Unconventional high temperature superconductivity in cubic zinc-blende transition metal compounds

Qiang Zhang¹, Kun Jiang¹,², YuHao Gu¹,³, and JiangPing Hu¹,⁴*

¹Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China;
²Department of Physics, Boston College, Chestnut Hill, MA 02467, USA;
³Beijing National Laboratory for Molecular Sciences, State Key Laboratory of Rare Earth Materials Chemistry and Applications, Institute of Theoretical and Computational Chemistry, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China;
⁴Kavli Institute of Theoretical Sciences, University of Chinese Academy of Sciences, Beijing 100190, China

Received November 4, 2019; accepted December 11, 2019; published online March 30, 2020

We consider possible high temperature superconductivity (high-$T_c$) in transition metal compounds with a cubic zinc-blende lattice structure. When the electron filling configuration in the d-shell is close to $d^{7}$, all three $t_{2g}$ orbitals are near half filling with strong nearest neighbor antiferromagnetic (AFM) superexchange interactions. We argue that upon doping, this electronic environment can be one of “genes” to host unconventional high-$T_c$ with a time reversal symmetry broken $d_{2z^2-x^2-y^2}$ pairing symmetry. With gapless nodal points along the diagonal directions, this state is a direct three-dimensional analogue to the two-dimensional $B_{1g}$ $d$-wave state in cuprates. We suggest that such a case may be realized in electron doped CoN, such as CoN$_{1-x}$O$_{x}$ and (H, Li)$_{1-x}$CoN.

high temperature superconductivity, zinc-blende structure, three-dimensional $d+id$ wave

PACS number(s): 74.10.+v, 74.20.Mn, 74.20.Rp, 71.10.Li

1 Introduction

The superconducting mechanism of unconventional high-$T_c$ in cuprates and iron-based superconductors [1] remains one of the most challenging problems in condensed matter physics [2]. A correct answer to this problem should be able to guide us to predict new materials with potential high-$T_c$. 

Recently, we have identified that a key character, called the electronic gene, which separates these two classes of high-$T_c$ materials from other transitional metal compounds, is that the d-orbitals with the strongest in-plane d-p couplings in both high-$T_c$ families are isolated near Fermi energy [3]. The gene can only be realized by a specific collaboration through cation-anion complexes, global lattice structures, and specific electron filling configurations in the d-shell of transition metal atoms. In cuprates, the $d_{x^2-y^2}$ orbital is isolated near Fermi energy in a two-dimensional (2D) Cu-O square lattice formed by corner-shared CuO$_6$ octahedra (or CuO$_4$ square planar) in a $d^9$ filling configuration of Cu$^{2+}$. In iron-based superconductors, there are two $t_{2g}$ $d_{xy}$-type orbitals which are isolated near Fermi energy with the $d^6$ filling configuration of Fe$^{2+}$ in a square lattice formed by edge-shared Fe(Se/As)$_4$ tetrahedra [3, 4]. In order to justify the above idea, we have suggested to realize the gene condition with the $d^7$ configurations in a 2D hexagonal layer formed by edge-shared trigonal bipyramidal complexes or in a square lattice formed by...
the corner-shared tetrahedra [5], and the $d^8$ configuration in a square lattice formed by Ni-based mix-anion octahedra [6]. Unfortunately, all these proposals have not been materialized.

To realize the gene condition, a quasi-2D layer is generally required because of the nature of the d-orbital spacial configuration. In fact, all above examples are quasi-2D. However, there may be one exception. In the $d^7$ filling configuration with corner shared tetrahedra, all three $t_{2g}$ orbitals can participate in superconducting pairing. These three orbitals together form a three-dimensional (3D) irreducible representation in a cubic lattice structure. Therefore, even in a 3D cubic lattice structure, they can be fully isolated near Fermi energy.

