α–K_2AgF_4: Ferromagnetism induced by the weak superexchange of different e_g orbitals from the nearest neighbor Ag ions

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α-K_2AgF_4: Ferromagnetism induced by the weak superexchange of different e_g orbitals from the nearest neighbor Ag ions

Xiaoli Zhang,[1] Guoren Zhang,[1] Ting Jia,[1] Zhi Zeng,[2,a] and H. Q. Lin[3]
[1]*Key Laboratory of Materials Physics, Institute of Solid State Physics, Chinese Academy of Sciences, Hefei 230031, China*
[2]*Key Laboratory of Materials Physics, Institute of Solid State Physics, Chinese Academy of Sciences, Hefei 230031, China and University of Science and Technology of China, Hefei 230026, China*
[3]*Beijing Computational Science Research Center, Beijing 100084, China*

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We study the abnormal ferromagnetism in α-K_2AgF_4, which is very similar to high-T_C parent material La_2CuO_4 in structure. We find out that the electron correlation is very important in determining the insulating property of α-K_2AgF_4. The Ag(II) $4d^9$ in the octahedron crystal field has the $t_{2g}^6 e_g^3$ electron occupation with e_g x^2-y^2 orbital fully occupied and $3z^2$-r^2 orbital partially occupied. The two e_g orbitals are very extended indicating both of them are active in superexchange. Using the Hubbard model combined with *N*th-order muffin-tin orbital (NMTO) downfolding technique, it is concluded that the exchange interaction between e_g $3z^2$-r^2 and x^2-y^2 from the first nearest neighbor Ag ions leads to the anomalous ferromagnetism in α-K_2AgF_4. [http://dx.doi.org/10.1063/1.4942793]

I. INTRODUCTION

Fluoroargentates(II) have attracted much attention due to the pursuit of superconductivity in transition-metal compounds other than cuprates.[1] Fluoroargentates(II) exhibit several similarities to oxocuprates(II), which are precursors of high-T_C superconductors. Ag is the heavier congener of Cu, possessing S=1/2 divalent transition-metal cation (Ag^{2+} $4d^9$ vs Cu^{2+} $3d^9$). Furthermore, previous studies of fluoroargentates have shown that Ag(II)-F bonds appear to be substantially covalent.[2] States in the vicinity of the Fermi level in fluoroargentates usually have Ag-F $pd\sigma$ antibonding characteristics. Therefore, holes might be doped into the F $2p$ band, providing potential superconductivity.

A new layered perovskite-related fluoroargentates(II), K_2AgF_4, has been synthesized by Z. Mazej *et al*.[3,4] Here after, as described in Ref. 4, we will refer to the quasi-two-dimensional polymorph of K_2AgF_4 as α-K_2AgF_4, which is isostructural to the parent compound of high-T_C cuprate La_2CuO_4. La_2CuO_4 is an antiferromagnetic (AFM) insulator. However, in contrast to La_2CuO_4, α-K_2AgF_4 was reported as a ferromagnetic (FM) insulator with $T_C \sim 26$ K.[3,4] In general, magnetic ions are often antiferromagnetically coupled through superexchange interaction in insulators, while ferromagnetically coupled through Stoner itinerant electrons band model in metal. Therefore, FM in insulator is abnormal in transition metal compounds. One possible explanation of the origin of the ferromagnetism in α-K_2AgF_4 would be AFM type orbital ordering (OO) induced by the cooperative Jahn-Teller effect, which exhibits in its sister compound Cs_2AgF_4.[5,6] However, the cooperative Jahn-Teller effect and OO were not found in α-K_2AgF_4 by Z. Mazej *et al*. both from experimental

[a]zzeng@theory.issp.ac.cn

and First-principles studies.[3] Therefore the origin of the ferromagnetism in α-K_2AgF_4 is interesting but not clear. In this work, we are going to investigate the origin of the ferromagetism in α-K_2AgF_4 using the combination of electronic structure and model calculations.

