ with $0.05 < y < 0.1$.[5]

The patterns shown in Fig. 2 are time-dependent dynamic characteristic obtained from Eqs. (7)-(9). Without long-range Coulomb interactions, the PS effect would make the SC (or AF) droplets enlarge with time under the condition that the total area of these droplets remain unchanged. However, the long-range Coulomb repulsion between holes always exists in the cuprates and they are unfavorable to the tendency of PS. The competition between PS and the Coulomb interactions will give rise to frustrated PS with large-amplitude, low-energy fluctuations in hole density. We wish to point out that the picture given in this paper is basically suitable also for a frustrated PS system. Although the Coulomb interactions are not explicitly included in the present phenomenological calculation and so it is difficult to obtain the accurate size of the SC (or AF) droplets, we can simply show the growth process of the SC phase on the AF background and how to give rise to a insulting-metallic (SC) transition with increasing doping concentration.

In summary, we have used the Ginzburg-Landau approach for the doped-hole PS and its effect on the phase diagram of the cuprate oxide. Owing to the occurrence of PS, the hole-rich SC phase and the hole-poor insulating AF phase can coexist with each other, so that the SC behavior of the sample will appear at lower doping concentrations and there will be a step doping dependence of T_c. It is shown that the SC droplets gradually enlarge in the AF background with increasing doping density; at the percolation threshold, they form connected SC channels, resulting in a insulator-metal transition. The theoretical picture is qualitatively consistent with experimental results of photodoped and oxygen-doped cuprate superconductors.

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