The zinc-blende lattice structure which is formed by corner shared tetrahedra is an ideal lattice structure to test this potential exception. Different from the previous examples and proposals, the lattice of the shared tetrahedra in the zinc-blende structure is essentially 3D. Locally, the tetrahedra symmetry is fully respected. The three $t_{2g}$ orbitals are degenerate and have kinematics in all three spacial directions. If we consider a transition metal compound with the zinc-blende structure, the transition metal atoms form a face center cubic (FCC) lattice as shown in Figure 1(a). Antiferromagnetic superexchange couplings can be generated through anions among all three $t_{2g}$ d-orbitals due to the crystal field splitting in a tetrahedron complex. Thus, in the first-order approximation, such an electronic environment can be described by a 3D $t$-J model.

### 2 One-orbital model

We first consider a one-orbital nearest neighbor (NN) $t$-$J$ model in a FCC lattice, with the effective interactions between the d-orbitals being mainly through d-p couplings. As we will show later, if we ignore the inter-orbital hopping, the kinematics of each $t_{2g}$ orbital in the zinc-blende lattice is close to that of an isotropic s-orbital. By setting the second NN distance as one, the kinetic part of the Hamiltonian can be written as:

$$H_k = \sum_{\alpha x} t_{\alpha x} c_{\alpha x}^\dagger c_{\alpha x} + \mu,$$

where $\alpha \equiv \cos(k_{\alpha}/2)$, $\alpha = x, y, z$ and $\sigma$ is the spin index. Here $t$ is the nearest neighbor hopping amplitude and $\mu$ is the chemical potential, with $\mu/t = -0.92$ at half filling. The band structure along the high symmetry moments is shown in Figure 1(c). Assuming the NN AFM superexchange coupling $J$, the total Hamiltonian for a standard $t$-$J$ model can be written as

$$H = \hat{P}(H_k) + J \sum_{\langle i,j \rangle} (S_i S_j - \frac{1}{2} n_i n_j),$$

where $\hat{P}$ is the projection operator to forbid double occupancy at a single site and $S_i (n_i)$ denotes the spin (density) at site $i$.

In a mean field solution, the above Hamiltonian in 2D is known to result in a phase diagram between a long range AFM state and a superconducting state, which is qualitatively consistent with experimental results in cuprates [7] and iron-based superconductors [8]. In 3D, the antiferromagnetism and frustration in the FCC structure have already been extensively studied [9]. Therefore, we will solely focus on the superconducting state of the above model.

Upon doping, the superconducting state of the above 3D model is more interesting because the lattice symmetry is much larger. The FCC lattice is governed by the $O_h$ point group. As the superconducting pairing is induced by the NNAFM interaction, the superconducting order must be in the spin-singlet pairing channel and carry specific momentum form factors, as the even irreducible representations of $O_h$ point group. Considering the equal pairing strength for all NN bonds, we have:

$$\Delta^4 = 4\delta_s(c_x c_y + c_x c_z + c_y c_z),$$
$$\Delta^{F_2} = 2\delta_d(2c_x c_y - c_x c_z - c_y c_z \pm i\sqrt{3}(c_x c_z - c_y c_y)),$$
$$\Delta^T = -4\delta_d(s_x s_y + e^{i\theta_s} s_y s_z + e^{i\theta_s} s_z s_x),$$