II. COMPUTATIONAL DETAILS

The electronic structure of α-K_2AgF_4 are studied using the full-potential linearized augmented plane-wave (FP-LAPW) method, as implemented in the WIEN2k code.[7] In the calculation, the generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof form is adopted.[8] The Coulomb interaction of the Ag 4*d* orbitals is also considered. The muffin-tin sphere radii are chosen to be 2.45, 2.05, and 1.82 bohr for K, Ag and F atoms, respectively. The value of $R_{MT}K_{max}$ is set to 7.0. The 500 k points are used for the integration over the Brillouin zone of the primitive cell.

To understand and evaluate the various hopping integrals in α-K_2AgF_4, we use the *N*th-order muffin-tin orbital (NMTO) based downfolding method, which generates localized Wannier functions and derives a few-orbital effective Hamiltonian from the full LDA Hamiltonian by integrating out high-energy degrees of freedom.[9] Fourier transformation of the orthonormalized NMTO effective Hamiltonian $H^{LDA}(k)$ in a Wannier representation yields on-site energies and hopping integrals. The LDA potential is generated with the Stuttgart TB-LMTO-ASA code.[10]

III. RESULTS AND DISCUSSION

The layered perovskite-related α-K_2AgF_4 crystalizes in orthorhombic structure with space group *Cmca*. The $GdFeO_3$-type AgF_6 octahedron tilted about *a* and rotated around *b* in alternating directions making the AgF_4 planes (in the *ac*-plane) slightly puckered.[3] The distorted octahedron has two short apical (2.084 Å) and four long inplane (2.259 Å) Ag-F bonds. We will use F_{ap} and F_{pl} to denote the F atoms in and out-of the puckered AgF_4 layer respectively. As the inter-layer magnetic coupling is too weak to be captured by the present total energy calculations, we consider three kinds of intra-layer magnetic structures: nonmagnetic (NM), FM and AFM coupling in α-K_2AgF_4.

We first carry out the spin polarized GGA calculations, which show the FM metallic ground state. However, the metallic ground state disagrees with the insulating nature of α-K_2AgF_4.[3] Consequently, we carried out the *GGA* + *U* calculations by considering the strong correlated effect, within which the insulating behavior appears when the value of *U* is larger than 4 eV. This value is in accordance with the commonly used electron correlation about 3 - 6 eV for Ag 4*d* electrons in first-principles calculations. In particular, the FM state is the ground state. This result implies that the electron correlation of Ag 4*d* is very important in determining the FM insulating behavior in α-K_2AgF_4.

Naturally, we are wondering the origin of the ferromagnetism in α-K_2AgF_4. In general, ferromagnetism in insulator can be originated from the cooperative Jahn-Teller effect induced AFM-type OO as that in Cs_2AgF_4, which, however, does not exist in α-K_2AgF_4 because each Ag ion has the same compressed octahedron crystal field as well as the $t_{2g}^6 e_g^3$ electron occupation. The e_g x^2-y^2 orbitals is fully occupied while the e_g $3z^2$-r^2 oribital is partially occupy, which can be clearly seen from the partial density of states for Ag 4*d* orbitals with $U = 4.5$ eV as shown in Fig. 1. In Fig. 1, the solid and dashed lines represent the density of states of the spin-up and spin-down states, respectively. The top panel is the total density of states of α-K_2AgF_4, the second and the third panels are the partial density of states of apical and in-plane F atoms, and the panels from four to eight are the partial density of states of five e_g orbitals of Ag ion. From the fourth and fifth panels in Fig. 1 we can also see that the states of the two e_g orbitals are very extended. Therefore, we expect that both of the two e_g orbitals engage in the superexchange in α-K_2AgF_4. The three electrons on the two e_g orbitals can be treated as one hole on the two e_g orbitals. As a result, the superexchange between the two Ag ions can be understood from the hole-hole interaction. Therefore, the Hamiltonion of the two interacted Ag ions can be written using two-band Hubbard model:

