Periodic charge-density modulations and gap anisotropy in chiral $d + id$ and $f$-wave superconductors

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Abstract

We identify a novel type of periodic charge-density modulation in triangular-lattice materials near an incommensurate filling. These charge modulations are suppressed by a strong pairing interaction, leaving the pairing modulations with the same periodicity. We also explore the competition between charge-density waves and superconductivity in chiral $d + id$ or $f$-wave superconductors, and we discuss the implications for cobaltate and organic superconductors. Furthermore, we self-consistently calculate the local density of states around impurities and show that the gap anisotropy of the chiral $d + id$ state is doping-dependent, which naturally explains the close-to-nodal gap features of cobaltate superconductors as indicated by experiments.

1. Introduction

Over the past two decades, neutron diffraction and scanning tunneling microscopy (STM) experiments have revealed the presence of stripe or checkerboard modulations in high-temperature superconductors (HTSCs) [1–6]. In response to these discoveries, theorists have proposed that the effect may be understood in terms of quasiparticle interference due to scattering on impurities [7], or in terms of stripes [8, 9]. This has also led to discussions of the existence of a hidden-order phase for the pseudogap region of HTSCs [10, 11]. Recently a number of experiments have shown evidence pointing to the existence of a charge-density-wave (CDW) order competing with superconductivity in cuprates [12–15]. The similar energy scales of these two competing orders have led to the conjecture that high-temperature superconductivity emerges from a pre-existing CDW environment. This provides a mechanism for the formation of small Fermi surface pockets, which explains the negative Hall and Seebeck effects [16] and the T$_c$ plateau [17] in underdoped cuprates.

Compared with the widely studied square lattice, the triangular lattice is more complex in that there are more choices for the spin pairing pattern, and the density-wave modulations in triangular-lattice materials (TLMs) are largely experimentally unexplored. Stimulated by findings of large thermoelectric power at higher doping $x$ [18–21] as well as superconductivity for Na doping level $1/4 < x < 1/3$ upon intercalation with water [22], the cobaltate Na$_x$CoO$_2$ has triggered intensive research [23–43] as a result of the geometric frustration and the strong electron correlation inherent in systems with a triangular lattice. Experimentally, the NMR Knight-shift measurement [32] has recognized unambiguously that the electron pairing in the superconducting (SC) state of Na$_x$CoO$_2$ · $\gamma$H$_2$O (NCO) is in the spin-singlet form. On the other hand, theories of the $t - J$ or Hubbard model regarding a triangular lattice have suggested a chiral $d + id$ state with time reversal symmetry breaking [34–39, 41–43]. Actually, this $d + id$ state has also been proposed as the pairing mechanism of graphite-intercalated materials [44–50], which has generated a surge of interest recently [51–55]. Moreover, a variety of charge-ordering patterns have been considered for TLMs on the basis of the extended Hubbard model [56–58]. In particular, it has been shown that a large nearest-neighbor (NN) Coulomb repulsion can cause the so-called $\sqrt{3} \times \sqrt{3}$ charge order. An angle-resolved photoelectron spectroscopy (ARPES) study shows evidence that this scenario of charge modulations may be realized for $x = 1/3$ in the NCO system [31]. Recent neutron
diffraction and x-ray measurements of the triangular antiferromagnet AgNiO$_2$ also display evidence of charge order in the Ni triangular lattice while the system remains metallic [59, 60]. However, although much progress has been made in the understanding of TLMs many issues are still open. In particular, the extent to which charge or spin fluctuations [61] can act in expanding the range of pairing possibilities is much less understood.

Spurred by these important advances, we investigate here ordering modulations pinned by impurities in TLMs as well as the competition between superconductivity and charge-density waves (CDWs) in $d + id$ or $f$-wave superconductors, with possible relevance to NCO and organic superconductors. Based on the $t - t' - J - V$ model, we theoretically demonstrate that the appropriate breaking of the commensurability can induce charge fluctuations and show that charge-density modulations with a period of roughly $4.5\sqrt{3}$ lattice constants around impurities near an incommensurate filling can appear in TLMs. To the best of our knowledge, these interesting modulations have not been reported previously. Moreover, we also consider the competition between CDW and superconductivity in $d + id$ or $f$-wave superconductors and explore the local density of states around the impurity. It is found that low-energy quasiparticle resonance states appear at the impurity site in both pairing cases and meanwhile the asymmetric SC coherence peaks are strongly suppressed. The LDOS spectra gradually recover the bulk feature at sites far from the impurity, which show a $V$-shape in the $f$-wave case. In contrast, the far-site LDOS of the $d + id$ state shows a doping-dependent gap anisotropy, which is fully gapped at low doping levels but gradually evolves into close-to-nodal gap features as the doping increases. These results may be helpful in understanding some exotic properties of cobaltate and organic materials.

