Predicting Diamond-like Co-based Chalcogenides as Unconventional High Temperature Superconductors

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We predict Co-based chalcogenides with a diamond-like structure can host unconventional high temperature superconductivity (high-\(T_c\)). The essential electronic physics in these materials stems from the Co layers with each layer being formed by vertex-shared Co\(_{\text{A}}\text{A}_4\) (A=S,Se,Te) tetrahedra complexes, a material genome proposed recently by us to host potential unconventional high-\(T_c\) close to a \(d^9\) filling configuration in 3d transition metal compounds. We calculate the magnetic ground states of different transition metal compounds with this structure. It is found that (Mn,Fe,Co)-based compounds all have a G-type antiferromagnetic(AF) insulating ground state while Ni-based compounds are paramagnetic metal. The AFM interaction is the largest in the Co-based compounds as the three \(t_{2g}\) orbitals all strongly participate in AFM superexchange interactions. The abrupt quenching of the magnetism from the Co to Ni-based compounds is very similar to those from Fe to Co-based pnictides in which a C-type AFM state appears in the Fe-based ones but vanishes in the Co-based ones. This behavior can be considered as an electronic signature of the high-\(T_c\) gene. Upon doping, as we predicted before, this family of Co-based compounds favor a strong d-wave pairing superconducting state.

I. INTRODUCTION

To solve the mystery of unconventional high-\(T_c\) superconductivity, a necessary step is to understand why cuprates[1] and iron-based superconductors[2] are two special types of materials to host high-\(T_c\) while other materials, in particular, many other transition metal compounds that share similar structural, magnetic and electronic properties, do not become high-\(T_c\). A correct understanding should also be able to guide us to search for new high-\(T_c\) superconductors, in particular, those based on other 3d transition metal compounds.

Recently, based on the mechanism that superconductivity is induced by the AFM superexchange interaction, we have suggested that there is an electronic gene that separates the two high-\(T_c\) families from other correlated electronic materials. Those d-orbitals that make the strongest in-plane d-p couplings in the cation-anion complexes in both high-\(T_c\) families are isolated near Fermi surface energy[3–5]. This property makes the effective AFM superexchange interactions to maximize their contribution to superconducting pairing. The electronic gene can only be realized in very limited special cases[4]. It requires a perfect collaboration between local building blocks, global lattice structures, as well as specific electron filling configurations in the d-shell of transition metal atoms. In the cuprates, the gene is realized because the \(d_{x^2−y^2}\) and \(e_g\) orbital can be isolated near Fermi energy in a two dimensional Cu-O square lattice formed by corner-shared Cu\(_x\text{O}_y\) octahedra( or CuO\(_2\) square planar) with a \(d^9\) filling configuration of Cu\(^{2+}\). In iron-based superconductors, we have shown that the gene condition is satisfied because two \(t_{2g}\) \(d_{xy}\) -type orbitals are isolated near a \(d^9\) filling configuration of Fe\(^{2+}\) in a Fe(Se/As) two dimensional square lattice formed by edge-shared Fe(Se/As)\(_4\) tetrahedra[3, 4, 6].

Following the above idea, as the d-orbitals with the strongest d-p couplings in a cation-anion complex gain energy and move up in the energy spectra of the d-orbitals, it is natural for us to ask first whether we can realize the gene condition in the \(d^7\) and \(d^8\) filling configurations. Up to now, we have predicted that the \(d^7\) gene condition can be realized in a two dimensional hexagonal layer formed by edge-shared trigonal bipyrimidal complexes[3] or in a two dimensional square lattice formed by the conner-shared tetrahedra[7], and the \(d^8\) gene condition exists in a two dimensional square lattice formed by Ni-based mix-anion octahedra[8]. Unfortunately, all these proposals have not been materialized.