$$H = \sum_{i=1,2} H_i + H_{e_g}^{LDA} \tag{1}$$

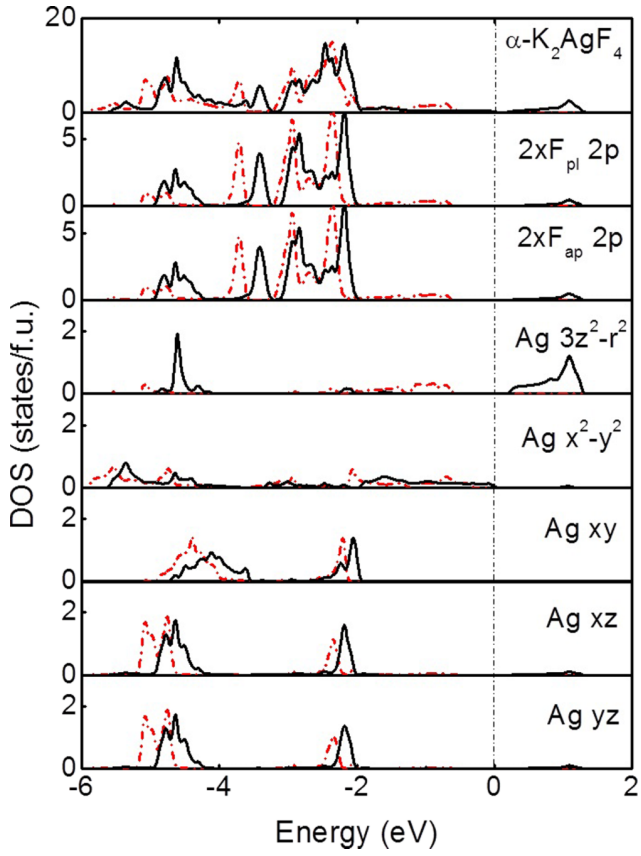

FIG. 1. The total and partial density of states of α-K_2AgF_4 in the FM state with $GGA+U$ (U=4.5 eV). The solid black lines denote the spin-up states while the dashed red lines denote the spin-down states. The Fermi level is set at zero energy.

$$H_{e_g}^{LDA} = \sum_{\langle i\neq j\rangle\alpha,\beta\sigma} t_{\alpha\beta}^{ij} c_{i\alpha\sigma}^{\dagger} c_{j\beta\sigma} \tag{2}$$

$$\begin{aligned} H_i = {} & U\sum_{\alpha} n_{i\alpha\uparrow}n_{i\alpha\downarrow} + (U'-J)\sum_{\sigma} n_{i1\sigma}n_{i2\sigma} + U'\sum_{\sigma\sigma'} n_{i1\sigma}n_{i2\sigma'} \\ & + J\sum_{\sigma\sigma'} c_{1\sigma}^{\dagger}c_{2\sigma'}^{\dagger}c_{1\sigma'}c_{2\sigma} + J'\sum_{\alpha\neq\beta} c_{\alpha\uparrow}^{\dagger}c_{\alpha\downarrow}^{\dagger}c_{\beta\downarrow}c_{\beta\uparrow} \end{aligned} \tag{3}$$

Where the $H_{e_g}^{LDA}$ is the one-hole hopping Hamiltonian and the H_i is the hole-hole interaction term. $c_{i\alpha\sigma}^{\dagger}$ ($c_{j\beta\sigma}$) represents the generation (annihilation) of a hole with spin σ ($\uparrow$,$\downarrow$) on orbital α (β) (=1, 2) and site i (j) (=1, 2). The $n_{i\alpha\sigma}$ is the hole number operator. The U and U' represent the Coulomb interaction of the intra-orbital and inter-orbital of the e_g orbitals of a Ag ion, while J and J' represent the Hund's coupling and the para-hopping respectively. In this paper we use $J = J'$ and $U = U' + 2J$.

Since $t^2/U << 1$ as will be seen later in this paper, we treated the $H_{e_g}^{LDA}$ hopping term in Eq. (1) as the perturbation to the $\sum_{i=1,2} H_i$. We can calculate the exchange constants in α-K_2AgF_4 using second-order perturbation theory. For the two Ag sites R′=(000) and R=(x, y, z), between which we want to compute the exchange constant J_{ex}, the states with no double hole occupancy, i.e. e_g^1+e_g^1 are $|1\rangle \sim |4\rangle$ in Fig. 2, and the states with one Ag ion double hole occupancy, i.e. e_g^2 are the six states $|5\rangle \sim |10\rangle$ in Fig. 2. Therefore, the eigenfunctions of e_g^2 can be obtained by diagonalizing $\sum_{i=1,2} H_i$, which involves the combination of $|5\rangle$ and $|6\rangle$ into a singlet and triplet states and the same for $|9\rangle$ and $|10\rangle$. The corresponding eigenvalues are listed in the Eq. (4) and the crystal-field splitting Δ has been included. The 6 new e_g^2 bases $|n\rangle$ (n=5-10, as shown in Eq. (4)) do not couple to the singly occupied states $|1\rangle \sim |4\rangle$. Considering the perturbation Hamiltonian $H_{e_g}^{LDA}$, we get the