The rest of the paper is organized as follows. In section 2, we formulate the physical model and introduce Bogoliubov–de Gennes equations. In section 3, we consider the charge-density modulations in the non-SC state. We then discuss in section 4 the competition between CDW and superconductivity in $d + id$ or $f$-wave superconductors with an incommensurate or $1/3$ filling. The results of the local density of states are presented in section 5. A schematic phase diagram is proposed in section 6. Finally we conclude in section 7.

2. Physical model and general formalism

Within the slave-boson mean-field framework, we write the Hamiltonian as $H = H_0 + H_{\text{imp}}$, where $H_0$ and $H_{\text{imp}}$ describe the superconductor [29, 38] and impurity, respectively, which are given by

$$H_0 = -\sum_{ij} t_{ij} \left( \sqrt{x_i} x_j f_i^\dagger f_j + H.c. \right) + \sum_{i\sigma} \sum_{\tau} \left( \sigma m_{i+\tau} \right) + V_{\text{nn}} \left( 1 - x_{i+\tau} \right) f_i^\dagger f_{i+\tau} + \sum_{ij} \left( \sigma \Delta^\pm \bar{f}_{ij}^\dagger \bar{f}_{ij} \right) + \mu \sum_{i\sigma} f_i^\dagger f_i, \quad H_{\text{imp}} = \sum_i V_{\text{M}}(i) \left( f_i^\dagger f_{i+1} - f_{i+1}^\dagger f_i \right) + \sum_{i\sigma} V_{\text{NM}}(i) \left( f_i^\dagger f_i \right).$$

where $t_{ij} = t$ and $t'$ are the NN and NNN hopping integrals, respectively. Hereafter, we set $\beta = 1$ and measure the length in units of the lattice constant $a$. $(ij)$ denotes the sum over NNN pairs, and $\tau$ is the unit vector directing along the six NN bonds. $J$ is the antiferromagnetic coupling strength between NN sites. $\pm$ denotes the spin-triplet and spin-singlet pairings, respectively. The NN repulsion interaction $V_{\text{nn}}$ is a key parameter in determining the fate of the charge-ordering state. For instance, increasing $V_{\text{nn}}$ in $H_0$ may cause a $\sqrt{3} \times \sqrt{3}$ charge order to occur near $x = 1/3$ doping. The effective field $V_{\text{M}}(i)$ is introduced to model the exchange coupling between conducting electrons and the impurity spin. Although more-complex scenarios can be envisioned, we limit ourselves here to impurity fields acting along the $z$ direction. $V_{\text{NM}}(i)$ denotes the scattering potential of the non-magnetic impurity on site $i$. The self-consistent mean-field parameters are given by $x_i = 1 - \sum_{\sigma} \left( f_i^\dagger f_i \right)$, the magnetization $m_i = \left( 1/2 \right) \left( \left( f_i^\dagger f_i \right) - \left( f_i^\dagger f_i \right) \right)$, and the SC order parameter $\Delta^\pm = \left( V_{\text{eff}}/2 \right) \left( f_i^\dagger f_{i+1} \pm f_{i+1}^\dagger f_i \right)$, with $V_{\text{eff}}$ the phenomenological attractive pairing interaction.