where $s_\alpha = \sin(k_{\alpha}/2)$. $\Delta^4$ represents the extended s-wave, $\Delta^{F_2}$ represents a time reversal symmetry broken superconducting state $d_{2\pm 2\pm 2\pm 2}$ that belongs to a 2D $E_g$ irreducible representation. It can also be written symmetrically as $4\delta_d(c_x c_y + e^{i2\pi/3} c_x c_z + e^{i4\pi/3} c_y c_z)$. Obviously, this $d \pm id$ gap function vanishes along the diagonal lines $|k_x| = |k_y| = |k_z|$ as a 3D analogue of the 2D $B_{1g}$ d-wave for the cuprates. However, in this one-orbital model, near half filling upon hole doping, there is no Fermi surface along the $\Gamma$-$L$ lines as depicted in Figure 1(c), leaving its superconducting state fully gapped. $\Delta^T$ represents a $t$-wave superconducting state that belongs to a 3D $T_{2g}$ irreducible representation. In the $\Delta^T$ state, besides the pairing strength $\delta_t$,
we have two additional phase parameters $\theta_1, \theta_2$. From the standard Ginzburg-Landau theory analysis [10] (see the Supporting Information), we have two types of $t$-wave phases: $T_{20}$, the time reversal invariant ($\theta_1 = \theta_2 = 0$) and $T_{21}$, the chiral ($\theta_1 = 2\theta_2 = 4\pi/3$) phases.

We use the slave slave boson mean-field approach [7, 11, 12] to calculate the superconducting states in the hole doped region. As shown in Figure 2(a) and (c), the extended $s$-wave quickly diminishes with doping while the superconducting orders in the $d \pm id$ wave $E_g$ state and the $t$-wave states appear to be comparable. However, as shown in Figure 2(b) and (d), the $E_g$ state has much lower energy than the $t$-wave states in relevant doping regions. We also notice that the time reversal symmetry broken phases generally gain more condensation energy than the unbroken counterparts. For example, the chiral $t$-wave state has lower energy than the TRI $t$-wave state.

This result can be easily understood by the Hu-Ding principle [13], which states the favored pairing symmetry is determined by the overlap strength between the momentum form factors of pairing functions and Fermi surfaces. The $E_g$ state can open bigger gaps near $X$, $W$ and $K$ points, and thus wins near half filling upon hole doping. Yet, with heavy electron doping to reach the $L$ (saddle) points, the $t$-wave can eventually become favored.

### 3 Three-orbital model

Now we consider all three $t_{2g}$ orbitals. In this case, it is important to note that due to the lack of inversion symmetry, zinc-blende structure belongs to the space group $F43m$ (No.216) and its point group is $T_d$ instead of the $O_h$. This symmetry difference allows additional hopping terms.

Taking the zinc-blende cobalt nitrogen (CoN) with a lattice constant 4.27 Å [14] as an example, its band structure from density function theory (DFT [15]) is shown in Figure 3(b) with the dotted gray line.1). The half-filled $t_{2g}$ orbital is achieved if we dope one more electron per Co atom into this material. We simplify the band structure in a tight binding model with only the NN hopping among three orbitals. We find that the model is a very good approximation to describe the band dispersion as indicated by the red solid lines in Figure 3(b). To be specific, we define the hopping matrix along $a_1$, directions $T(a_1)$ in the basis $\psi(r) = (d_{x^2}, d_{xy}, d_{xz})$. Due to the time reversal, the mirror and the two-fold rotation symmetries, there are only four free hopping parameters:

$$T(a_1) = \begin{pmatrix} t_1 & t_3 & t_4 \\ t_3 & t_1 & t_4 \\ -t_4 & -t_4 & t_2 \end{pmatrix},$$

with $t_{1,2,3,4}$ being real numbers. The kinetic matrix can be

![Figure 2](image2.png)

**Figure 2** (Color online) The results from the slave boson mean-field solution of the single-orbital $t$-$J$ model. (a), (c) The pairing strength $\delta_{s/d}$; (b), (d) the ground state energy $SE$ with respect to the normal state versus hole doping at $J/t=0.3, 0.5$; here $T_{20}$ and $T_{21}$ denote the TRI and chiral $t$-wave pairing states, respectively; (e), (f) the pairing strength $\delta_d$ and the ground state energy as a function of $J/t$ with a hole doping level $x = 0.1$.

