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Unconventional pairing in doped band insulators on a honeycomb lattice: the role of the disconnected Fermi surface and a possible application to superconducting β-MNCl (M = Hf, Zr)

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Abstract
We investigate the possibility of realizing unconventional superconductivity in doped band insulators on the square and honeycomb lattices. The latter lattice is found to be a good candidate due to the disconnectivity of the Fermi surface. We propose applying the theory to the superconductivity in doped layered nitride β-MNCl (M = Hf, Zr). Finally, we compare two groups of superconductors with disconnected Fermi surface, β-MNCl and the iron pnictides, which have high critical temperature T_c, despite some faults against superconductivity are present.

Keywords: β-MNCl, superconductivity, band insulator, Fermi surface, spin fluctuations, pnictides

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Layered nitride β-MNCl [1] (M = Hf, Zr) doped with carriers is one of the most interesting superconductors. The mother compound β-MNCl is composed of alternate stacking of honeycomb MN bilayer and Cl bilayer [2]. It is a band insulator which becomes a superconductor upon electron doping through Na or Li intercalation. The critical temperature T_c is relatively high, up to $\sim$25 K for M = Hf and $\sim$15 K for M = Zr. The bilayer honeycomb lattice consisting of M and N (figure 1) is considered the main cause of superconductivity, and the two-dimensional nature of the superconductivity has been revealed by nuclear magnetic resonance [3] and muon spin relaxation studies [4, 5]. Despite the relatively high T_c, both experimental and theoretical studies indicate extremely low density of states (DOS) at the Fermi level [6–8]. In fact, β-MNCl has the highest T_c among materials with the specific heat γ as small as $\sim$1 mJ (mol K)^2. The electron–phonon coupling is also estimated to be weak [6, 8–10], and the isotope effect is found to be small [11, 12]. In the superconducting state, the density of states recovers rapidly upon increasing the magnetic field [7], suggesting some kind of anisotropic pairing. As for the doping dependence, the DOS at the Fermi level stays nearly constant, but, for Li$_x$ZrNCl, T_c shows an increase upon lowering the carrier concentration until a sudden superconductor-insulator transition [13]. On the other hand, in Li$_x$HfNCl, T_c stays nearly constant in the doping range $x < 0.5$ [14]. Furthermore, for Li$_x$HfNCl, an

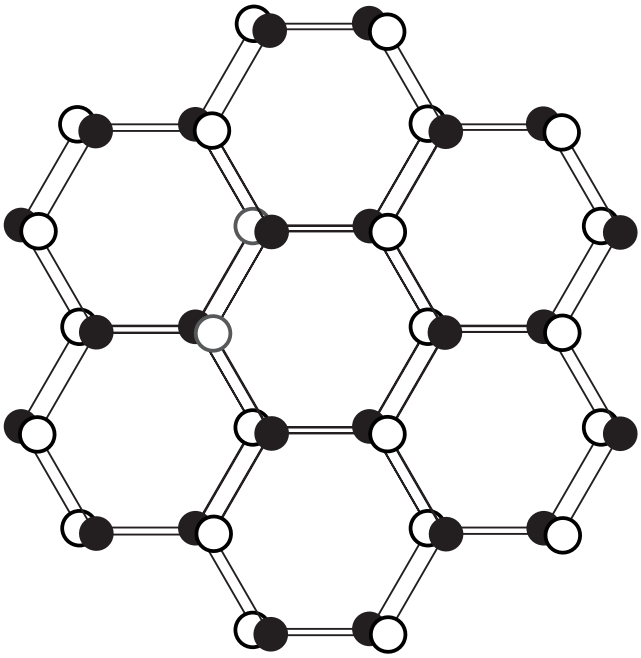

Figure 1. The bilayer honeycomb lattice. The black and white circles represent M(= Hf, Zr) and nitrogen atoms, respectively.

intercalation of organic (tetrahydrofuran) molecules between the layers enhances T_c [14]. These experiments suggest some kind of unconventional pairing. On the contrary, scanning tunneling spectroscopy experiments find an s-wave like, fully open gap [15, 16]. Specific heat measurements also suggest an s-wave like gap, but again, the doping dependence of the gap value is unusual. In the underdoped regime, the gap is large, while the gap becomes small as the doping level is increased, varying from a 'strong coupling' to an 'extremely weak coupling' regime [18].