The mean-field Hamiltonian $H$ can be diagonalized by solving the following Bogoliubov–de Gennes (BdG) equations:

$$\begin{bmatrix} H_{0,1} & \Delta^\pm \tau \varepsilon \pm H_{0,1}^\dagger \end{bmatrix} \begin{bmatrix} u_1 \\ v_1 \end{bmatrix} = E \begin{bmatrix} u_1 \\ v_1 \end{bmatrix}$$

where the spin-dependent single-particle Hamiltonian reads $H_{\text{imp}} = \sqrt{x_i} x_j \left( -t \delta_{i+\tau, j} - t' \delta_{i+\tau', j} \right) + \left( \sigma \right) \sum_{i\tau} m_{i+\tau} + V_{\text{nn}} \sum_i \left( 1 - x_{i+\tau} \right) + \sum_{i\sigma} \sigma V_{\text{M}}(i) \delta_{i-i_0} - \mu \right) \delta_{i_0}$. The subscripts $\tau$ and $\tau'$ denote the unit vectors directing
along six NN and NNN bonds respectively, and \( i_{\text{m}} \) is the position of the impurity site. The self-consistent parameters are given by \( n_{\text{m}} = \sum_{\nu} u_{\nu m}^2 f (E_{\nu}) \), \( n_{\text{m}} = \sum_{\nu} v_{\nu m}^2 f (E_{\nu}) \), and \( \Delta_{\mu} = \frac{1}{2} \sum_{\nu} [u_{\nu m}^2 v_{\nu m}^2 - v_{\nu m}^2 u_{\nu m}^2] \cosh \left( \frac{\beta E_{\nu}}{2} \right) \), where \( f (E) = 1 / (1 + e^{\beta E}) \) is the Fermi distribution function.

The BdG equations are self-consistently solved for a triangular lattice composed of 27 \( \times \) 27 sites (rhombus-like shape) under the periodic boundary conditions. The numerical calculations are performed at a very low temperature \( (T = 10^{-6} \text{ K}) \) to extract the low-energy physics. The \( f \)-wave SC (FSC) order parameter \([29, 40]\) at the ith site is defined as \( \Delta_f = (1/6) \sum \sin (3\theta_{ij}) \Delta_{ij,a} \), where \( \theta_{ij} \) is the azimuthal angle of six NNN lattice vectors, whereas for the \( d + id \) pairing the SC order parameter is \( \Delta_{d+id} = \sum \Delta_{ij,a} e^{2i\theta_{ij}} \), with \( \theta_{ij} = 2\pi/3 \). The gap functions of the \( d + id \) and \( f \)-wave pairing states are given by (i) \( \Delta_{d+id} = \cos \left( \sqrt{3} k_x \right) \) - \( \cos \left( \sqrt{3} k_y \right) \) - \( \sqrt{3} \sin k_x \sin \frac{\sqrt{3} k_y}{2} \); (ii) \( \Delta_f = \sin \left( \sqrt{3} k_x \right) \left( \cos k_y - \cos \frac{\sqrt{3} k_y}{2} \right) \), both of which clearly exhibit six-fold symmetry, as shown in Figure 1. Here we show the general gap symmetry of the \( d + id \) and \( f \)-wave states which may be achieved in triangular-lattice superconductors. For the \( d + id \) state, we only displayed the absolute value of the complex gap function (i.e., \( |\Delta| \)). Detailed analysis of the nodes in the NNN \( d + id \) state was carried out in \([41]\). As the doping level is increased, the Fermi surface shrinks accordingly. In particular, one finds that the Fermi surface near \( x = 0.4 \) in the \( d + id \) state may pass through the six nodes inside the first Brillouin zone (BZ), and thus this is in agreement with the recent NMR experiment \([32]\). This gap anisotropy of the \( d + id \) state near \( x = 0.4 \) is also confirmed by our spectral calculations, as discussed hereafter. The spin order parameter is defined as \( M_i = m_i \), i.e., the ferromagnetic order, for the sake of frustrated antiferromagnetism in the triangular lattice.

### 3. Charge-density modulations in the non-SC state

The system is explored by dividing the triangular lattice into two sublattices: a honeycomb sublattice (blue-yellow dots) and a \( \sqrt{3} \times \sqrt{3} \) triangular sublattice (red dots), as shown in Figure 2(a). The triangular lattice is divided so as to conveniently handle the \( \sqrt{3} \times \sqrt{3} \) CDW near \( x = 1/3 \) because electrons can exactly occupy the \( \sqrt{3} \times \sqrt{3} \) triangular sublattice when the NN repulsion interaction is large enough. For the translation invariant case, the corresponding energy band is given by \( E(k) = -2t \left( 2 \cos \frac{\sqrt{3} k_x}{2} \cos \frac{k_y}{2} - 2t' \left[ \cos \left( \sqrt{3} k_x \right) \cos \frac{\sqrt{3} k_y}{2} \right] \right) - \mu \). To reproduce the large Fermi surface around the \( \Gamma \) point, we set the hopping parameters \((t, t')\) of the band dispersion to be \((-1, 0.25)\), which can be compared with angle-resolved photoemission spectroscopy (ARPES) experiments \([31, 33]\). In line with \([43]\), the pairing may be mediated by strong spin fluctuations along the antiferromagnetically ordered wave vector \( Q \) in the \( \Gamma \) to \( K \) direction (see Figure 2(b)). The resulting Fermi surfaces for \( x = 1/3 \) and \( x = 0.6 \) have nesting or nearly nesting features along the antiferromagnetic wave vector \( Q \) and thus favor CDW instability or lead to strong spin fluctuations.

