Distinct pairing symmetries of superconductivity in infinite-layer nickelates

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We report theoretical predictions on the pairing symmetry of the newly discovered superconducting nickelate Nd1−xSr2NiO2 based on the renormalized mean-field theory for a generalized model Hamiltonian proposed in [Phys. Rev. B 101, 020501(R)]. For practical values of the key parameters, we find a transition between a gapped \((d + is)\)-wave pairing state in the small doping region to a gapless \(d\)-wave pairing state in the large doping region, accompanied by an abrupt Fermi surface change at the critical doping. Our overall phase diagram also shows the possibility of a \((d + is)\)-to \(s\)-wave transition if the electron hybridization is relatively small. In either case, the low-doping \((d + is)\)-wave state is a gapped superconducting state with broken time-reversal symmetry. Our results are in qualitative agreement with recent experimental observations and predict several key features to be examined in future measurements.

Introduction. The recent discovery of superconductivity (SC) in the single crystal thin films of infinite-layer nickelates Nd1−xSr2NiO2 [1] has stimulated intensive debates on its underlying electronic structural properties and superconducting pairing symmetries [2–10]. Despite the similarities in the crystal structure and 3\(d^8\) configuration of the nickelate and cuprate superconductors, there are increasing evidences suggesting that these two systems might belong to different classes of unconventional SC. Earlier first-principles calculations have revealed subtle differences in their band structures [11–21]. In experiments, the parent compound NdNiO2 displays paramagnetic metallic behavior at high temperatures with a resistivity upturn below about 70 K, showing no sign of any magnetic long-range order [22]. This is in stark contrast with the cuprates whose parent compound is a charge-transfer insulator with antiferromagnetic (AF) long-range order. As a consequence, the nickelates may be modelled as a self-doped Mott insulator with two types of charge carriers [23], with the low-temperature upturn arising from the Kondo coupling between low-density conduction electrons and localized Ni-3\(d_x^2−r_y^2\) moments [24]. This produces both Kondo singlets (doubons) and holes moving through the lattice of otherwise nickel spin-1/2 background, suppressing the AF long-range order, and causing a phase transition to a paramagnetic metal [25]. Latest measurements [5, 25] and first-principle calculations [9, 13] confirm this scenario and reveal a special interstitial s orbital for the hybridization [9], which is missing in previous calculations.

We expect these differences to have an immediate impact on the candidate pairing mechanism. In cuprates, additional holes are doped on the oxygen sites in the CuO2 planes [26–29] and combine with the 3\(d_{x^2−r_y^2}\) spins of Cu-ions to form the Zhang-Rice singlets [30]. High temperature SC with robust \(d\)-wave pairing can be derived from an effective one-band \(t-J\) model [31–33]. In nickelates, Sr doping may not only introduce additional holes on the oxygen sites to form the Ni-O spin singlets or holons (a spin zero state) [3, 34], but also reduce the number of conduction electrons, thus tilting the balance between the electron and hole carriers of distinct characters. The Hall coefficient is then expected to vary gradually and change sign with doping or temperature. One thus anticipates more rich physics in the nickelate superconductors, whose pairing symmetry may be altered by the hybridization. Indeed, latest experiment has revealed a non-monotonic change of \(T_c\) in exact accordance with the sign change of the Hall coefficient [35, 36].

To further elucidate the pairing symmetry of the nickelate superconductors, we employ here the renormalized mean-field theory (RMFT) [37] and study the superconducting pairing symmetry based on a generalized \(K-t-J\) model [8] in Eq. (1) and Eq. (2). Our calculations lead to a global phase diagram depending on the hole concentration \(p\) and the conduction electron hopping \((t_c/K)\) which controls the effective strength of the Kondo hybridization. At small doping and with reasonable choices of parameters, our calculations reveal an unusual gapped \((d + is)\)-wave SC with the time-reversal symmetry breaking, which is distinctly different from the familiar cuprate superconductivity. For large doping, we find either extended \(s\)-wave pairing or pure \(d\)-wave pairing. The latter is quite robust and occupies a large region in the phase diagram. Comparison with experiment tends to favor a transition from the gapped \((d + is)\)-wave to gapless \(d\)-wave.
pairing states with increasing hole doping. We further predict that the SC transition is accompanied with an abrupt Fermi surface change associated with the breakdown of the Kondo hybridization, causing potentially a crossover line in the temperature-doping phase diagram as observed in recent Hall measurements 35, 36.