### Figure 3

![Figure 3](image3.png)

**Figure 3** (Color online) The zinc-blende structure for CoN (a) and its three-orbital tight-binding (solid red) and the DFT (dotted gray) dispersion (b). The slave boson mean-field results with $J = 0.2$ eV: (c) the pairing strength $\delta_{s/d}$ and (d) the ground state energy versus hole doping. The inset in (c) depicts the intraorbital isotropic ($\delta_1$) and anisotropic ($\delta_2$) pairing order parameters for the $E$ representation in eq. (8).

---

1) Our DFT calculations employ the VASP code with the PAW method and the PBE exchange-correlation functional [15]. The kinetic energy cutoff of 600 eV for the planewaves, Γ-centered $k$-mesh of $16 \times 16 \times 16$ and energy convergence criterion of $10^{-6}$ eV are adopted.
written as:

\[ H_{\text{BCS}}(k) = \sum_{\langle g \rangle} T(R_g a_1) e^{i k \cdot R_g a_1} - \mu, \]

where \( \langle g \rangle \in T_d \) ensures that \( R_g a_1 \) runs over all the 12 NN vectors and \( T(R_g a_1) = R_g T(a_1) R_g^{-1} \). In Figure 3(b), it fits reasonably well to the DFT calculations with \((t_1, t_2, t_3, t_4, \mu) = (0.214, 0.206, 0.235, 0.084, -0.889) \) eV. We notice that \( t_1 \approx t_2 \), which indicates that its band structure is similar to the single-orbital model if the interorbital hoppings are ignored. The interorbital \( t_3 \) and \( t_4 \) terms cause the splitting at \( L \) and \( W \) points, respectively. The small \( t_4 \) term stems from the absence of the inversion symmetry due to the existence of nitrogen atoms (see Supporting Information). The above band structure is rather qualitatively generic to \( t_2g \) d orbitals in the zinc-blende lattice structure. With the effective hoppings between the d-orbitals being mainly induced by the d-p couplings, the lattice symmetry qualitatively provides such a band structure.

By adding the AFM exchange interactions, we consider a multi-orbital t-J model \([12, 16]\) and study the possible superconducting states. As we only consider the spin-singlet pairing, the pairing symmetries from the representations of \( T_d \) group is the same to the single-orbital model in FCC structure. For the superconducting pairing in this multi-orbital t-J model, the intraorbital pairing is always dominant over the inter-orbital pairing as shown in previous work \([8, 16]\). Therefore, we can focus on the superconducting states with only intraorbital pairing. For the three \( t_2g \) orbitals, the pairing operators between them can be classified according to the irreducible representations of the \( T_d \) group as \( \hat{T}_2 \otimes \hat{T}_2 = \hat{A}_1 \oplus \hat{E} \oplus \hat{T}_1 \oplus \hat{T}_2 \), in which only \( \hat{A}_1 \) and \( \hat{E} \) are formed by the intraorbital pairings. Combining with the momentum form factors in eqs. (2)-(4), we can construct the BCS mean-field decoupling terms:

\[ H_{\text{BCS}}^{a} = \Delta_a(k) \hat{A}_1 + \delta_{2}[e(k)\hat{E}]_1, \]

\[ H_{\text{BCS}}^{b} = \Delta_b(k) \hat{A}_1 + \delta_{2}[a(k)\hat{E}]_1 + \delta_{x}[e(k)\hat{E}]_2, \]

\[ H_{\text{BCS}}^{c} = \Delta_c(k) \hat{A}_1 + \delta_{2}[t_2(k)\hat{E}]_1, \]

with the \( \delta_{x,3} \) terms defined in Supporting Information. The first terms in all above three BCS forms represent isotropic pairing among all three orbitals. As shown in the inset of Figure 3(c), this term is dominant over other pairing terms in our calculations. The pairing prefers to maintain equal amplitudes on different orbitals, consistent with the ”superconducting fitness” analysis \([17]\). Thus, we simply focus on the isotropic intraorbital pairings.