Here, we first study the possibility of unconventional superconductivity by doping band insulators on a square or honeycomb lattice[1]. We find that the honeycomb lattice is a good candidate for realizing superconductivity, where the disconnectivity of the Fermi surface is important. Secondly, we consider β-MNCl. The two bands, which are closest to the Fermi level in the first principles band calculation [8], can roughly be reproduced by a *single* honeycomb lattice model where the above general theory can be applied. Finally, we compare two groups of superconductors with disconnected Fermi surface, β-MNCl and the iron pnictides, which have high T_c despite some faults against superconductivity are present.

2. Square lattice

Hubbard Model is a model that considers the on-site repulsive interaction U in a tight binding model. Let us start with the Hubbard model on a square lattice, where we consider the hopping integral t only between nearest neighbors. When the band filling n (number of electrons/number of sites) is about half, which corresponds to $n = 1$, strong

[1] Theoretically, a possibility of unconventional pairing mediated by charge fluctuations has been proposed in [17].

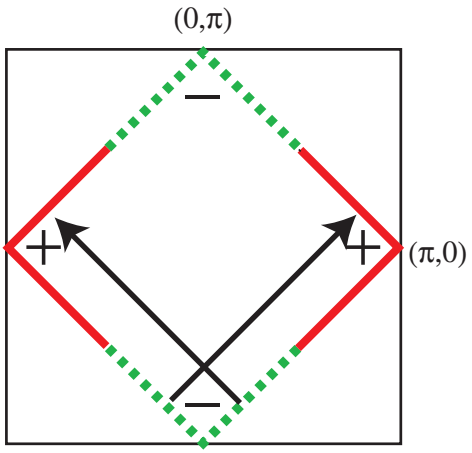

Figure 2. An explanation of the d-wave superconductivity due to spin fluctuations on the square lattice. The arrows represent the wave vector $\boldsymbol{Q}$ at which the spin fluctuations develop. The solid (dashed) lines are the portions of the Fermi surface where the gap has a positive (negative) sign.

antiferromagnetic spin fluctuations arise. The possibility of d-wave superconductivity mediated by these spin fluctuations has been discussed for the past several decades. The d-wave superconductivity can be understood as follows. Generally, superconductivity occurs due to pair scattering mediated by the pairing interaction $V(\boldsymbol{q})$. The gap equation can be written as

$$\Delta(\boldsymbol{k}) = -\sum_{\boldsymbol{k}'} \frac{\tanh[E(\boldsymbol{k}')/k_B T]}{2E(\boldsymbol{k}')} V(\boldsymbol{k}' - \boldsymbol{k})\Delta(\boldsymbol{k}'), \qquad (1)$$

where Δ is the gap, E is the quasiparticle dispersion, and T is the temperature. When the spin singlet pairing interaction is mediated by spin fluctuations, $V(\boldsymbol{k})$ is positive and takes large values at large $\boldsymbol{Q}$, where the spin fluctuations develop. For the square lattice, where the spin fluctuations develop near $\boldsymbol{Q} = (\pi, \pi)$, we have to change the sign of the gap between the wavevectors $\sim(\pi, 0)$ and $\sim(0, \pi)$ in order to have a finite Δ as a solution for the gap equation, which results in a d-wave gap as shown in figure 2. By applying fluctuation exchange (FLEX) approximation to this system, which is a kind of self-consistent perturbation theory that collects random phase approximation type diagrams, we can obtain the Green's function and the spin susceptibility [19]. These can be plugged into the Eliashberg equation, whose solution gives d-wave superconductivity with T_c of the order $0.01t$, where t is the nearest-neighbor hopping integral (if $t \sim 1$ eV, T_c is of the order of 100 K).