Model Hamiltonian and RMFT. - We start by first introducing the generalized $K-t$-J model for the nickelate superconductors, given by $H = H_{t-J} + H_K$. The $t$-$J$ part describes the hole doped lattice of Ni 3$d_{x^2-y^2}$ spins with the nearest-neighbor AF superexchange interactions.

$$H_{t-J} = - \sum_{\langle ij \rangle} \left( t_{ij} P_G d_{i \sigma}^\dagger d_{j \sigma} P_G + \text{h.c.} \right) + J \sum_{\langle ij \rangle} S_i \cdot S_j,$$

where $d_{i \sigma}$ and $d_{i \sigma}^\dagger$ are the annihilation and creation operators of the Ni 3$d_{x^2-y^2}$ electrons, respectively, $t_{ij}$ is the hopping integral between site $i$ and $j$, and $P_G$ is the Gutzwiller operator to project out doubly occupied electron states on the Ni sites. For simplicity, we consider only the nearest neighbor hopping (NN) $t$ and next-nearest neighbor (NNN) hopping $t'$. The AF superexchange $J$ is induced by the O-2$p$ orbitals but greatly reduced compared to that in cuprates. The Kondo hybridization part is given by,

$$H_K = -t_c \sum_{\langle ij \rangle, \sigma} \left( c_{i \sigma}^\dagger c_{j \sigma} + \text{h.c.} \right) + \frac{K}{2} \sum_{\langle j_{x,y,z} \rangle, \sigma, \sigma'} S_j^\sigma c_{j \sigma}^\dagger \tau_{\sigma \sigma'} c_{j \sigma'},$$

where $c_{i \sigma}$ ($c_{i \sigma}^\dagger$) are the annihilation (creation) operators of the conduction electrons from Nd 5$d$, interstitial $s$, or other extended orbitals, $t_c$ describes the effective hoping amplitude of the conduction electrons projected on the square lattice sites of the Ni$^{4+}$ ions, $\tau_{\sigma \sigma'}$ ($\alpha = x, y, z$) are the spin-1/2 Pauli matrices, and $K$ is the effective Kondo exchange coupling.

In the parent compounds LnNiO$_2$ (Ln=Nd, La, Pr), the total electron density ($n_c + n_d$) is one per unit cell, hence the total holon density $n_h = n_c$. For Sr doped compounds, the hole doping $p = n_h - n_c > 0$. Analyses of the Hall coefficients at high temperatures suggest that the average number of the conduction electrons is always small, i.e., $n_c = N^{-1} \sum_{\langle ij \rangle} \langle c_{i \sigma}^\dagger c_{j \sigma} \rangle \ll 1$, where $N$ is the total number of the lattice sites.

For the RMFT calculations, the Gutzwiller renormalization factor should be included to approximate the projection operator that projects out the doubly occupied states. We have $g_t = n_h/(1 + n_h)$ for the constraint electron hopping $t$ and $t'$, $g_J = 4/(1 + n_h)^2$ for the AF Heisenberg exchange $J$, and $g_K = 2/(1 + n_h)$ for the Kondo exchange coupling $K$. Four different mean-field order parameters are then introduced to decouple the quartic AF Heisenberg spin exchange and the Kondo exchange interactions:

$$\chi_{ij} = \langle d_{i \uparrow}^\dagger d_{j \uparrow} + d_{i \downarrow}^\dagger d_{j \downarrow} \rangle, \quad B = \frac{1}{\sqrt{2N}} \sum_k (u_{13}^k u_{24}^k + u_{14}^k u_{43}^k - u_{21}^k u_{34}^k - u_{22}^k u_{33}^k),$$

$$\Delta_{ij} = \langle d_{i \uparrow}^\dagger d_{j \downarrow}^\dagger - d_{i \downarrow}^\dagger d_{j \uparrow} \rangle, \quad D = \frac{1}{\sqrt{2N}} (c_{j \uparrow}^\dagger d_{j \uparrow} + c_{j \downarrow}^\dagger d_{j \downarrow}).$$