Let us now focus on exploring the aforementioned CDW. Figure 3 shows the typical charge-density modulations around an impurity for fixed \( x = 0.6 \) and \( J = 0.2 \). For a weak pairing interaction \( V_p = 0.3 \),
modulated CDW patterns with a period of roughly $4.5\sqrt{3}$ lattice constants are observed around impurities, accompanied by the destruction of superconductivity. This is interesting because it demonstrates that the appropriate breaking of the commensurability will induce large charge fluctuations. Clearly one also notices that the modulation period of these charge modulations is independent of the pairing symmetries because they are induced in the non-SC state. The dynamic pattern due to nesting by considering ordering wave vectors (see figures 1 and 2) can rotate in different pairing states (see figures 4 and 5 in section 4), but it does not affect the modulation period. The spatial distribution of the charge order around a magnetic impurity on the triangular lattice is plotted in figure 3(a), and the corresponding scattering-dot density plot is also presented. It is obvious that the maximum strength of the charge order parameter is induced at the central site. In contrast, the tendency is the opposite in the nonmagnetic impurity case, where the charge order vanishes at the central site due to the strong repulsive effect of the nonmagnetic impurity (see figure 3(b)). Notice that in both cases pronounced periodic modulations with six-fold symmetry are clearly seen around the impurity, with the satellite peaks or valleys regularly spaced throughout the triangular lattice. This implies a long correlation length ($\sim 4.5\sqrt{3}$), which is estimated to be about two nanometers (nm) if one assumes the lattice constant $a \sim 0.28$ nm. These results are expected to be detected by the x-ray diffraction or scattering measurements. As the pairing interaction is further increased, superconductivity occurs whereas the CDW modulations gradually disappear, as discussed hereafter.

4. Competing orders in chiral $d + id$ and $f$-wave superconductors

Let us begin by considering the $x = 0.6$ case for larger values of the pairing interaction which will lead to the emergence of superconductivity. In figure 4, we plot the spatial distribution of the $d + id$, charge, and spin order parameters around a magnetic impurity for $V_{so} = 0.9$ and $V_p = 0.6$. Clearly the $d + id$ order is suppressed to a vanishing value at the impurity site and is not uniform beyond a long distance from the central impurity.
Instead, the $d + id$ order also displays weakly modulated patterns with the same period as the charge modulations. Similar results are seen in the $f$-wave case, as shown in figure 5. To further verify the physical relevance of superconductivity to the charge fluctuations, we have again also performed self-consistent calculations of the superconductivity, charge, and spin order parameters for representative situations in both the $d + id$ and $f$-wave cases. It is found that for intermediate strength of the pairing interaction (not shown), CDW modulations may still persist in the charge order parameter, with a weaker modulation amplitude in comparison.
with those shown in figures 4 and 5. Furthermore, according to the calculations, the periodic charge modulations appear to be a robust feature for large $V_{nn}$, whereas the pairing interaction is kept not strong; this shares some similarities with the checkerboard modulations observed in cuprates [2]. A closer examination of the spatial distribution of the SC and charge order parameters reveals that as the SC order becomes more stable, the charge modulations are weakened by degrees. Given that the pairing interaction is larger than 0.68, i.e., $V_p > 0.68$, the $d + id$ SC order develops robustly whereas the CDW modulations tend to disappear thanks to the strong suppression of the charge fluctuations by superconductivity, as shown in figure 6. Similar behaviors are observed in the $f$-wave case (not shown). In the meantime, the charge density exhibits a Friedel-type oscillation only within a limited range around the impurity. As a side remark, it is also interesting to observe that a further

![Figure 5](image1.png)  
Figure 5. The same as figure 4 but for the $f$-wave pairing case.