The square lattice with only the nearest-neighbor hopping is a bipartite lattice which can be separated into A and B sublattices. Let us see what happens to the superconductivity if we introduce a level offset Δ between A and B sublattices. The introduction of Δ opens up a gap at the center of the band, so this amounts to investigating the possibility of unconventional superconductivity by doping carriers in band insulators (figure 3(a)). As shown in figure 4, we find that the introduction of Δ rapidly suppresses superconductivity. Thus, in case of the square lattice, chances are small for realizing unconventional superconductivity in the above sense.

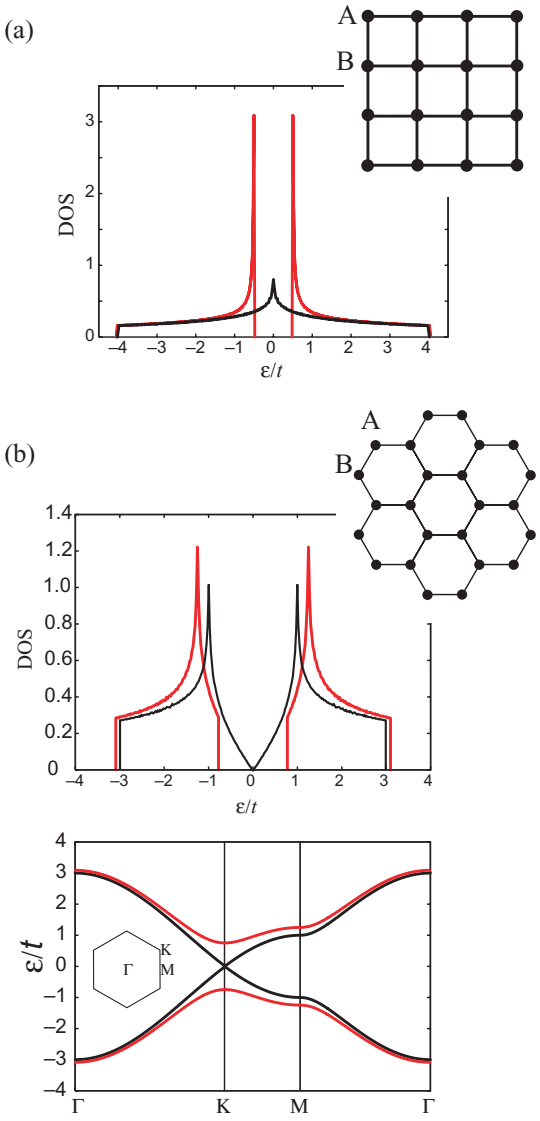

Figure 3. (a) The density of states for the square lattice with $\Delta = 0$ (black) and $\Delta = t$ (red). (b) The density of states (upper) and the band dispersion (lower) for the honeycomb lattice with $\Delta = 0$ (black) and $\Delta = 1.5t$ (red). The hexagonal Brillouin zone of the honeycomb lattice is shown in the inset of the lower panel.

3. Honeycomb lattice

Let us compare the above result for the square lattice with those for another two-dimensional bipartite lattice, namely the honeycomb lattice. In the honeycomb lattice, there are two sites in a unit cell, in which the two bands make point contact at K and K′ points of the Brillouin zone, resulting in a zero gap density of states (figure 3(b)). We show in figure 5(a) the maximum value of the spin susceptibility as a function of temperature for the band filling of $n = 1.08$, which corresponds to small electron doping. Surprisingly, we find that the spin susceptibility is nearly independent of T, which is in sharp contrast to the square lattice. For example, for the square lattice with $n = 0.7$, which is already substantially far from half-filling, we still have a strong enhancement of the spin susceptibility upon lowering the temperature. Upon further hole doping to $n = 0.65$, the spin susceptibility is suppressed, but even in that case, there is a moderate increase of the spin susceptibility upon lowering the temperature. In figure 5(b), we show the eigenvalues λ of the linearized Eliashberg equation as a function of temperature. T_c is the temperature where λ reaches unity. The density of states at Fermi level is nearly the same for the square lattice with