In this paper, we identify a family of Co-based Chalcogenides with a diamond-like lattice structure, for example, CuInCo\(_3\)(S, Se, Te)\(_4\) with a stannite or primitive-mixed CuAu(PMCA) structure, in which the Co two-dimensional layer is formed exactly by corner shared tetrahedra. The electronic gene is realized in the \(d^7\) filling configuration of Co\(^{2+}\) as we have proposed in ref.[7]. The successful synthesesizations of the type of transition metal compounds were reported in the past[9, 10]. However, very few measurements have been made to study their electronic properties. Here we calculate their electronic and magnetic properties under the formula CuMn\(_{2}\)\(_\text{A}_4\)(S, Se, Te)\(_4\) with M = Mn, Fe, Co and Ni. In all these materials, the electronic physics near Fermi energy stems from the M(S,Se,Te)\(_2\) layer and is attributed to the d-orbitals of the transition metal elements. In the Co case, the three \(t_{2g}\) orbitals are near degenerate and close to half-filling, and make the dominating contribution near Fermi energy. The (Mn,Fe,Co)-based compounds all have a checkerboard (G-type) AFM insulating ground state while Ni-based

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compounds are paramagnetic metal. The AFM exchange interaction is the largest in the Co-based compounds. This magnetic trend from the Co to Ni based compounds is very similar to those from Fe to Co-based pnictides in which a C-type AFM state appears in the Fe-based ones but vanishes in the Co-based ones[11]. This result indicates that the Co-based parental compounds are multi-orbital Mott insulators. However, upon electron doping, the magnetic long-range order can quickly be diminished and possible d-wave superconductivity can arise as we predicted in ref.[7, 12]. Experimental results appear to be consistent with our calculation results[10]. The new materials closely resemble both cuprates and iron-based superconductors, and can bridge the gap between their electronic properties. We believe that this family of materials can display a variety of novel electronic phases and can be a fertile new ground to study strongly correlated electronic physics.

II. DIAMOND-LIKE TRANSITION METAL CHALCOGENIDES

The diamond-like quaternary chalcogenides with formula I-II₃-III-VI₄ and I-II-IV-VI₄ can be considered as the derivatives of zinc-blende chalcogenides by sequential cation cross-substitution[13, 14]. There are a variety of possible compositions with I = Cu, Ag; II=Zn, Cd, Mn, Fe, Co; III=Al, Ga, In; IV=Si, Ge, Sn; VI = S, Se, Te[9, 13–22]. In the past, a great attention was paid to study Zn/Cd compounds for their semiconducting properties due to potential applications for photovoltaics[21], non-linear optics[14, 22] and so on. However, the transition metal compounds have not been well studied.

Here we consider the I-II₂-III-VI₄ quaternary chalcogenides with II=Mn, Fe, Co and Ni, namely, transition metal elements. There are three different possible structures for this formula, kesterite, stannite and PMCA[13]. We focus on the last two structures, stannite and PMCA because in these two structures, the transition metal chalcogenide tetrahedra form a square lattice through corner-sharing as shown in Fig.1 (a) and (b).

It is obvious that in both stannite and PMCA structures, the electronic physics is carried out by the partially filled 3d-shell of the transition metal atoms. A simple picture is that by changing II=Zn to II=transition metal elements in these structures, the bands of the d-orbitals are filled in the semiconductor gap. Therefore, both stannite and PMCA structures support almost identical electronic physics. As the electronic physics is carried out by the partially filled 3d-shell of the transition metal atoms. A simple picture is that by changing II=Zn to II=transition metal elements in these structures, the bands of the d-orbitals are filled in the semiconductor gap. Therefore, both stannite and PMCA structures support almost identical electronic physics. As the electronic physics is carried out by the partially filled 3d-shell of the transition metal atoms. A simple picture is that by changing II=Zn to II=transition metal elements in these structures, the bands of the d-orbitals are filled in the semiconductor gap. Therefore, both stannite and PMCA structures support almost identical electronic physics. As the electronic physics is carried out by the partially filled 3d-shell of the transition metal atoms. A simple picture is that by changing II=Zn to II=transition metal elements in these structures, the bands of the d-orbitals are filled in the semiconductor gap. Therefore, both stannite and PMCA structures support almost identical electronic physics. As the electronic physics is carried out by the partially filled 3d-shell of the transition metal atoms. A simple picture is that by changing II=Zn to II=transition metal elements in these structures, the bands of the d-orbitals are filled in the semiconductor gap. Therefore, both stannite and PMCA structures support almost identical electronic physics. As the electronic physics is carried out by the partially filled 3d-shell of the transition metal atoms. A simple picture is that by changing II=Zn to II=transition metal elements in these structures, the bands of the d-orbitals are filled in the semiconductor gap. Therefore, both stannite and PMCA structures support almost identical electronic physics. As the electronic physics is carried out by the partially filled 3d-shell of the transition metal atoms. A simple picture is that by changing II=Zn to II=transition metal elements in these structures, the bands of the d-orbitals are filled in the semiconductor gap. Therefore, both stannite and PMCA structures support almost identical electronic physics.

