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Article

A possible new family of unconventional high temperature superconductors

Jiangping Hu [a,b,c,*], Congcong Le [a]

[a] Beijing National Laboratory for Condensed Matter Physics, and Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China
[b] Collaborative Innovation Center of Quantum Matter, Beijing 100871, China
[c] School of Physics, University of Chinese Academy of Sciences, Beijing 100049, China

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ABSTRACT

We suggest a new family of Co/Ni-based materials that may host unconventional high temperature superconductivity (high-T_c). These materials carry layered square lattices with each layer being formed by vertex-shared transition metal tetrahedra cation–anion complexes. The electronic physics in these materials is determined by the two dimensional layer and is fully attributed to the three near degenerated t_{2g} *d*-orbitals close to a d^7 filling configuration in the *d*-shell of Co/Ni atoms. The electronic structure meets the necessary criteria for unconventional high T_c materials proposed recently by us to unify the two known high-T_c families, cuprates and iron-based superconductors. We predict that they host superconducting states with a *d*-wave pairing symmetry with T_c potentially higher than those of iron-based superconductors. These materials, if realized, can be a fertile new ground to study strongly correlated electronic physics and provide decisive evidence for superconducting pairing mechanism.

1. Introduction

Successful theoretical predictions of high temperature superconducting materials rarely happen. The two known families of high T_c materials, cuprates [1] and iron-based superconductors [2], were discovered accidentally without any theoretical guide. Theoretical studies have been mainly devoted to explain rich phenomena observed in experiments. After almost three decades of intensive research, it has become extremely clear that if there is any chance to solve the elusive high T_c mechanism, a successful theoretical prediction of new high T_c materials is necessary.

Recently, we suggest that a special electronic trait that separates the two high T_c families from other correlated electronic materials is that in both high T_c families, those *d*-orbitals that make the strongest in-plane *d*-*p* couplings in the cation–anion complexes are isolated near Fermi surface energy [3–5]. In magnetically-driven superconducting mechanism, this property makes the effective antiferromagnetic (AFM) superexchange interactions to maximize their contribution to superconducting pairing and simultaneously reduces other unwanted side effects from other orbitals. We also further argued that this property can only be realized in very limited special cases [4]. Realizing such a property requires a strict symmetry match between local building blocks and global lattices, as well as a specific electron filling configuration in the *d*-shells of transition metal atoms. In cuprates, which possess perovskite or perovskite-like structures, the speciality is only realized near the d^9 filling configuration in an octahedra (or square) complex to isolate the e_g $d_{x^2-y^2}$ orbital near Fermi energy. In iron-based superconductors, it is only realized near the d^6 filling configuration of a tetrahedra complex to isolate two t_{2g} d_{xy} -type orbitals [3,4]. Therefore, this speciality allows us to explain why high T_c is such a rare phenomenon. It can be considered as a gene type character to guide us to search for or predict possible new high T_c materials [3].

Following the above analysis, we have predicted that the gene exists in a two dimensional hexagonal lattice formed by edge-shared trigonal bipyramidal complexes with a d^7 electron filling configuration, which suggests that Co^{2+}/Ni^{3+} based materials containing this type of hexagonal lattices are promising new high T_c materials [3]. However, confirming such a prediction can be very difficult due to the rare appearance of trigonal bipyramidal complexes in material databases.

Here we propose a new family of Co/Ni-based materials that carry the special electronic property to be promising unconventional high-T_c candidates. The materials are constructed by layered square lattices with each layer being formed by vertex-shared tetrahedra cation–anion complexes. When it is close to the d^7 filling configurations in the *d*-shell, namely those of Co^{2+} or Ni^{3+}, the electronic physics in these materials are fully attributed to the three near degenerated t_{2g} *d*-orbitals. The new materials

* Corresponding author.
E-mail address: jphu@iphy.ac.cn (J. Hu).

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closely resemble both cuprates and iron-based superconductors, and thus can bridge the gap between their electronic properties. In fact, we predict that the materials have the same d-wave pairing symmetry in superconducting states as cuprates and can reach a maximum T_c higher than those of iron-based superconductors. The new family of materials, if synthesized, can be a fertile new ground to study strongly correlated electronic physics and test various ideas on both cuprates and iron-based superconductors.

2. Material design

Our proposal is deeply related to iron-based superconductors. Therefore, we first review the electronic structures of iron-based superconductors. In iron-pnictides, as shown in Fig. 1a, the two dimensional FeAs layer is constructed by edge sharing between two nearest neighbour (NN) $FeAs_4$ tetrahedra complexes. As explicitly pointed out before [3,4,6], the edge sharing between two sublattices has a profound effect on electronic structures of iron-pnictides. It makes one combination of d_{xz} and d_{yz} orbitals noted as $d^{**}_{xz/yz}$ strongly couples with the e_g $d_{x^2-y^2}$ orbital. Such a coupling creates an energy gap between their binding and antibinding bands to allow the d_{xy} and the other combination of d_{xz} and d_{yz} orbital noted as $d^{*}_{xz/yz}$, the two pure t_{2g} orbitals, separated from all other d-orbitals. As shown in Fig. 1a, the d^6 filling configuration makes these two pure t_{2g} orbitals isolated near Fermi energy, which explains why Fe^{2+} is specially required to realize high T_c in iron-based superconductors [4]. In this analysis, the superconducting pairing essentially is confined between two t_{2g} orbitals within each sublattice.