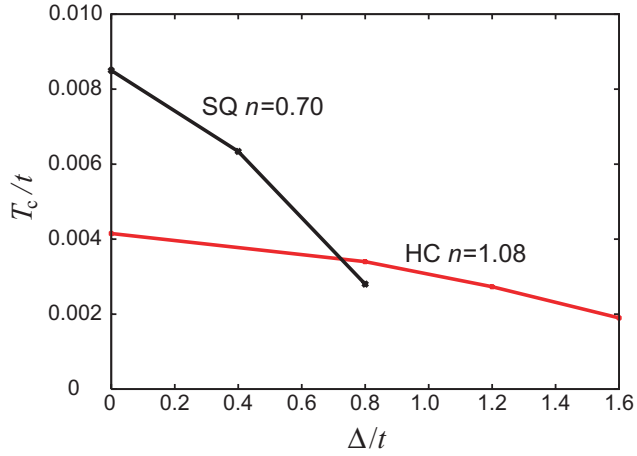

Figure 4. T_c as a function of the level offset Δ obtained by FLEX + Eliashberg equation for the square lattice with $U = 6t$, $n = 0.7$ (black) or for the honeycomb lattice with $U = 6t$ and $n = 1.08$ (red).

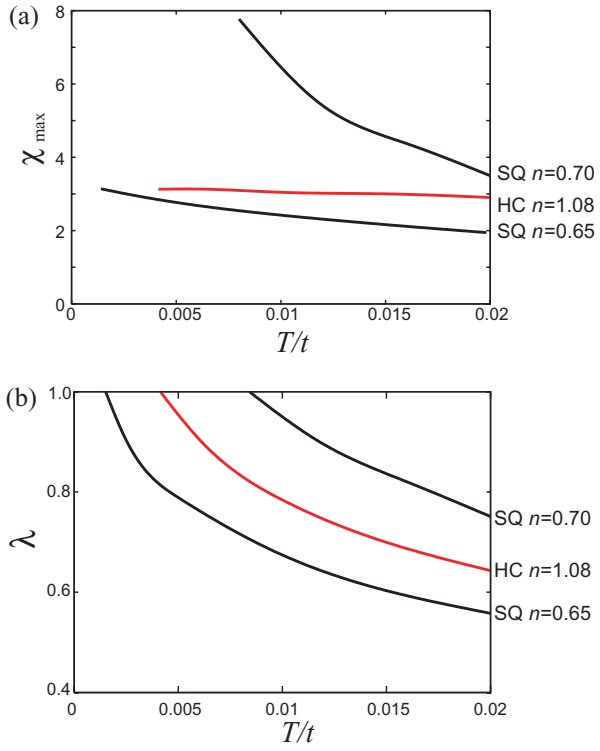

Figure 5. (a) The maximum value of the spin susceptibility as a function of temperature, obtained by FLEX for the square lattice with $n = 0.7$ or $n = 0.65$ and for the honeycomb lattice with $n = 1.08$. $U = 6t$ in all cases. HC and SQ stand for the honeycomb and the square lattices, respectively. (b) The eigenvalue of the linearized Eliashberg equation with the same parameters as in (a). The temperature at which $\lambda = 1$ is the T_c.

