First-principles calculations of the electronic and magnetic properties of Cs₂AgF₄

Er-Jun Kan, Lan-Feng Yuan, Jinlong Yang,* and J. G. Hou

Hefei National Laboratory for Physical Sciences at Microscale, University of Science and Technology of China, Hefei, Anhui 230026,

People's Republic of China

(Received 12 February 2007; revised manuscript received 3 June 2007; published 13 July 2007)

 Cs_2AgF_4 forms a layered perovskite structure and contains $4d^9$ metal ions, similar to the $3d^9$ Cu cuprates. However, the cuprates are antiferromagnetic, while Cs_2AgF_4 is ferromagnetic. Here we investigate the electronic and magnetic properties of Cs_2AgF_4 using density functional theory (DFT) to clarify the origin of its ferromagnetism. The ground state is found to be ferromagnetic and nearly semimetallic. Because of Jahn-Teller distortions in the $[AgF_6]^{4-}$ octahedron, the ground state has a staggered order of z^2-x^2 and z^2-y^2 orbitals. The superexchange interaction through the $Ag(z^2-x^2)-F-Ag(z^2-y^2)$ bridge stabilizes the ferromagnetism. In order to take into account the on-site Coulomb interaction, we also perform DFT+U calculations. The insulating state becomes the ground state, while the ferromagnetism and orbital order of z^2-x^2 and z^2-y^2 are still preserved.

DOI: 10.1103/PhysRevB.76.024417

PACS number(s): 75.10.Lp, 75.50.-y, 71.20.-b

I. INTRODUCTION

In the high- T_c superconductors of layered cuprates such as La₂CuO₄, it is generally believed that two-dimensional (2D) antiferromagnetic (AFM) order is an essential aspect of their superconductivity.^{1,2} In order to extend our understanding of high- T_c superconductors, other layered transition-metal materials have also been studied.³⁻⁶ As an ideal isostructural analog of La₂CuO₄, Cs₂AgF₄ was first synthesized by Odenthal *et al.*,⁷ where featured d^9 metal ions and AgF₂ square lattices are presented. Therefore, it is natural to guess Cs₂AgF₄ as a 2D square-lattice Heisenberg antiferromagnet and possible high- T_c superconductor. However, measurements of magnetism reveal that Cs₂AgF₄ is ferromagnetic (FM),^{2,7} and no high- T_c superconductivity has been reported. The unexpected FM coupling has attracted great interest.

In order to explain the puzzling difference between the cuprates and Cs₂AgF₄ in magnetism, some theoretical works have been done. Kasinathan et al. obtain a FM ground state which is 6 meV below the spin-unpolarized solution within the generalized gradient approximation (GGA) in the framework of density functional theory (DFT).⁸ They do not obtain any orbital order in their calculations and conclude that ferromagnetism may arise from a Stoner⁹ mechanism. Also based on the GGA. Dai et al. find that the FM state is preferred to the AFM state by 28 meV.¹⁰ They conclude that the ferromagnetism in Cs₂AgF₄ is caused by the spin polarization of the $x^2 - y^2$ bands originating from the $3z^2 - r^2 - p - x^2 - y^2$ superexchange interactions through the Ag-F-Ag bridges. In the above calculations, the single-crystal structure of Cs₂AgF₄ is I4/mmm according to the measurements of Odenthal *et al.*,⁷ so $[AgF_6]^{4-}$ octahedra have no tilted or displaced distortions from center symmtry in the Ag-F sheets. However, recently McLain et al. refine the crystal structure of Cs_2AgF_4 in the space group *Bbcm* by neutron diffraction,² where in-plane F atoms are displaced from central positions between Ag atoms in the Ag-F square lattices. The Bbcm orthorhombic lattice is related to an associated I4/mmm tetragonal lattice by, approximately, a_{Bbcm} = $\sqrt{2a_{I4/mmm}}$, $b_{Bbcm} = \sqrt{2b_{I4/mmm}}$, and $c_{Bbcm} = c_{I4/mmm}$. Just as in the I4/mmm structure, Ag and F atoms form layers of edgeshared $[AgF_6]^{4-}$ octahedra. But displacement of F atoms from the central positions between the nearest-neighbor Ag atoms lowers the crystal symmetry and leads to alternate Ag-F bond lengths. They suggest that alternate Ag-F distances possibly cause staggered orbital order of $z^2 - x^2$ and $z^2 - y^2$ orbitals in the Ag-F sheets and the superexchange interaction between staggered Ag 4*d* orbitals through F atoms makes FM solution stable.