![Fig. 1](image-url) (a) and (b) are the CuInCo₂A₄ (A=S, Se, Te) Stannite and PMCA crystal structures. (c) show the checkerboard AFM state. (d) Crystal energy splitting configurations and the required electron filling configuration.

| System          | a(Å) | c(Å) | η=ε/2a | Co-A(Å) | Co-A-Co(°) |
|-----------------|------|------|-------|---------|-----------|
| CuInCo₂Te₄ exp[9] | 6.20 | 12.38 | 1.00  | 2.69    | 108.96    |
| CuInCo₂Te₄ opt  | 6.06 | 12.10 | 1.00  | 2.54    | 114.91    |
| CuInCo₂Se₄ opt  | 5.66 | 11.35 | 1.00  | 2.38    | 114.21    |
| CuInCo₂S₄ opt   | 5.34 | 10.80 | 1.01  | 2.25    | 114.25    |

This result indicates that the stannite-type CuInCo₂Te₄ has already been synthesized[9]. According to the Shannon ionic radii table[23], the radii of cations are quite close. The cation-anion radius ratios determine the favorable coordination number (C.N.). In this case, C.N.=4 (tetrahedral coordination) is favored in CuInCo₂A₄ for A=S,Se,Te and the tetragonal distortion(η) = ε/2a in CuInCo₂Te₄ is very small.

Our DFT calculations employ the Vienna ab initio simulation package (VASP) code[24] with the projector augmented wave (PAW) method[25]. The Perdew-Burke-Ernzerhof (PBE)[26] exchange-correlation functional was used in our calculations. The crystal structures of were fully relaxed with a kinetic energy cutoff (ENCUT) of 600 eV for the planewaves and the force convergence criterion is 0.01 eV/Å.

The experimental and optimized lattice parameters of the CuInCo₂A₄ quaternary chalcogenides are listed in the Table.I. The optimized crystal parameters are about 2% smaller than the experimental values for CuInCo₂Te₄. This is a very typical result for DFT calculations as the calculation result is for lattice at zero temperature and the electron-electron correlation effect is underestimated.

III. MAGNETISM

In the study of magnetism of CuInM₂A₄, the GGA plus on-site repulsion U method (GGA+U) in the formulation of Dudarev et al.[27] is employed to describe the associated electron-electron correlation effect. The effective Hubbard U (U_{eff}) is defined by U_{eff} = U - J_{Hund} and the Hund exchange parameter J_{Hund} is 0.5eV when U > 0 in this paper. We consider four different magnetic states, the paramagnetic state, the ferromagnetic(FM) state, the G-type AFM
state (shown in Fig.1(c) ) and the AFM* state (AFM in the a-b plane with FM along the c axis) as the initial guess of the relaxation.