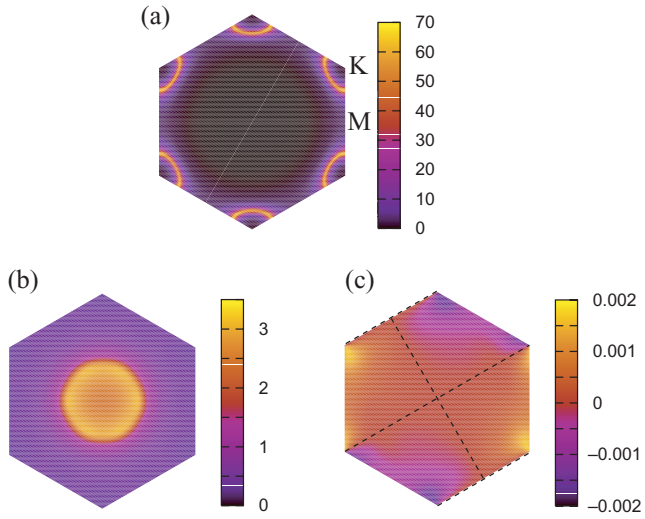

Figure 6. The contour plots of the FLEX result at the lowest Matsubara frequency for the honeycomb lattice in the hexagonal Brillouin zone with $U = 6t$, $n = 1.08$, and $T = 0.01t$ (a) The Green's function of the upper band squared, (b) the spin susceptibility, (c) the superconducting gap function.

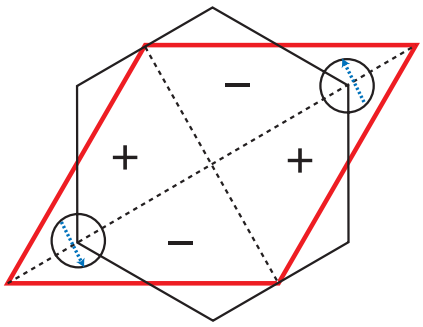

Figure 7. The Fermi surface (the two circles) and the sign of the gap function are schematically shown in the extended zone scheme. The dashed arrows represent the wave vectors at which the spin fluctuations develop.

$n = 0.65$ and the honeycomb lattice with $n = 1.08$, and also the spin susceptibility has similar values at low temperature, but still, the honeycomb lattice has larger λ and higher T_c. Thus, the Hubbard model on the honeycomb lattice has relatively high T_c despite the low density of states and weak, temperature independent spin fluctuations.

Figure 6(a) shows the contour plot of the Green's function squared, whose ridge corresponds to the Fermi surface. We see here two disconnected parts of the Fermi surface. The spin susceptibility (figure 6(b)) is maximized at wave vectors that bridge the opposite sides of each part of the Fermi surface. As can be seen more clearly in figure 7, the gap has a d-wave form, i.e. it changes sign across the wave vector at which the spin susceptibility is maximized. Note that one of the nodes of the gap does not intersect the Fermi surface because of its disconnectivity, which may be one reason why superconductivity is favored despite the low density of states and weak spin fluctuations. By symmetry, there are two degenerate d-wave gaps (say, d_{xy} and $d_{x^2-y^2}$, or any two linearly independent combinations), and the most probable