The resulting mean-field Hamiltonian has a bilinear form and can be expressed in the momentum space,

$$\mathcal{H}_{mf} = \sum_k \Psi_k^\dagger \left( \begin{array}{cccc} \chi(k) & K_D & \Delta^*(k) & K_B^* \\ K_D^* & \epsilon_c(k) & K_B & 0 \\ \Delta(-k) & K_B & -\chi(-k) & -K_B^* \\ K_B & 0 & -K_D & -\epsilon_c(-k) \end{array} \right) \Psi_k,$$

where the Nambu spinors are defined as $\Psi_k^\dagger = (d_{k \uparrow}^\dagger, c_{k \uparrow}^\dagger, d_{-k \downarrow}, c_{-k \downarrow})$, and the matrix elements are

$$\chi(k) = -\sum_\alpha \left( t g_{\ell} + \frac{3}{8} J g_{\delta} \chi_\alpha \right) \cos(k \cdot \alpha)$$

$$-t' g_{\ell} \sum_\delta \cos(k \cdot \delta) + \mu_1,$$

$$\epsilon_c(k) = -t_c \sum_\alpha \cos(k \cdot \alpha) + \mu_2,$$

$$\Delta(k) = \frac{3}{8} J g_{\delta} \sum_\alpha \Delta_\alpha \cos(k \cdot \alpha),$$

$$K_D = -\frac{3}{4} g_K K \frac{D}{\sqrt{2}}, \quad K_B = -\frac{3}{4} g_K K \frac{B}{\sqrt{2}}.$$
FIG. 1: Theoretical phase diagram of the superconductivity with varying hopping $t_c/K$ and hole concentration $p$. At small doping, the pairing symmetry is primarily $(d + is)$-wave SC. At large doping, the pairing is either $s$-wave SC for small $t_c/K$ or $d$-wave SC for large $t_c/K$.

where $u_{ij}^k$ are given by the matrix elements of $U_k$, and the last two equations fix the chemical potentials $\mu_1$ and $\mu_2$, respectively.

**Numerical results.** For clarity, we define $\Delta_s = |\Delta_x + \Delta_y|/2$ and $\Delta_d = |\Delta_x - \Delta_y|/2$ to represent the $s$ and $d$-wave pairing amplitudes, respectively. To numerically solve these self-consistent equations, we first fix the practical parameters based roughly on the experimental analyses and first-principle results. The Kondo coupling $K$ is considered to be the largest energy scale and thus chosen as the energy unit ($K = 1$). To simplify the discussions, only the numerical results for the NN hopping $t = 0.2$, the NNN hopping $t' = -0.05$, and the AF Heisenberg spin exchange $J = 0.1$ are presented. The density of the conduction electrons is set to $n_c = 0.1$. These parameters may vary among different systems but the qualitative physical features will not be changed.

First of all, the overall phase diagram is displayed in Fig. 1 with the values of $t_c/K$ and the hole concentration $p$. We find a dominant $d$-wave pairing symmetry in the phase diagram, which, for small $t_c/K$ and large doping, turns into an extended $s$-wave state. Most intriguingly, we find a large region of the $(d + is)$-wave pairing for small hole doping. This exotic pairing state breaks the time-reversal symmetry and its presence reflects a unique feature of the nickelate superconductivity due to the interplay of the Kondo and Mott physics in comparison with the cuprates.

Details on the transition from the mixed $(d + is)$-wave SC to the pure $d$-wave SC can be found in Fig. 2(a) for an intermediate $t_c/K = 0.25$. The critical hole doping is $p^* \approx 0.13$, which is comparable with the experiment but may vary with $t_c$ and other controlling parameters. The transition is accompanied with vanishing Kondo mean-field parameters $B$ and $D$, implying a breakdown of the Kondo hybridization in the large doping side. It also implies that the $s$-wave component is primarily associated with the Kondo hybridization effect and the $d$-wave component is from the usual $t$-$J$ model. The corresponding Fermi surface structures in these two different doping regions can be extracted from the minimal energy contour of the SC quasiparticle excitation energy. Two typical dopings for $p = 0.05$ and $p = 0.2$ are plotted in Figs. 2(b) and 2(c), and the corresponding SC gap functions are plotted in Figs. 2(d) and 2(e). For small doping $p < p^*$, the normal state has a large hole-like Fermi surface around four Brillouin zone corners, while for large doping, two types of charge carriers are effectively decoupled and give rise to two separate electron-like Fermi surfaces around the Brillouin zone center. The physics of the pure $d$-wave pairing region is similar to that of heavily hole-doped cuprates for this particular doping. We have...
pure doping effect as in cuprates. Associated with the breakdown of the hybridization but shitz transition of the Fermi surfaces, but it is no longer tions displayed in Figs. 3(d) and 3(e). We still see a Lifshitz transition. Again, the Fermi surfaces for finite. Hence the hybridization effect is not affected across parameter region in our generalized model. Discussions and Conclusion. The generalized $K$-$t$-$J$ model contains several key energy scales that need to be fixed for better experimental comparison in each individual compound. While the conduction electron hopping $t_c$ may be roughly estimated from band calculations, the constraint electron hoppings $t$ and $t'$ are strongly renormalized due to the background AF correlations. Following our previous analyses, the Heisenberg superexchange $J$ is expected to be roughly the order of 10-100 meV, which is smaller than that of cuprates due to the larger charge transfer energy between O-2$p$ and Ni-$3d_{x^2−y^2}$ orbitals. The Kondo exchange interaction $K$ is estimated to be the order of 100-1000 meV [8, 9]. This justifies our choice of $J/K$ in current numerical calculations. In any case, our results may serve as a qualitative guide for future studies on nickelate superconductors.