![Figure 6](image2.png)  
Figure 6. The same as figure 4 but for $V_p = 1.0$.  

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increase in pairing interaction (for instance, $V_p > 1.0$) is accompanied by the gradual disappearance of the pairing modulations, leaving a homogenous SC order. Noticeably, no visible periodic modulations are observed in the spin order (for instance, as shown in figures 4(c) and 5(c)). This feature is fundamentally different from that in cuprates, where robust spin-density modulations are observed around impurities [63–66]. In light of the physics in the cuprates, one of the main questions that needs to be addressed is whether a triangular-lattice system exhibits a pseudogap, although little attention has been given to this [67–72]. Thus subsequent works are desired to clarify whether there is a connection between the pseudogap and periodic charge modulations in strongly correlated TLMs far away from half-filling.

The ordering processes just discussed indicate that charge order and superconductivity can compete with each other in triangular-lattice superconductors. To the best of our knowledge, these interesting modulations have not been reported previously for TLMs and are markedly different from those results obtained at low doping levels [40, 62], as discussed hereafter. Therefore, these results may be useful in understanding the charge ordering or modulated patterns observed in TLMs, as well as superconductivity near the charge order instability with an incommensurate filling.

Next we explore the system at $x = 1/3$ doping which is a natural commensurate value of the triangular lattice, and discuss the possible relevance to cobaltate superconductors. As shown by ARPES experiments [31, 33], the scenario of $\sqrt{3} \times \sqrt{3}$ charge modulations may be achieved near $x = 1/3$ doping in NCO. Theoretically, the charge dominant mechanism based on the $t$–$V$ model or $t$–$J$–$V$ model for NCO near $x = 1/3$ doping has been suggested [29, 40, 58, 62], which predicts spin-triplet $f$-wave superconductivity in the vicinity of charge instability. Unfortunately, the spin-triplet pairing mechanism is in conflict with the NMR measurement [32] which has convincingly demonstrated that the electron pairing of NCO is in the spin-singlet form. Therefore, we focus on the chiral $d + id$ pairing state possibly realized in NCO with $x = 1/3$. To achieve the appropriate critical temperature ($T_C$) consistent with experiment, we set $V_p = 0.6$ and $J = 0.2$. The NN repulsion interaction is chosen as $V_{nn} = 0.3$ so that superconductivity is favorable in the vicinity of charge instability. Figure 7 displays the typical spatial distributions of competing orders around a magnetic impurity in a $d + id$ wave superconductor. As expected, the $d + id$ SC order is strongly diminished at the impurity site, indicating the destruction of superconductivity by impurity scattering (see figures 7(a) and (d)). Additionally, the gap suppression is strongly localized near the impurity site and extends over several lattice sites from the impurity. These features resemble the images seen in the $f$-wave case (see figures 2 and 3 in [62]). In view of the similarities between the spatial distributions of competing orders in the $d + id$ and $f$-wave states, it is difficult to definitely distinguish the two pairing cases. Therefore, one should further calculate the quasiparticle spectra, as investigated in the following.
5. Local density of states at or near the impurity

It is known that nanoscale inhomogeneity or impurities can strongly affect the local density of states (LDOS) which is more directly related to the measured scanning-tunneling spectrum. By employing the supercell techniques, we compute the LDOS with energy $E$ at the site $i$ as

$$
\rho_i(E) = -\frac{1}{M_x M_y} \sum_{n,k} \left[ |u_{nk}^{\alpha d}|^2 \delta(E_{nk} - E) + |v_{nk}^{f}|^2 \delta(E_{nk} + E) \right],
$$

where $n$ is the index of the eigenstates and $k$ is the Bloch wave vectors to the impurity unit cells. In this work, we take $M_x \times M_y = 15 \times 15$. The system Hamiltonian $H$ is invariant under a supercell translation.