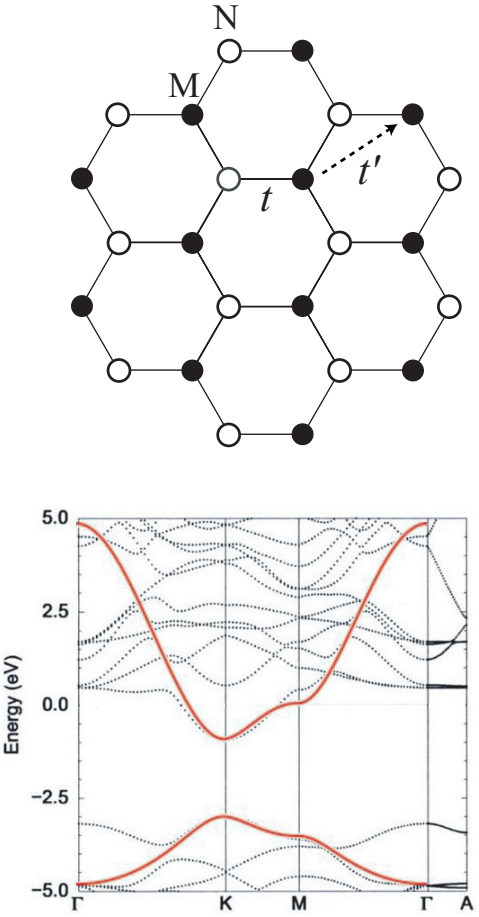

Figure 8. Upper panel: the tight binding model considered for β-MNCl. Lower panel: the first principles band calculation taken from [8] and the band dispersion of the tight binding model.

form of the gap below T_c is the form $d + id$, where the two d-wave gaps mix with a phase shift of $\pi/2$. Since the two d-wave gaps have nodal lines at different positions, this kind of mixture leads to a gap that has a finite absolute value on the entire Fermi surface. An important point is that if such a state is realized, the time reversal symmetry should be broken.

Now we introduce the level offset between A and B sites as we did for the square lattice. In this case, a band gap also opens in the center (figure 3(b)), so we once again investigate the possibility of superconductivity by doping band insulators. In this case, we find that superconductivity is relatively robust against the introduction of Δ. This may be because the density of states is already low in the original honeycomb lattice, so that the introduction of Δ does not affect superconductivity so much.

4. Application to β-MNCl

Here we apply the above theory to β-MNCl. Although β-MNCl has a bilayer honeycomb lattice, we find that the two bands closest to the Fermi level, obtained in the first principles calculation [8, 10, 20, 21], can roughly be reproduced by a *single* layer honeycomb lattice model consisting of alternating 'M' and 'N' orbitals with a level offset as shown in figure 8.

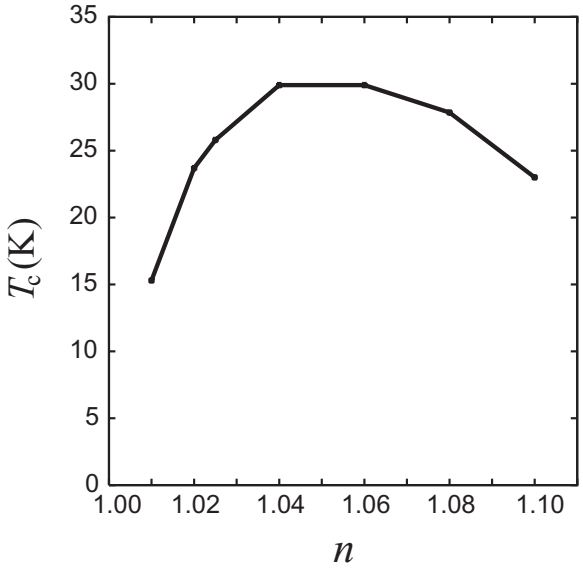

Figure 9. T_c plotted as a function of the band filling for the model shown in figure 8.

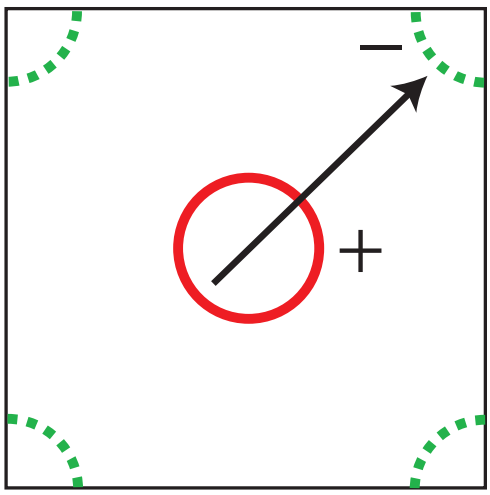

Figure 10. An example of fully open sign reversing gap on a disconnected Fermi surface is shown. The arrow shows the nesting vector at which the spin fluctuations develop.