In this paper, we use first-principles calculations to elucidate the electronic and magnetic properties of Cs_2AgF_4 , based on recent refinements of crystal structure. The possible orbital order and stabilization of the FM state are investigated with both DFT and DFT+U.

II. COMPUTATIONAL METHOD

Our electronic calculations are performed with the Vienna ab initio simulation package (VASP), which implements DFT using a plane-wave basis set.^{11,12} The Perdew-Wang functional form of the GGA is adopted.¹³ The projector augmented-wave14 (PAW) method in its implementation of Kresse and Joubert¹⁵ is used to describe the electron-ion interaction. The Kohn-Sham equations are solved via a Davidson-block iteration scheme.¹² The plane-wave kinetic energy cutoff is fixed at 500 eV. Brillouin zone (BZ) integrations are performed on a well-converged grid of 8×8 \times 4 Monkhorst-Pack¹⁷ special points. The total energy is converged to 10^{-6} eV/cell. The geometry optimizations start from the experimental structure and reach convergence until all the forces vanish within 0.002 eV/Å. During the optimizations, the cell parameters are fixed to the experimental values (a=6.435 Å, b=6.439 Å, and c=14.150 Å). The total energy and density of states (DOS) are calculated using the linear tetrahedron method with Blochl corrections.¹⁶ The approach of Dudarev et al.¹⁸ is adopted for DFT+U calculations. Since this DFT+U functional depends only on the difference of the Hubbard parameter U and screened exchange parameter J, J is fixed at 1 eV in all DFT+U calculations. The Hubbard on-site Coulomb interaction is applied to Ag 4d orbitals only. Geometry relaxation is performed at a spinpolarized GGA level.



FIG. 1. (Color online) Crystal structure of Cs_2AgF_4 . The left one is a side view of the crystal structure, and the right one is a top view of the Ag-F sheet.

III. RESULTS AND DISCUSSIONS

A. GGA results

In our calculations, we consider four kinds of magnetic structures: nonmagnetic (NM), FM, and two different AFM coupling denoted as A and G type. A-type AFM coupling represents the FM coupling in the Ag-F sheets plus AFM coupling between the Ag-F layers along the [001] direction, while G-type AFM corresponds to the situation that all Ag atoms are antiferromagnetically coupled to their nearest-neighbor ones.

In Cs₂AgF₄, there are two types of F sites (as shown in Fig. 1). One is apical along the [001] direction (named as F_1), and the other is in the Ag-F sheets (named as F_2). An F_1 site only connects to one Ag, and an F_2 site bridges two Ag atoms with 180° in the Ag-F square lattices. The optimized atomic positions in FM coupling (as listed in Table I) have only minor differences from the experimental ones. The calculated Ag-F distances in the Ag-F sheets are 2.178 and 2.374 Å, while the experimental values are 2.113 and

TABLE I. Structural parameters of *Bbcm* Cs_2AgF_4 in the FM state. Experimental values are presented in parentheses.

Atom	X	у	Z
Ag	0.0 (0)	0.0 (0)	0.0 (0)
Cs	0.0 (0)	0.0 (0)	0.3559 (0.3567)
F_1	0.0 (0)	0.0 (0)	0.1534 (0.1492)
F ₂	0.2388 (0.2382)	0.2386 (0.2256)	0.0 (0)

2.440 Å. In the A-type AFM coupling, the calculated Ag-F distances in the Ag-F sheets are 2.150 and 2.402 Å, close to the ones in the FM states, and the A-type AFM state lies only 8 meV above the FM state. In the nonmagnetic state, which is about 74 meV above the FM state, F_2 atoms are located at central positions of the nearest-neighbor Ag atoms, and the calculated Ag-F distances are identical (2.277 Å) in the Ag-F square lattices. After geometric relaxations, we find that the *G*-type AFM solution is not stable and converges to NM state.