Figure 8 shows the calculated LDOS spectra at or near the impurity. In both the $d + id$ and $f$-wave states, in-gap states are observed at the impurity site, reflecting resonances caused by magnetic scattering (see figure 8(a)). In contrast, the absence of in-gap resonances is observed in the CDW state, and the weight of the Van Hove singularity (VHS) peak near $E = 0.6$ seemingly shifts to the lower energy side due to $V_{nm}$. These results bear resemblance to those obtained in [40, 62]. At the NN site (see figure 8(b)), the LDOS spectra almost have their bulk characteristics restored, with VHS peaks near $E = 0.6$. Remarkably, the LDOS of the CDW state exhibits a nonzero value at $E = 0$, indicating that the ground state is metallic. For the FSC state, a notable feature is the nodal (called V-shape) gap structure near $E = 0$ in the LDOS, which is the signature of gapless SC states. In contrast with the $f$-wave state, the LDOS of the $d + id$ state is fully gapped (called U-shape) at low energies. The LDOS spectra at the NNN site exhibit a feature similar to that of the NN case, but more spectral weight transfers to the low-energy side (see figure 8(c)). For the fifth neighbor of the impurity site, one finds that the LDOS spectra gradually recover the bulk feature of the SC and CDW states, as shown in figure 8(d).

Now let us turn to the case of $x = 1/3$ doping, which is closely related to NCO. Because the triplet $f$-wave case was studied in our previous paper [40, 62], we concentrate in this discussion mainly on the singlet $d + id$ state, which is consistent with the NMR experiment [24, 32]. For comparison, the LDOS spectrum of the $f$-wave case [62] is also presented, as shown in figure 9. It is seen in figure 9(a) that a sharp resonant peak is created near $E = 0$.
at the impurity site in addition to another peak forming at the positive higher energy, which is analogous to the $f$-wave case (see the dashed red line). In addition, humps develop at the negative-energy side in both cases, as a result of the suppression of coherence peaks. Despite these similarities, the LDOS spectra at the NN, NNN, and fifth neighbor sites in these two cases show marked differences. In the $f$-wave case, the LDOS has its bulk feature rapidly restored, with the V-shape near $E = 0$ besides additional peaks at the high energy in the NN-site LDOS. Nevertheless, in the $d + id$ state, intra-gap resonant peaks are also observed in the LDOS at NN and NNN sites near $E = 0$. Strikingly, the far-site LDOS of the $d + id$ state is fully gapped (U-shape) at low energies but reverts back to V-shape above the energy gap. This may give rise to a crossover of the Knight shift from power law behaviors below $T_C$ to exponential decays at low temperatures. We show this interesting characteristic in more detail hereafter.

To see this crossover more clearly, we now proceed to investigate the LDOS spectra for various doping levels and show the gap anisotropy of the $d + id$ state. As explored in the functional RG calculation in [42], we also find the strong doping dependence of the gap anisotropy in this paper. However, there are still marked differences; [42] finds that the NN $d + id$ state is the most energetically preferred and that the higher harmonic contributions in the d-wave sector are irrelevant throughout the parameter space. However, our analysis (based on the $t - J - V$ model) indicates that the NNN $d + id$ state is energetically favorable and consistent with the conclusion of [41]. The reason for the discrepancy may lie in the fact that the multi-orbital effects are included in [42], whereas the single-band $t - J - V$ model is considered in the present work. On the whole, doping-dependent gap anisotropy is observed in all these studies on the basis of different models, which is in agreement with experiments. Physically, one finds that a generic NN chiral wave SC state has a full gap and the nodes are pinned to the first BZ center and boundary. As a result, the Knight shift or spin-lattice relaxation rate is expected to decrease exponentially below $T_C$ due to its nodeless character. In contrast, new nodes in the gap function of the NNN $d + id$ state may occur inside the BZ and thus can support a nodal or anisotropic $d$-wave SC state [41].