TABLE III: The calculated magnetic moments and the band gaps in the AFM state for CuInM* (M = Mn, Fe, Co, Ni; A = S, Se, Te) with the stannite-type structure (space group \( I\bar{4}2m \)) from the initial guess of the AFM state using PBE[26].

| System    | \( \mu_B \) (\( \mu_B \)) | Gap (eV) | \( \mu_B \) (\( \mu_B \)) | Gap (eV) |
|-----------|-----------------|---------|-----------------|---------|
| CuInMnSe4 | 4.1             | 0.76    | 4.6             | 0.76    |
| CuInFeSe4 | 3.0             | 0.17    | 3.6             | 0.75    |
| CuInCoSe4 | 1.9             | 0.19    | 2.5             | 1.07    |
| CuInNiSe4 | 0               | 0       | 1.0             | 0       |
| CuInMnTe4 | 4.0             | 0.80    | 4.6             | 0.90    |
| CuInFeTe4 | 3.0             | 0       | 3.6             | 0.92    |
| CuInCoTe4 | 1.7             | 0.02    | 2.4             | 1.04    |
| CuInNiTe4 | 0               | 0       | 0.9             | 0       |

We find that the G-type AFM state is generally favored in the Mn, Fe and Co-based compounds. The lattice parameters at the AFM state are listed in the Table.II. The ordered magnetc moments and the band gaps are strongly dependent on \( U_{\text{eff}} \).

The Mn, Fe and Co atoms are, in general, in high spin states. The magnetic moments slightly increase as \( U_{\text{eff}} \) increases. Although CuInFe*Te4 and CuInCo*Te4 are metallic as shown in Fig.2 when \( U_{\text{eff}} = 0 \), we believe that all these compounds should be insulating because PBE often underestimates the band gap for transition metal compounds[28]. The gaps in the DFT calculations for Fe and Co-based compounds are strongly dependent on \( U_{\text{eff}} \). They increase rapidly when \( U_{\text{eff}} \) is switched on. We plot the electronic band structures in the AFM state for the Co-based compounds in Fig.2 when \( U_{\text{eff}} = 2.0 \text{eV} \). The Ni-based compounds, the magnetic states gain little energy up to \( U_{\text{eff}} = 2 \text{eV} \), which indicates that the Ni-based materials are paramagnetic (or very weak FM) metals. The moment is developed fully only when \( U_{\text{eff}} > 4 \text{eV} \). But even at \( U_{\text{eff}} = 5 \text{eV} \), the material remains to be a metal. This abrupt quenching of the magnetic order from the Co-based to Ni-based compounds resembles the similar quenching of the magnetic order in iron-based superconductors in which the

AFM order vanishes completely when Fe is replaced by Co.

If we use an effective Heisenberg model to describe the AFM exchange interaction, as the dominant AFM interactions are between two nearest neighbor (NN) sites, the model can be written as

\[
H = J \sum_{<ij>} \mathbf{S}_i \cdot \mathbf{S}_j + J_z \sum_{<ij,z>} \mathbf{S}_i \cdot \mathbf{S}_j
\]

where \( <ij> \) labels the in-plane nearest neighbor (NN) links and \( <ij,z> \) labels the out of plane NN links. The classical energies of the above magnetic states are

\[
E_{FM} = NS^2(2J + J_z) + E_0,
\]

\[
E_{AFM} = NS^2(-2J - J_z) + E_0,
\]

\[
E_{AFM_2} = NS^2(-2J + J_z) + E_0
\]

From the calculated energies of the four different magnetic states, we can extract the effective magnetic exchange interactions. The interaction between the Co layers, \( J_z \), is very small. It is about an order of magnitude smaller than the in-plane interaction, \( J \). The values of \( J \) in CuInM*Te4 are plotted in Fig.3 as a function of M, transition metal elements. \( J \) reaches the maximum value when M=Co. For M=Ni, the estimation is not reliable as the moment is too small. The results in CuInM*Se4 are very similar. These qualitative results do not depend on U. Here, the physics of J is exactly identical to the next NN AFM interactions, \( J_{2z} \), in iron based superconductors. For a comparison, we also insert a picture in Fig.3 to show \( J_2 \) in BaM*As2 with M=Cr, Mn, Fe, Co[11].