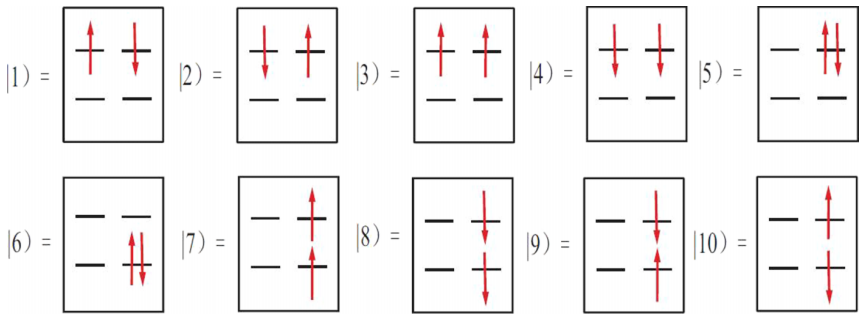

FIG. 2. The schematic show of the states with two holes occupying the two Ag sites. The up and down arrows denote the spin-up and spin-down holes respectively.

hopping integrals, which is the matrix elements of the Hamiltonian $H_{e_g}^{LDA}$ between states $|1) \sim |4)$ and $|5\rangle \sim |10\rangle$ in the space of 10 two-hole states. As a result, the off-diagonal elements of H-$2\epsilon_2$ (relative to the on site energy of $3z^2$-r^2) are then:

$$\begin{pmatrix}
 & \frac{\sqrt{2}}{2}(|5)+|6)) & \frac{\sqrt{2}}{2}(|5)-|6)) & |7\rangle & |8\rangle & \frac{\sqrt{2}}{2}(|9)+|10)) & \frac{\sqrt{2}}{2}(|9)-|10)) \\
(1| & \frac{t_{1,1}^{xyz}}{\sqrt{2}} & \frac{t_{1,1}^{xyz}}{\sqrt{2}} & 0 & 0 & \frac{t_{1,1}^{xyz}}{\sqrt{2}} & \frac{t_{1,1}^{xyz}}{\sqrt{2}} \\
(2| & \frac{t_{1,1}^{xyz}}{\sqrt{2}} & \frac{t_{1,1}^{xyz}}{\sqrt{2}} & 0 & 0 & \frac{t_{1,1}^{xyz}}{\sqrt{2}} & -\frac{t_{1,1}^{xyz}}{\sqrt{2}} \\
(3| & 0 & 0 & t_{1,2}^{xyz} & 0 & 0 & 0 \\
(4| & 0 & 0 & 0 & t_{1,2}^{xyz} & 0 & 0 \\
\langle 5| & U+J+\Delta & 0 & 0 & 0 & 0 & 0 \\
\langle 6| & 0 & U-J+\Delta & 0 & 0 & 0 & 0 \\
\langle 7| & 0 & 0 & U-3J+\Delta & 0 & 0 & 0 \\
\langle 8| & 0 & 0 & 0 & U-3J+\Delta & 0 & 0 \\
\langle 9| & 0 & 0 & 0 & 0 & U-J+\Delta & 0 \\
\langle 10| & 0 & 0 & 0 & 0 & 0 & U-3J+\Delta
\end{pmatrix} \tag{4}$$