![Figure 9. The LDOS spectra at (a) the impurity site, and (b) its NN site (c) NNN site, and (d) fifth neighbor (5NN) in the $x = 1/3$ doping case, with $V_{nn} = 0.3$, $J = 0.2$, and $V_p = 0.6$ for the $d + id$ state (solid blue line). Data from the $f$-wave case in [62] are also shown for comparison (the dashed red line).]
Our numerical calculations confirm this general analysis. Typical results are presented in figure 10. In all doping cases, the magnetic impurity produces resonant states inside the \( d + id \) gap at the impurity site, and particularly sharp peaks show up in the low doping cases of \( x = 0.16 \) and 0.25 (see figure 10(a)). Moreover, there are two resonant peaks inside the gap at NN and NNN sites in the cases of \( x = 0.16 \) and 0.25, whereas the nonexistence of resonant peaks is observed in the \( x = 0.4 \) case, as shown in figures 10(b) and (c). For a low doping \( x = 0.16 \), the \( d + id \) state develops a full gap (U-shape) in the far-site LDOS as in an isotropic s-wave superconductor (see figure 10(d)). As a result, the spin-lattice relaxation rate \( T_1 \) will follow an exponential temperature dependence at temperatures below \( T_c \). On the other hand, for a higher doping of \( x = 0.4 \), a nearly V-shaped LDOS occurs for sites far from the impurity, which reflects the close-to-nodal feature of the bulk DOS at this doping level. Thus, one expects good agreement with the power law behavior in \( 1/T_1 \) at low temperatures as reported by NMR experiment [24, 32]. As for the \( x = 0.25 \) case, the far-site LDOS bears a close resemblance to the \( x = 1/3 \) doping site, with a crossover from a full gap to a near-V-shaped one, as previously illustrated. These results indicate that the gap anisotropy of the chiral \( d + id \) state is doping-dependent, and they naturally explain the close-to-nodal gap features of cobaltate superconductors as reported by experiments.

6. Phase diagram

According to the present calculations and previously related results of our group, we propose a rough temperature versus doping (\( T-x \)) phase diagram for doped triangular lattices, as shown in figure 11. This phase diagram encompasses a number of interesting phases, including frustrated antiferromagnetic (AFM), paramagnetic (PM), superconducting, and metal (M) phases. Since we cannot determine for certain whether it is a magnetic or a normal metal, we collectively call it ‘metal phase’ in this paper. The phase diagram can be explained as follows: antiferromagnetism disappears with increasing doping to give birth to superconductivity. \( T_c \) takes its maximum value near \( x = 0.3 \), but this SC phase is also suppressed for several degrees where a PM metallic phase is stabilized. This reflects the fact that the AFM correlations play roles in the SC state, similar to the

![Figure 10](https://i.imgur.com/3J5Q5Q.png)

**Figure 10.** Change of the \( d + id \)-wave gap anisotropy with doping. The LDOS spectra are calculated at (a) the center impurity site and (b) its NN site, (c) NNN site, and (d) fifth neighbor (5NN). The solid blue, solid red, and dashed-dotted green lines represent the LDOS of a doping level for \( x = 0.16, 0.25, \) and 0.4, respectively.
high $T_C$ cuprates. In addition, the AFM correlations depress $T_C$ much more in the low-doping than in the high-doping case; hence the asymmetric shrinking of the SC dome. Peculiarly, the outstanding feature in the phase diagram is that there are remarkable CDW fluctuations in the vicinity of $x = 0.13$ and 0.6, indicating the important role of charge dynamics. Generally, one can understand this as follows. The NN repulsive interaction repels electrons from NN sites, and as a result, there is a tendency for the electrons to occupy the NNN sites, which leads to the three-fold pattern. Since the electron density is equal or close to 1/3 in cobaltate superconductors, one expects that the three-fold CDW will be strong. Physically, the screening of the sodium ordering potential [73–76] by water molecules in NCO might suppress the tendency toward developing a charge ordering in the CoO$_2$ layer, which may then lead to the emergence of an SC state over other competing phases at low temperature. On the other hand, the new finding of the CDW fluctuations near $x = 0.6$ confirms that appropriate breaking of the commensurability will induce strong charge fluctuations which can compete with superconductivity. As a result, one may expect that these charge-density modulations near $x = 0.6$ may provide some clues to understanding the electronic or magnetic properties of NCO near $x = 2/3$. For instance, the nonexistence of a charge-ordered insulating state near $x = 0.6$ (see figure 8, the dashed green) is in agreement with experiments [25, 26]. Further diffraction measurements of NCO are desired to check these results. It is worth mentioning that these charge-density modulations or fluctuations can even exist without an impurity because they are not necessarily static charge orders. Instead, they may be dynamic and can be pinned by impurities so that they are more likely to be observed around impurities experimentally.