Here we take $t = 1.2$ eV, $\Delta/t = 2.7$, and $t'/t = 0.35$. If we consider on-site repulsive interaction $U = 6t$ on both M and N orbitals[2], the model is similar to the one studied in section 2, except that distant hopping integrals t' have to be considered so as to reproduce the first principles band structure. Consequently, within the FLEX + Eliashberg equation approach, we obtain relatively high T_c of around 30 K as shown in figure 9.

Now we compare the present scenario with the experiments for β-MNCl. As mentioned in the Introduction, relatively high T_c is obtained despite the extremely low density of states and weak electron–phonon coupling [6–10], which can be explained within the present theory. The isotope effect is small [11, 12], which again seems consistent since the the present pairing mechanism is purely electronic. The cointercalation of organic molecules enhances T_c [14], and this also seems to be understandable within this kind of spin fluctuation mediated pairing, where the quasi two dimensionality is favored [22, 23]. As for the pairing symmetry, a fully open gap is observed in the experiments [15, 16], and this is consistent with the present scenario provided that the $d + id$ state is realized. It is hence interesting to investigate experimentally the possibility of time reversal symmetry breaking in the superconducting state of this material. The rapid recovery of the specific heat by applying the magnetic field [7], and also the unusual doping dependence of both the T_c and the magnitude of the gap [13, 14, 18] remain as interesting future problems.

5. Superconductivity in systems with disconnected Fermi surface

Finally, let us go back to the d-wave superconductivity on the square lattice. As mentioned, T_c obtained by FLEX is the order of $0.01t$, where t is the hopping integral. This can correspond to a high T_c in actual materials because t can be of the order of electron volt, but still, this is low compared to the original energy scale t. There are several reasons for the 'low' T_c, and one of them is that we have to have nodes of the gap *intersecting* the Fermi surface, because sign change of the gap is required in the case of spin fluctuation mediated pairing. In this context, we proposed some time ago that if there are disconnected parts of Fermi surface nested to some extent, we can change the sign of the gap between the disconnected peaces without the nodes intersecting the Fermi surface, and this can result in a high-T_c superconductivity [24, 25]. An example of such a Fermi surface is shown in figure 10. Possibilities of the disconnected Fermi surface playing important role in the occurrence of superconductivity or the determination of the pairing symmetry have been discussed for a cobaltate Na_xCoO_2 [26] and an organic superconductor $(TMTSF)_2X$ [27].

Quite recently, superconductivity has been found in iron-based pnictides [28, 29]. The highest T_c of this series of materials have reached 55 K [30]. Band calculations show that there are several disconnected parts of the Fermi surface in this material [31], where spin fluctuations can arise due to the nesting between them [32]. According to our Eliashberg theory calculation that takes into account such kind of spin fluctuations [33], the gap changes sign across the nesting vector of the Fermi surface, and the magnitude of the gap is especially large on the portion of the Fermi surface where the $d_{x^2-y^2}$ orbital character is strong as shown in figure 11. The nearest-neighbor hopping of this orbital is about 0.15 eV, which is quite small, and the experimentally observed maximum $T_c = 55$ K corresponds to about $0.04t$ which is higher than that can be reached in the single band square lattice.

Thus the two groups of materials seem to exhibit high T_c although some faults against superconductivity are present: for β-MNCl, relatively high T_c is obtained despite the extremely low DOS and weak spin fluctuations (and

[2] Generally, the on-site repulsion on the M site and N site can be different, but here, for simplicity, we take them equal.