The different structural behaviors of the four kinds of magnetic structures provide clues to pursuing the origin of FM order in Cs_2AgF_4 . The small energy difference between the FM and A-type AFM solutions implies that the interaction between the Ag-F sheets is weak. As shown in Fig. 2, the bands of FM states around Fermi energy are very flat along the [001] direction, confirming this observation. In the Ag-F sheets, a large dispersion of the bands reveals the existence of strong interactions between the Ag and F atoms. In the spin-majority channel, the valence bands are fully occupied, with the Fermi energy being near the valence band edge, while partly occupied in the spin-minority channel. Thus, the electronic structure has nearly semimetallic character.

The total and projected DOS are presented in Fig. 3. Since the only difference between the A-AFM and FM is the very weak magnetic coupling inter-Ag-F sheets, here we only dis-



FIG. 2. (Color online) Band structure of Cs_2AgF_4 in FM solution. The dotted red line represents the Fermi level.



FIG. 3. (Color online) Calculated total and projected DOS of Cs_2AgF_4 in FM (a) and nonmagnetic (b) states.

cuss the electronic structures of the FM and nonmagnetic solutions. The valence bands have mixed Ag-F character. The interaction between Ag and F atoms involves both F_1 and F_2 atoms. For the FM state, F_1 and F_2 atoms have different spin-polarized behaviors. From -1 to 1 eV (relative to E_F), F_1 and F_2 atoms have a similar hybridization with Ag atoms and F_1 atoms mix more strongly than F_2 atoms from -2.5 to -1 eV and the situation is opposite from -4.5 to -2.5 eV. The calculated spin magnetizations are $0.10\mu_B$ and $0.12\mu_B$, for F_1 and F_2 atoms, respectively. Similar with previous results, ^{19,20} we find that Ag-F bonds have significant covalency.

The projectied DOS presented in Fig. 3(b) reveals that the electronic structure becomes metallic in NM solution. F_1 and F_2 atoms show little difference from the DOS figures near the Fermi energy. It is easily found that the hybridization between Ag and F has similar character with that in FM coupling.

Since the ferromagnetism in Cs_2AgF_4 is obtained, the next question is its origin. As an analog of K_2CuF_4 (Ref. 21) and Rb_2CuCl_4 (Ref. 22), strong superchange interaction through different orbitals is proposed as the reason.² In our calculations, because the Ag-F distances are not equivalent in the Ag-F sheets and F2 atoms are displaced from central positions, the Ag-F distances are alternately distributed in the Ag-F square lattices and the shorter ones are almost identical with those along the [001] direction (2.176 Å). The Jahn-Teller distortions cause staggered orbital order of $z^2 - x^2$ and z^2 - y^2 orbitals in the Ag-F sheets just as that in LaMnO₃ (Ref. 23) and $(C_2H_5NH_3)_2CuCl_4$ (Ref. 24). In Fig. 4, we present the occupied- and unoccupied-band charge densities around the Fermi level. It is clear that both occupied and unoccupied bands have the same orbital order of $z^2 - x^2$ and $z^2 - y^2$ orbitals because nine electrons locate in the Ag 4d orbitals. There-



FIG. 4. (Color online) Occupied (a) side view and (b) top view of one single Ag-F sheet and unoccupied (c) side view and (d) top view of one single Ag-F sheet band charge densities in FM solution. The energy window of 0.5 eV width is shown just below the Fermi level for occupied states and 0.5 eV width above the Fermi level for unoccupied states.

fore, the origin of ferromagnetism in Cs₂AgF₄ is likely to be superexchange interaction the through the $Ag(z^2-x^2)$ -F- $Ag(z^2-y^2)$ bridge. The staggered orbital ordering obviously derives from the staggered Ag-F distances in the Ag-F sheets which are absent in other calculations.^{8,10,19,20} On the other hand, in the nonmagnetic state, there is no orbital order of Ag atoms as shown in Fig. 5. From the occupied-band charge density, we clearly see that all Ag atoms are equal and the occupied bands are constituted with mixed d_{z^2} and $d_{x^2-v^2}$ character. We also perform calculations with the experimental geometric structures. The results show the magnetic ordering is FM, just as the optimized structures. The occupied- and unoccupied-band charge densities around Fermi level in FM solution have the same situation.