FIG. 2: (color online) The band structures under the GGA+U calculations for CuInCo*Te4: (a) \( U_{\text{eff}} = 2 \text{eV} \); (b) \( U_{\text{eff}} = 4 \text{eV} \).

IV. ELECTRONIC STRUCTURES AND EFFECTIVE HAMILTONIAN AT LOW ENERGY

In the ref.[7], we have studied the CoS* layer in ZnCoS2. As the electronic physics in CuInCo*A4 is also controlled by the CoA* layer, their electronic physics should be described by the same model derived in ref.[7]. However, in CuInCo*A4, the unit cell is doubled at least. The doubling of the unit cell stems from the CuIn layer due to the inequivalence of Cu and In atoms. We will show that the effect of
The Hamiltonian $H$ is converged to a nonmagnetic state. The elements of the $3 \times 3 H$ matrix is specified as

$$\begin{align*}
H_{11} &= \epsilon_1 + 2t_{11}^x \cos(k_x) + 2t_{11}^y \cos(k_y) + 4t_{11}^{xy} \cos(k_x) \cos(k_y) + 2t_{11}^{xz} \cos(2k_x) + 2t_{11}^{yz} \cos(2k_y), \\
H_{12} &= -4t_{12}^x \sin(k_x) \sin(k_y), \\
H_{13} &= 2t_{13}^x \sin(k_x) + 4it_{13}^{xy} \sin(k_x) \cos(k_y) + 2it_{13}^{xz} \sin(2k_x), \\
H_{22} &= \epsilon_2 + 2t_{22}^x \cos(k_x) + 2t_{22}^y \cos(k_y) + 4t_{22}^{xy} \cos(k_x) \cos(k_y) + 2t_{22}^{xz} \cos(2k_x) + 2t_{22}^{yz} \cos(2k_y), \\
H_{23} &= 2t_{23}^y \sin(k_y) + 4it_{23}^{xy} \sin(k_y) \cos(k_x) + 2it_{23}^{yz} \sin(2k_y), \\
H_{33} &= \epsilon_3 + 2t_{33}^x \cos(k_x) + \cos(k_y) + 4t_{33}^{xy} \cos(k_x) \cos(k_y) + 2t_{33}^{xz} \cos(2k_x) + \cos(2k_y),
\end{align*}$$

where the hopping parameters are specified in ref.[7]. In the first order approximation, the electronic band structures of CuInCo$_2$A$_4$ can also be described by this model. Rather than making a detailed fitting to this model and extracting all parameters for CuInCo$_2$A$_4$, we list the most important intra-orbital NN hopping parameters and the orbital band widths in the Table IV. The NN hopping parameters are slightly larger than those in ZnCoS$_2\,[7]$. 

In ref.[7, 12, 29], we have argued that it is inevitable that the superconducting pairing symmetry in this model is a $d$-wave in which there should be gapless nodes along the diagonal direction in the momentum space. To obtain a qualitative understanding of the $d$-wave state, we can make a rough estimation by fixing the relative intra-orbital pairing strength for three orbitals according to their hopping energy scales. In Fig. 5, we draw the three orbital band structure of the effective model in both folded and unfolded Brillouin zones and sketch the $d$-wave gap form factors in the momentum space by taking $\frac{1}{2} \Delta_0 (\cos(k_x) - \cos(k_y))$ for $d_{xy}$ and $\Delta_0 \cos(k_y)$ for $d_{yz}$, $-\Delta_0 \cos(k_x)$ for $d_{xz}$, where $\Delta_0$ is a superconducting gap parameter. This state is simply a multi-orbital version of the $d$-wave state in cuprates.