The energy difference between the Néel state and the FM state is that between the 2nd-order-perturbation energy of $|3)$ and $|1)$, we thus obtain:

$$\begin{aligned}
\Delta E &= \sum_{n=5}^{10} \frac{|\langle n|H_{e_g}^{LDA} - 2\epsilon_1|3)|^2}{E - E_n^0} - \sum_{n=5}^{10} \frac{|\langle n|H_{e_g}^{LDA} - 2\epsilon_1|1)|^2}{E - E_n^0} \\
&= |t_{1,1}^{xyz}|^2\left(\frac{\frac{1}{2}}{U+J+\Delta} + \frac{\frac{1}{2}}{U-J+\Delta}\right) + |t_{1,2}^{xyz}|^2\left(\frac{\frac{1}{2}}{U-J+\Delta} + \frac{\frac{1}{2}}{U-3J+\Delta}\right)
\end{aligned} \tag{5}$$

To obtain the value of ΔE, we need the values of hopping integrals between the R′=(000) and R=(x, y, z) Ag ions, especially the $t_{1,2}^{xyz}$ and $t_{1,1}^{xyz}$, which can be obtained using NMTO downfolding scheme.

We show the LDA band structure of α-K_2AgF_4 in Fig. 3(a), in which the e_g states lying in the -2.0 ~ 0.5 eV are active. The NMTO downfolded Ag e_g bands is shown in Fig. 3(b). The agreement of the LDA and NMTO downfolded Ag e_g bands suggests that the Hamiltonian is indeed physically reasonable and is suitable to capture the low energy physics of the α-K_2AgF_4. In Fig. 4, we show one layer of Ag ions in a unit cell of α-K_2AgF_4. The hopping integrals up to the third nearest neighbor (NN) are shown in Fig. 4 with $t^{1/201/2}$, t^{001} and t^{100} are the first, second and third NN hopping integers respectively. The xyz are the local coordinates used in this paper with z axis perpendicular to the xy-plane and is not shown here. The abc are the lattice coordinates with b-axis perpendicular to the ac-plane and is also not shown here. The values of hopping integers within the e_g Wannier representation are as follows:

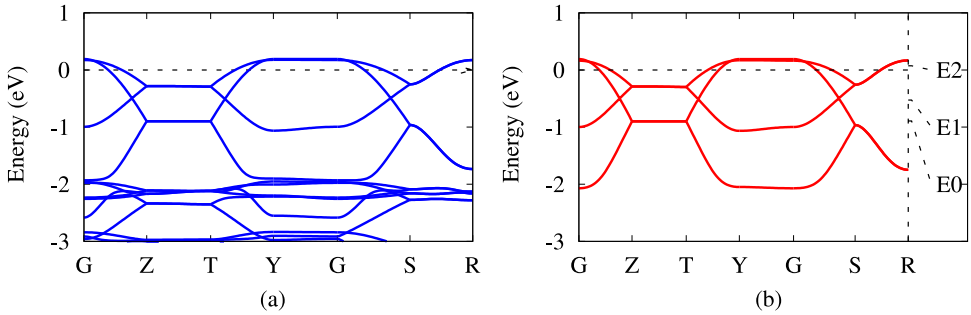

FIG. 3. (a) The band structure of non-spin-polarized α-K_2AgF_4 obtained with the full LDA basis. (b) The downfolded Ag e_g bands with NMTO basis. E_0, E_1 and E_2 are energy grids used in the downfolding procedure.

NMTO basis set:

$$|\chi^{\perp}\rangle = \{|3z^2 - r^2\rangle, |x^2 - y^2\rangle\} \tag{6}$$

The on-site term:

$$t^{000}_{\alpha,\beta} = \begin{pmatrix} -336 & 0 \\ 0 & -1008 \end{pmatrix} \tag{7}$$

The first NN:

$$t^{1/201/2}_{\alpha,\beta} = \begin{pmatrix} -147 & -215 \\ -215 & -284 \end{pmatrix} \tag{8}$$

The second NN:

$$t^{001}_{\alpha,\beta} = \begin{pmatrix} -11 & 0 \\ 0 & 43 \end{pmatrix} \tag{9}$$