It is worthwhile comparing our results with the available experiment. Recent systematic measurements on the resistivity and Hall coefficients in Nd$_{1−x}$Sr$_x$NiO$_2$ have revealed a non-monotonic doping dependence of the superconducting $T_c$, whose local minimum coincides with the sign change of the Hall coefficient [35, 36]. The latter further gives rise to a crossover line in the temperature-doping phase diagram of the nickelate superconductors. A straightforward comparison suggests that the experimental observation may correspond to our derived transition from the $(d + is)$-wave pairing to the $d$-wave or $s$-wave paring. The concurrent change in the Hall coefficient therefore marks a potential Fermi surface change, in resemblance of that observed in some heavy fermion systems owing to the breakdown of the Kondo hybridization [38]. The latter also leads to a delocalization line in the temperature-pressure or temperature-doping phase diagram [39, 40]. It is thus attempted to link the experiment with our theoretical proposals, predicting the SC transition from a gapped $(d + is)$-wave state to a gapless $d$-wave pairing state, with the crossover line in the temperature-doping plane potentially associated with the Fermi surface change due to the Kondo hybridization.

If this is the case, one may further expect several key features to be examined in future experiment: 1) a superconducting transition between gapped and gapless pairings with increasing doping to be best revealed by the scanning tunneling spectroscopy or the penetration depth measurement; 2) time-reversal symmetry breaking in the low-doping gapped SC phase to be detected in the $\mu$SR or Kerr experiments; 3) Fermi surface reconstruction accompanying the superconducting transition to be measured by the quantum oscillation experiments or angle-resolved photoemission spectroscopy. Additionally, there may also exist other exotic properties associated with the quantum critical point, besides the non-Fermi liquid behavior which has been observed in superconducting nickelate thin films with $\rho \sim T^\alpha$ and $\alpha = 1.1 − 1.3$ [8]. It will be interesting to see if future measurements will confirm these preliminary predictions or suggest a different parameter region in our generalized model.

In conclusion, we have discussed the pairing symmetry of the newly discovered superconducting nickelate Nd$_{1−x}$Sr$_x$NiO$_2$ based on the RMFT for a generalized $K$-
$t$-$J$ model. Our calculations reveal an interesting interplay between the Kondo and Mott physics. For practical choices of the parameters, we find a transition from a gapped $(d + i s)$-wave state to a gapless $d$-wave state with increasing doping. An extended $s$-wave pairing has also been predicted but requires sufficiently small hopping and large doping. For the former transition, our calculations suggest a concurrent Fermi surface change and a corresponding crossover line in the temperature-doping phase diagram due to the breakdown of the Kondo hybridization. Our proposal is in good agreement with available experiments and gives several key predictions for further verification.

Note Added. As we are finishing this manuscript, single particle tunneling measurements \cite{11} were reported on superconducting nickelate thin films with $T_c \approx 9.1\,K$, and two distinct types of tunneling spectra were revealed: a V-shape feature with a gap maximum 3.9 meV, a U-shape feature with a gap about 2.35 meV, and some spectra with mixed contributions of the two components. These spectra were ascribed to different Fermi surfaces from the conduction and Ni $3d_{x^2−y^2}$ orbitals. However, according to our present calculations, these distinct tunneling spectra observed at different locations on the thin films may be caused by different hole doping concentrations due to surface effects, so the different spectral shapes may correspond to the different pairing states in our theory. In this sense, the tunneling experiment is supportive of our theoretical prediction of multiple superconducting phases.

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