Due to the high degeneracy of the three \( t_2g \) orbitals, under the slave boson mean-field approach, the carrier occupancies in these orbitals are identical, leading to an equal renormalization factor for all the hopping interactions \([12]\). Adopting the hopping parameters fitted to CoN and \( J = 0.2 \) eV, the results are reported in Figure 3(c) and (d). Similar to the single-orbital model, the time reversal symmetry broken \( d_{x^2-y^2} \) wave is the most favored state. Following the Hu-Ding principle \([13]\), the \( t \)-wave pairing is expected to be weaker in the three-orbital model than in the one-orbital model because of the band splitting at the \( L \) points. Our calculation confirms this result. Even in the heavy electron doped region, the \( t \)-wave never wins over the \( d \pm i d \) wave. Moreover, the splitting at \( L \) points results in one Fermi surface along the \( \Gamma-L \) lines. Thereafter, in the three-orbital model, eight gapless points appear in the \( d \pm i d \) wave state, resembling the nodal \( d \)-wave state in cuprates.

4 Conclusions

In summary, guided by the recent ideas on searching for potential new high temperature superconductors, we studied the superconducting states of a 3D t-J model in both one and three orbital cases under the slave boson mean-field approximation. It was found that the time reversal symmetry broken \( d_{x^2-y^2} \pm i d_{x^2-y^2} \) wave superconducting state wins over all other superconducting states upon hole doping. The state has gapless nodal points along the diagonal directions, being a direct 3D extension of the \( d \)-wave superconducting state of cuprates. Similar 3D \( d \pm i d \) pairing symmetry was theoretically suggested previously for the \( \beta \)-pyrochlore CsW₂O₆ from a weak coupling approach \([18]\) without conclusive experimental evidence.

To materialize, we must have a zinc-blende transition metal compound with a \( d^0 \) filling configuration at transition metal atoms. The zinc-blende CoN was experimentally known to be a very good metal \([20]\), however, with \( d^6 \) filling configuration. The zinc-blende CoO with \( d^9 \) configuration has an AFM ground state \([9, 19]\) but is metastable. Therefore, assuming that the zinc-blende structure is not drastically modified locally, we can suggest that the potential superconductivity may be realized in \( \text{CoO}_{1-x}\text{N}_x \) \([20]\) in which \( x \) describes the concentration of doped hole carriers. Under the same assumption, we may also consider materials by adding electron carriers to CoN, such as (H, Li)\(_{1-x}\)CoN \([21]\), to realize potential superconducting states.

Qiang Zhang was supported by the International Young Scientist Fellowship of Institute of Physics, Chinese Academy Sciences (Grant No. 2017002), and the Postdoctoral International Program from China Postdoctoral Science Foundation (Grant No. YBBK131T61). YuHao Gu was supported by the High-performance Computing Platform of Peking University. Jiang-Ping Hu was supported by the National Basic Research Program of China (Grant Nos. 2015CB921300, and 2017YFA0303100), the National Natural Science Foundation of China (Grant No. NSFC-11334012), and the Strate-
Supporting Information

The supporting information is available online at phys.scichina.com and link.springer.com. The supporting materials are published as submitted, without typesetting or editing. The responsibility for scientific accuracy and content remains entirely with the authors.