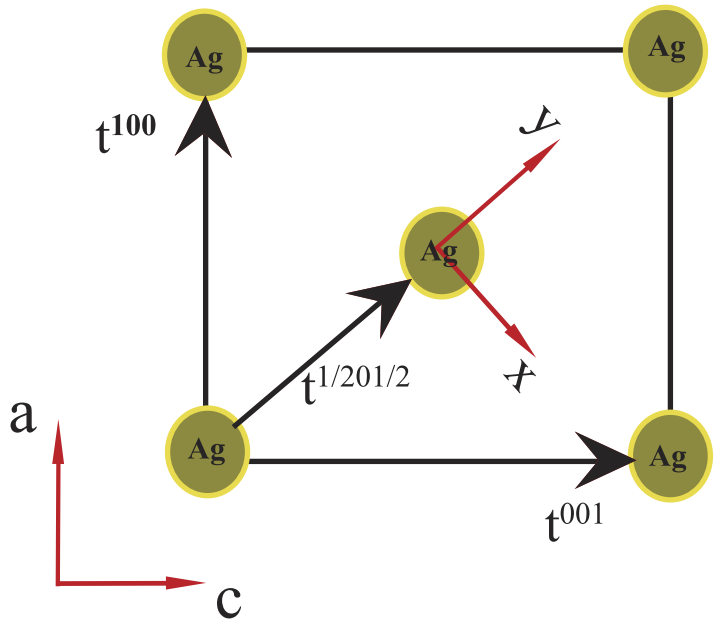

FIG. 4. The schematic show of the pathes of the first ($t_{12}^{1/201/2}$), second (t_{12}^{001}) and third (t_{12}^{100}) NN hopping integrals.

The third NN:

$$t^{100}_{\alpha,\beta} = \begin{pmatrix} -2 & 0 \\ 0 & 26 \end{pmatrix} \tag{10}$$

where the unit is meV. The α and β represent the $3z^2$-r^2 and x^2-y^2, respectively. The hopping integral of the first, second and third NN between Ag ions are shown in Fig. 4. The on-site energies for $3z^2$-r^2 and x^2-y^2 are ϵ_2=-336 and ϵ_1=-1008 meV, respectively, which indicate that the crystal-field splitting of $3z^2$-r^2 and x^2-y^2 are Δ = 672 meV. The non-zero off-diagonal values of the first NN hopping integrals in Eq. (8) ($t^{1/201/2}_{12} = t^{1/201/2}_{21}$ = -215 meV) indicate that the hoppings between $3z^2$-r^2 and x^2-y^2 of the first NN Ag ions are allowed along all the directions. Further away NN hoppings are much smaller and will not be considered here.

Now we can evaluate the magnetic exchange constants in terms of Heisenberg Hamiltonian:

$$H = J_{ex} \sum_{\langle i,j \rangle} S_i \cdot S_j \tag{11}$$

For $E = 2\epsilon_2$ and $S = \frac{1}{2}$, ΔE is of $\frac{1}{4}$ the exchange constant J_{ex} between the two sites considered, so

$$J_{ex} = 4\Delta E \tag{12}$$

J<0 represents FM coupling, J>0 represents AFM coupling. From the expression of ΔE in Eq. (5) we can see that the first term is always positive, which is caused by the superexchange between $3z^2$-r^2 orbitals of the two Ag ions and will lead to AFM alignment. The second term might be negative, which is caused by the superexchange between $3z^2$-r^2 and x^2-y^2 orbitals of the two Ag ions and will lead to FM alignment. We calculate the exchange constant up to third NN within U=4.5 and J=1 eV, which show that J_1 = -1 meV, J_2 and J_3 are negligible. This indicates the weak FM coupling of the NN Ag ions, which is in accordance with the extremely low ferromagnetic transition temperature (T_C = 26 K). Therefore, the origin of the weak FM in α-K_2AgF_4 is caused by the superexchange between $3z^2$-r^2 and x^2-y^2 orbitals of the first NN Ag ions.

In summary, we have successfully explained the origin of the ferromagnetism in α-K_2AgF_4. First, we have proved that the electron correlation in Ag $4d^9$ is very important in determining the insulating behavior of α-K_2AgF_4. Second, we have proposed that both of the two e_g orbitals engage in the superexchange interaction by determining the Ag $4d^9$ configuration in the form of $t^6_{2g}e^3_g$, in which the two e_g orbitals show very delocalization features. Last, we reach a conclusion that the exchange interaction between e_g $3z^2$-r^2 and x^2-y^2 from the first NN Ag ions leads to the anomalous ferromagnetism in α-K_2AgF_4.

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