Since the values of $V_p$ and $V_{nn}$ vary, we plotted the T-x phase diagram only for fixed $J = 0.2$, $V_p = 0.6$, and $V_{nn} = 0.6$. AFM, PM, SC, and M denote the antiferromagnetic, paramagnetic, superconducting, and metal phases, respectively. CDW I stands for CDW fluctuations near $x = 1/3$ (dashed red line), where a three-fold charge pattern may be strong. CDW II refers to the CDW metal state near $x = 0.6$ (dashed blue line). Notably, a weaker pairing strength or a larger NN repulsive interaction can lead to the shrinking of the SC dome, as discussed in the text.

7. Conclusion

In summary, we have studied ordering modulations and gap anisotropy in chiral $d + id$ and $f$-wave superconductors by including the competition or coexistence between superconductivity and the charge and spin orders. An intriguing result is that a type of periodic charge-density modulations pinned by impurities is observed in chiral $d + id$ and $f$-wave superconductors near an incommensurate filling $x = 0.6$ for a weak pairing interaction. In particular, we must point out that the modulation period of these charge modulations is...
independent of the pairing symmetries because they are induced in the non-SC state, which might be detected by x-ray diffraction measurements of TLMs. Although the pattern can rotate in different pairing states, it does not affect the modulation period. As the pairing interaction is increased, the charge modulations are gradually suppressed, whereas a weakly modulated SC order with the same periodicity shows up. This confirms that the appropriate breaking of the commensurability will induce strong charge fluctuations which can compete with superconductivity. Notice that in both the $x = 1/3$ and $x = 0.6$ doping cases, chiral $d + id$ or $f$-wave superconductivity can be realized in a 2D doped triangular lattice for appropriate parameter ranges. Fermi surface topology and magnetic fluctuations play a crucial role in the emergence of the unconventional superconductivity. Physically, the $f$- and $d$-wave states are the natural candidates for superconductivity in triangular lattices, given that they are electronically mediated. Furthermore, we also computed an experimentally accessible quantity, the LDOS. It is shown that the resonant quasiparticle peaks are created at the magnetic impurity site, and a crossover from full gap to near-V shape is seen in the far-site LDOS spectra of the $d + id$ state, indicating that the gap anisotropy is doping-dependent. These results may be helpful in explaining the close-to-nodal gap features of NCO as a chiral $d + id$-wave superconductor. Therefore, our findings support the existence of chiral $d + id$ or $f$-wave superconductivity in a doped triangular lattice in the strongly correlated regime, and they provide insights into the SC phases of NCO as well as organic compounds.

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Appendix A. Size independence of the CDW modulations

Here we discuss the size independence of the CDW modulations near $x = 0.6$. As shown in figure A1, the CDW modulations share the same period with that exhibited in figure 3 where the triangular lattice is composed of 27 × 27 sites. Therefore, one verifies the size independence of the CDW modulations near $x = 0.6$. Indeed, similar situations are encountered in [63, 66] in which the 4a × 4a checkerboard CDW modulations in cuprates were shown to be independent of the lattice size. Thus this provides an explanation for the CDW modulations revealed by experiments [1–6].

References

[1] Tranquada J, Sternlieb B, Axe J and Nakamura Y 1995 Nature 375 561
[2] Hoffman J E, Hudson E W, Lang K M, Madhavan V, Eisaki H, Uchida S and Davis J C 2002 Science 295 466
[3] Howald C, Eisaki H, Kaneko N, Greven M and Kapitulnik A 2003 Phys. Rev. B 67 014533
[4] Vershinin M, Misra S, Ono S, Abe Y, Ando Y and Yazdani A 2004 Science 303 1995
[5] Hanaguri T, Lupien C, Kohsaka Y, Lee D H, Azuma M, Takano M, Takagi H and Davis J C 2004 Nature 430 1001
[6] Wise W D, Boyer M C, Chatterjee K, Kondo T, Takeuchi T, Ikuta H, Wang Y and Hudson E W 2008 Nat. Phys. 4 696
[7] Wang Q-H and Lee D-H 2003 Phys. Rev. B 67 020511
[8] Kivelson S A, Bindloss I P, Fradkin E, Oganesyan V, Tranquada J M, Kapitulnik A and Howald C 2003 Rev. Mod. Phys. 75 1201
[9] Vojta M 2009 Adv. Phys. 58 699
[10] Chakravarty S, Laughlin R B, Morr D K and Nayak C 2001 Phys. Rev. B 63 094503