V. DISCUSSION

We have identified a family of Co-based chalcogenides as potential high-$T_c$ superconductors. The parent compounds of these materials are multi-orbital Mott insulators with AFM ground states. As we have calculated theoretically in ref.[7], a $d$-wave pairing symmetry is favored in these materials upon doping. Verifying these predictions does not only add a new family of high-$T_c$ superconductors, but also provides a clear picture and a roadmap to settle illusive high-$T_c$ mechanism.
The Co-based chalcogenides can serve as a bridge to unify cuprates and iron-based superconductors. On one side, the materials share many similarities with iron-based superconductors. The electronic physics in both materials are carried out by $t_{2g}$ multi-orbitals. The Co square lattice in the former is simply a sublattice of the Fe square lattice of the latter. They both share common AFM interactions. As we have pointed in this paper, the trend of the magnetism as a function of transition metal elements is also very similar. On the other side, the materials share a common AFM ground state as cuprates and have strong Mott physics as well. Both materials are expected to have a common d-wave superconducting state upon doping.

We have mentioned in the introduction that the structure of the Co-based chalcogenides can be considered as a derivative of the insulating zinc-blende chalcogenides by replacing the entire Zn layer by Co completely. Electronically, this replacement inserts the d-orbitals into the insulating gap, which is also the case for iron-based superconductors, for example, BaFe$_2$As$_2$ can be considered as a derivative of the insulating BaZn$_2$P$_2$ by replacing Zn by Fe entirely[2]. This simple understanding can be used to design and find other possible high-$T_c$ materials.

The abrupt quenching of magnetism from the Co to Ni compounds is a natural characteristics of the electronic structure required by the proposed gene condition[3, 4]. Both cuprates and iron-based superconductors clearly display the same quenching phenomena. The phenomena can be understood as follows. In the proposed gene condition, as all d-orbitals around Fermi surfaces are near half-filling and have been delocalized through the large d-p hybridization, adding an electron to the d-shell drastically weakens the electron-electron correlation effect to quench magnetism.

Our theoretical results on the magnetism of the Co and Ni compounds appear to be consistent with experimental results[10]. In the measured curve of spin susceptibility on the Co-based compounds[10], the susceptibility increases as temperature increases in the measured temperature window up to 400K. This indicates that the material is in an AFM state with a Neel transition temperature, $T_N$, higher than 400K which is consistent with our calculated AFM coupling strength. The measured curve for the Ni-based compounds does not exhibit such an AFM behavior[10].

Comparing the Co-based compounds to the previous theoretical compound, ZnCoS$_2$[7], the CoSe$_2$ layer is slightly distorted due to the doubling of the unit cell. The distortion can affect superconducting transition temperatures $T_c$ as the buckling of CuO layer in cuprates is known to be a strong factor to affect $T_c$[30]. Here the effect could be even larger because the unit cell doubling in a d-wave pairing state can cause the mixture between two bands with opposite pairing signs, which is a destructive reconstruction for pairing. Therefore, for this family of Co-based materials, the material quality can be key factor in obtaining high-$T_c$. Nevertheless, from $T_N > 400K$, the energy scale of the AFM interactions is quite large. We do expect the maximum $T_c$ in this compound should exceed those of iron-based superconductors.

The electron doping can be achieved by substituting Co with Ni, just like the substitution of Fe by Co or Ni in iron-based superconductors. The carriers can also be introduced by modifying CuIn layers. In principle, we may consider a modified formula as $\text{Cu}_{1-x}\text{In}_{x}\text{Se}$, $\text{CuIn}_{1-x}\text{Sn}$, or $\text{CuIn}_{1-x}\text{Sr}$ to introduce electron carriers or hole carriers.

In summary, we identify a new family of Co-based high temperature superconductors with a diamond-like stannite or PMCA structure. The parental materials have been already synthesized and the measured magnetic properties are consistent with our predictions. The materials can serve a bridge to unify the two known high-$T_c$ superconductors, cuprates and iron-based superconductors, and provide us a first falsifiable test to the gene condition proposed for unconventional high-$T_c$[4] to settle the elusive high-$T_c$ mechanism.

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