It is interesting to investigate why we can get FM solution but not *G*-type AFM solution. In the perfect AgF₆ octahedron, six Ag-F bonds are of equal length and the local point group is O_h . Its e_g levels (i.e., the z^2 and x^2-y^2 levels) are degenerate, while in the *Bbcm* lattices with *G*-type AFM state, each AgF₆ octahedron is accompanied by axial compression along the [001] direction. This distortion makes the z^2 level higher than the x^2-y^2 level, and all Ag atoms have the same orbital occupancy. Because of the extended nature of



FIG. 5. (Color online) Occupied bands charge densities in nonmagnetic state: (a) side view and (b) top view of one single Ag-F sheet. The energy window of 0.5 eV width is shown just below the Fermi level for occupied states.



FIG. 6. (Color online) (a) The calculated spin magnetization (M) within DFT+U. The top line is relative to F atoms, while the bottom one is relative to Ag atoms in FM solution. U=0 means GGA results. (b) Electronic structure of Cs₂AgF₄ in FM solution with Hubbard U at 3 eV.

Ag 4*d* orbitals relative to 3*d* electrons and deficiency of the GGA function, the 4*d* electrons of Ag atoms are artificially delocalized. Therefore, through the Ag–F–Ag bridge, the interaction between the same z^2 orbitals of nearest neighbors is artificially strengthened and makes the 4*d* electrons of z^2 orbitals itinerant. The local exchange effect of z^2 orbitals is removed, so the *G*-AFM state converges into a nonmagnetic solution. In the FM state, because of the distortion in the Ag-F sheets, Ag atoms have staggered orbital occupation of z^2-x^2 and z^2-y^2 orbitals in each Ag-F square. The interaction through the Ag–F–Ag bridge cannot eliminate the difference of z^2-x^2 or z^2-y^2 orbitals in different spin channels, so FM solution can be achieved.

B. DFT+U results

Although Ag 4*d* electron wave functions are more extended than 3*d* electrons, the electron-correlation effect may still be important. Therefore, we also study the stability of ferromagnetism, using DFT+U calculations. Because of the weak coupling between the Ag-F sheets, FM and A-type AFM states almost have the same electronic properties. Thus, we only consider the FM and G-type AFM states and treat the Coulomb U as a parameter (we use a value of U as 3, 4, 5, 6, 7 eV). One of the important results is that meta-stable G-type AFM solution is obtained and Ag atoms have a magnetic moment as large as $0.38\mu_B$ even at U=3 eV. Thus the.

In the DFT+U calculations, the FM solution is always preferred over the *G*-type AFM state by 0.4 eV with all *U* used in the calculations. Compared with GGA results, the FM solution becomes more stable. In Fig. 6(a), we present the spin magnetization of Ag and F atoms in FM coupling under DFT and DFT+U calculations. It is interesting that the magnetization of Ag has a different tendency from that of F with the Hubbard *U*. The spin magnetization of Ag increases with an increase of U, indicating that Ag 4*d* electrons become more localized. The opposite tendency for F implies that the hybridization between Ag and F is reduced with an increase of U. For electronic properties, even with a small value of U (3 eV), Cs₂AgF₄ has switched from a nearly semimetallic to an insulating state. For 4*d* or 5*d* metal atoms, the DFT+U method has proved to be an effective way to get correct results.^{25–27} Their results reveal that the $U_{eff}=U-J$ should be at least about 3 eV for 4*d* or 5*d* metal atoms. Since this is a reasonable value for Ag 4*d* electrons in a screening environment, we conclude that Cs₂AgF₄ is an insulator.

FM solution is always favored at all Hubbard U parameter. Since FM ordering derives from the superexchange through the Ag(z^2-x^2)-F-Ag(z^2-y^2) bridge according to our GGA results, the staggered orbital order of z^2-x^2 and z^2-y^2 orbitals should be preserved. Our results confirm the above predictions. So the Hubbard U only affects the electronic structures and atom spin magnetization, but not the orbital order.

IV. CONCLUSION

In summary, we have performed DFT and DFT+U calculations on the electronic and magnetic properties of Cs_2AgF_4 . Based on the GGA, we obtain a FM ground state which has nearly semimetallic structure. Because of Jahn-Teller distortions of $[AgF_6]^{4-}$ octahedra, a staggered order of z^2-x^2 and z^2-y^2 orbitals is formed in the Ag-F square lattices. Due to the strong hybridization between Ag and F, the superchange interaction through the $Ag(z^2-x^2)$ -F- $Ag(z^2-y^2)$ bridge makes the FM solution favored. In order to take into account the on-site Coulomb interaction, DFT+U calculations are carried out. On the other hand, with all Hubbard U we use in DFT+U, the FM solution is always the ground state and the orbital order in the Ag-F sheets is preserved.