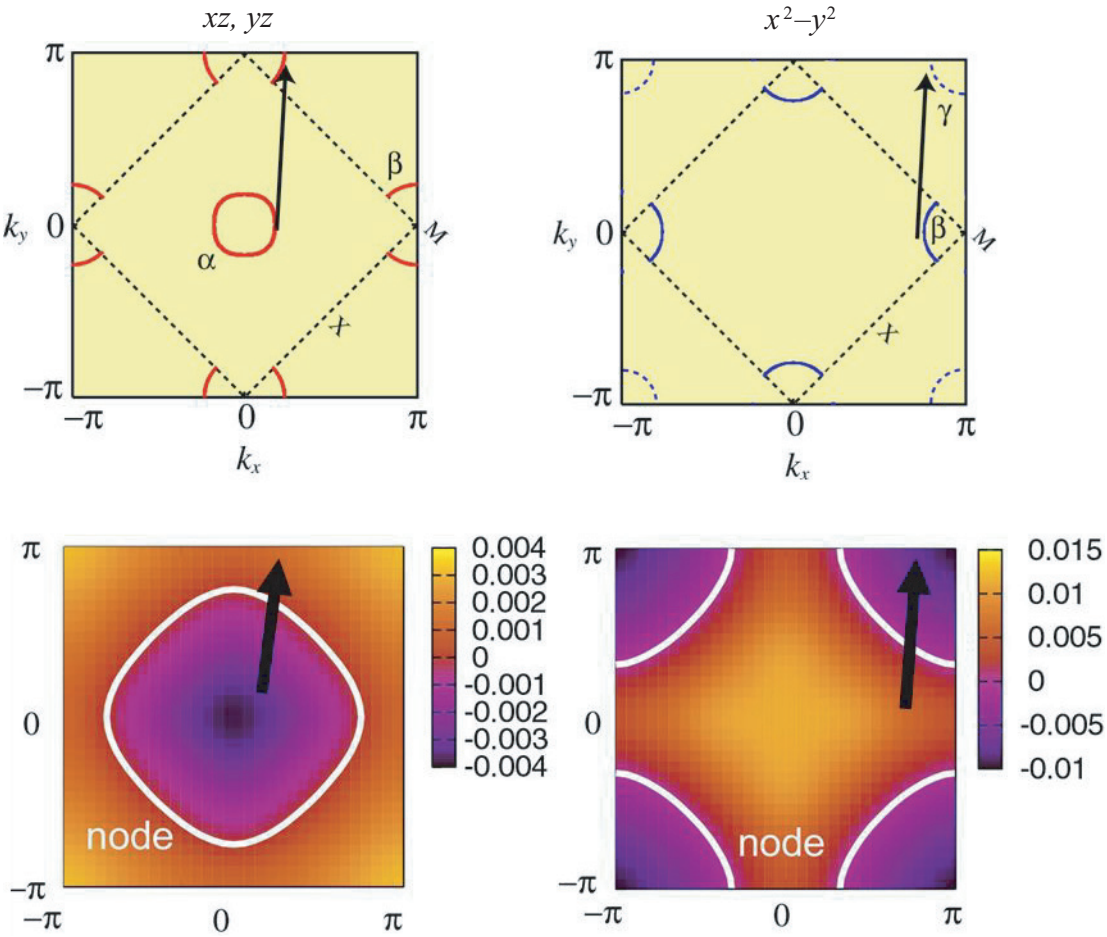

Figure 11. Upper panels: the portions of the Fermi surface of iron pnictides with strong d_{xz}, d_{yz} (left) or $d_{x^2-y^2}$ (right) orbital character. The dashed curve around (π, π) (at the corners of the Brillouin zone) is where the part of the band lies very close to the Fermi level, although it does not actually produce a Fermi surface. The arrows show the nesting vector of the Fermi surface. Lower panels: the gap function for the d_{xz}, d_{yz} (left) or $d_{x^2-y^2}$ (right) orbitals.

electron–phonon coupling), while for the pnictides, high T_c is obtained despite the low energy scale of the main band and competing spin and charge fluctuations due to the multiplicity of the orbitals. The disconnectivity of the Fermi surface may be one good reason why these faults are overcome. In the future, there may a possibility that we can get higher T_c by realizing disconnected Fermi surface on more ideal situations.

Acknowledgments

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