Following the above understanding of iron-based superconductors, logically we can simply keep one Fe sublattice without losing essential physics. If we divide Fe atoms into two sublattices, each sublattice as shown in Fig. 1b can be viewed as a structure constructed by vertex sharing between two NN tetrahedra. Thus a natural proposal is to study a material which has a lattice structure of Fig. 1b. This is exactly the main point of this paper. It is easy to notice that in this lattice there is no large coupling between e_g and t_{2g} orbitals. The e_g and t_{2g} orbitals are well separated in energy by crystal field energy splitting. All three t_{2g} orbitals are close to be degenerated. Therefore, as shown in Fig. 1b, a configuration close to a d^7 filling on transition metal ion meets the requirements to isolate the t_{2g} orbitals near Fermi energy. Thus, our goal is to construct Co^{2+} or Ni^{3+} based materials containing such a two dimensional lattice structure and predict possible properties.

The first question is that whether the lattice structure in Fig. 1b is feasible or not. The answer is positive. In fact, the layer structure exists in the popular zinc blende structure (β-ZnS). As shown in Fig. 2a, the zinc blende is a well known three dimensional cubic structure created by vertex-sharing tetrahedra. If we view the cubic structure layer by layer along any principle axis, each ZnS_2 layer is identical to the structure shown in Fig. 1b. For the purpose of theoretical demonstration, we can replace half Zn atoms in ZnS by Co atoms to create a prototype of material $ZnCoS_2$ that has alternating ZnS_2 and CoS_2 layers along c-axis, shown in Fig. 2b. We can also make extension of this material by replacing S atoms with other chalcogenide atoms to create materials such as $ZnCoO_2$ and $ZnCoSe_2$. However, for $ZnCoO_2$, we find that the lattice constant is only about 3.1 Å, much smaller than those of $ZnCo(S,Se)_2$. The short distance suggests that there are strong direct hoppings between d-orbitals which can destroy the superexchange processes. Therefore, we will focus on $ZnCo(S,Se)_2$. In these materials. the electronic physics near Fermi energy is expected to be dominated by the two dimensional $Co(S,Se)_2$ layer as Zn has a filled d-shell.

It is also possible to design materials with layered $Co(S,Se)_2$ structures. One possibility is to consider 1111 iron-pnictides, such as LaOFeAs. Following the above analysis, we can design related materials such as $(LaO)_2CoSe_2$, which include $CoSe_2$ layers.

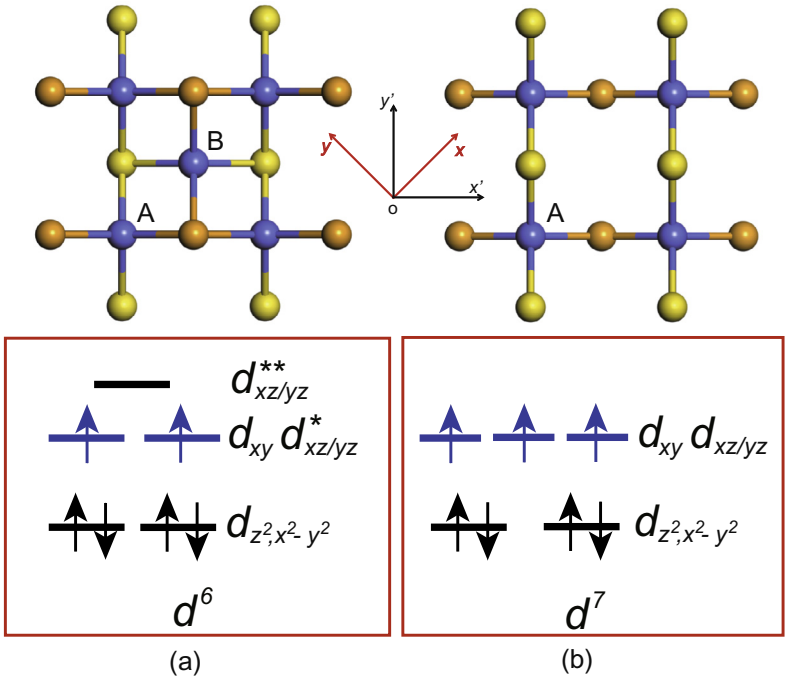

Fig. 1. (Color online) The two dimensional layer structures, the corresponding d-orbital crystal energy splitting configurations and the required electron filling configuration to realize high temperature superconductivity: (a) a FeAs(Se) layer in iron-based superconductors with the d^6 filling configuration; (b) the proposed layer by keeping only cation atoms at the A sublattice of (a) with the d^7 filling configuration.