ACKNOWLEDGMENTS

This work is partially supported by the National Natural Science Foundation of China (Grant Nos. 50121202,

20533030, and 10474087), by National Key Basic Research Program under Grant No. 2006CB922004, by the USTC-HP HPC project, and by the SCCAS and Shanghai Supercomputer Center.

*Corresponding author. jlyang@ustc.edu.cn

- ¹W. E. Pickett, H. Krakauer, R. E. Cohen, and D. J. Singh, Science **255**, 46 (1992).
- ²S. E. McLain, M. R. Dolgos, D. A. Tennant, J. F. C. Turner, T. Barnes, T. Proffen, B. C. Sales, and R. I. Bewley, Nat. Mater. 5, 561 (2006).
- ³R. L. Leheny, R. J. Christianson, R. J. Birgeneau, and R. W. Erwin, Phys. Rev. Lett. **82**, 418 (1999).
- ⁴W. Bao, Y. Chen, Y. Qiu, and J. L. Sarrao, Phys. Rev. Lett. **91**, 127005 (2003).
- ⁵P. A. Fleury and H. J. Guggenheim, Phys. Rev. Lett. **24**, 1346 (1970).
- ⁶T. Huberman, R. Coldea, R. A. Cowley, D. A. Tennant, R. L. Leheny, R. J. Christianson, and C. D. Frost, Phys. Rev. B 72, 014413 (2005).
- ⁷R.-H. Odenthal, D. Paus, and R. Hoppe, Z. Anorg. Allg. Chem. **407**, 144 (1974).
- ⁸D. Kasinathan, A. B. Kyker, and D. J. Singh, Phys. Rev. B **73**, 214420 (2006).
- ⁹E. C. Stoner, Proc. R. Soc. London, Ser. A 165, 372 (1938).
- ¹⁰D. Dai, M.-H. Whangbo, J. Kohler, C. Hoch, and A. Villesuzanne, Chem. Mater. **18**, 3281 (2006).
- ¹¹G. Kresse and J. Hafner, Phys. Rev. B **49**, 14251 (1994).
- ¹²G. Kresse and J. Furthmuller, Comput. Mater. Sci. 6, 15 (1996).
- ¹³J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, and C. Fiolhais, Phys. Rev. B 46, 6671

(1992).

- ¹⁴P. E. Blochl, Phys. Rev. B **50**, 17953 (1994).
- ¹⁵G. Kresse and D. Joubert, Phys. Rev. B **59**, 1758 (1996).
- ¹⁶P. E. Blochl, O. Jepsen, and O. K. Andersen, Phys. Rev. B 49, 16223 (1994).
- ¹⁷H. J. Monkhorst and J. D. Pack, Phys. Rev. B **13**, 5188 (1976).
- ¹⁸S. L. Dudarev, G. A. Botton, S. Y. Savrasov, C. J. Humphreys, and A. P. Sutton, Phys. Rev. B 57, 1505 (1998).
- ¹⁹R. Valiente, J. A. Aramburu, M. T. Barriuso, and M. Moreno, J. Phys.: Condens. Matter 6, 4515 (1994).
- ²⁰W. Grochala and R. Hoffmann, Angew. Chem., Int. Ed. **40**, 2742 (2001).
- ²¹W.-H. Li, C. H. Perry, J. B. Sokoloff, V. Wagner, M. E. Chen, and G. Shirane, Phys. Rev. B **35**, 1891 (1987).
- ²²F. Aguado, F. Rodríguez, R. Valiente, A Señas, and I. Goncharenko, J. Phys.: Condens. Matter 16, 1927 (2004).
- ²³H. Zenia, G. A. Gehring, and W. M. Temmerman, New J. Phys. 7, 257 (2005).
- ²⁴Y. Moritomo and Y. Tokura, J. Chem. Phys. **101**, 1763 (1994).
- ²⁵I. V. Solovyev, P. H. Dederichs, and V. I. Anisimov, Phys. Rev. B 50, 16861 (1994).
- ²⁶H. J. Xiang and M.-H. Whangbo Phys. Rev. B **75**, 052407 (2007).
- ²⁷N. Stojic, N. Binggeli, and M. Altarelli, Phys. Rev. B 73, 100405(R) (2006).