1. J. G. Bednorz, and K. A. Müller, Z. Phys. B-Condensed Matter 64, 189 (1986); Y. Kamihara, T. Watanabe, M. Hirano, and H. Hosono, J. Am. Chem. Soc. 130, 3296 (2008).
2. J. Zaanen, S. Chakravarty, T. Senthil, P. Anderson, P. Lee, J. Schmalian, M. Imada, D. Pines, M. Randeria, C. Varma, M. Vojta, and M. Rice, Nat. Phys. 2, 138 (2006); M. R. Norman, Science 332, 196 (2011); A. J. Leggett, Nat. Phys. 2, 134 (2006).
3. J. Hu, C. Le, and X. Wu, Phys. Rev. X 5, 041012 (2015); J. Hu, Sci. Bull. 61, 561 (2016); J. Hu, and J. Yuan, Front. Phys. 11, 117404 (2016).
4. J. Hu, and N. Hao, Phys. Rev. X 2, 021009 (2012).
5. J. Hu, and C. Le, Sci. Bull. 62, 212 (2017); G. E. Delgado, P. Grima-Gallardo, L. Nieves, H. Cabrera, J. R. Glenn, and J. A. Aitken, Mat. Res. 19, 1423 (2016); J. Hu, Y. Gu, and C. Le, Sci. Bull. 63, 1338 (2018).
6. C. Le, J. Zeng, Y. Gu, G. H. Cao, and J. Hu, Sci. Bull. 63, 957 (2018).
7. G. Kotliar, and J. Liu, Phys. Rev. B 38, 5142 (1988); J. Brinckmann, and P. A. Lee, Phys. Rev. B 65, 014502 (2001).
8. K. Seo, B. A. Bernevig, and J. Hu, Phys. Rev. Lett. 101, 206404 (2008); R. Yu, and Q. Si, Phys. Rev. B 86, 085104 (2012).
9. J. S. Smart, Phys. Rev. 86, 968 (1952); W. L. Roth, Phys. Rev. 110, 1333 (1958); M. E. Lines, Phys. Rev. 139, A1304 (1965); N. N. Sun, and H. Y. Wang, J. Magn. Magn. Mater. 454, 176 (2018).
10. M. Sigrist, and K. Ueda, Rev. Mod. Phys. 63, 239 (1991).
11. A. Rüegg, M. Ingersent, S. Pilgram, and M. Sigrist, Eur. Phys. J. B 48, 55 (2005); Q. H. Wang, D. H. Lee, and P. A. Lee, Phys. Rev. B 69, 092504 (2004).
12. Y. Gu, Q. Zhang, C. Le, Y. Li, T. Xiang, and J. Hu, Phys. Rev. B 100, 165405 (2019).
13. J. Hu, and H. Ding, Sci. Rep. 2, 381 (2012).
14. K. Suzuki, T. Kaneko, H. Yoshida, H. Morita, and H. Fujimori, J. Alloys Compd. 224, 232 (1995).
15. G. Kresse, and J. Furthmuller, Phys. Rev. B 54, 11169 (1996); G. Kresse, and D. Joubert, Phys. Rev. B 59, 1758 (1999).
16. K. Jiang, X. Wu, J. Hu, and Z. Wang, Phys. Rev. Lett. 121, 227002 (2018); Z. P. Yin, K. Haule, and G. Kotliar, Nat. Phys. 10, 845 (2014).
17. A. Ramires, D. F. Agterberg, and M. Sigrist, Phys. Rev. B 98, 024501 (2018).
18. D. F. Agterberg, V. Barzykin, and L. P. Gor'kov, Phys. Rev. B 60, 14868 (1999); S. V. Streltsov, I. I. Mazin, R. Heid, and K. P. Bohnen, Phys. Rev. B 94, 241101 (2016).
19. M. J. Redman, and E. G. Steward, Nature 193, 867 (1962); H. X. Deng, J. Li, S. S. Li, J. B. Xia, A. Walsh, and S. H. Wei, Appl. Phys. Lett. 96, 162508 (2010).
20. M. W. Lume, and R. Dronskowski, Adv. Funct. Mater. 14, 371 (2004); J. Takahashi, Y. Hirose, D. Oka, S. Nakao, C. Yang, T. Fukumura, I. Harayama, D. Sekita, and T. Hasegawa, Appl. Phys. Lett. 107, 231906 (2015).
21. M. V. Reddy, G. Prithvi, K. P. Loh, and B. V. R. Chowdari, ACS Appl. Mater. Interfaces 6, 680 (2014); H. Wang, X. Song, Y. Xu, and Z. Yang, Mod. Phys. Lett. B 32, 1850184 (2018).