Orbital ordering in the ferromagnetic insulator Cs_2AgF_4 from first principles

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We found, using density-functional theory calculations within the generalized gradient approximation, that Cs_2AgF_4 is stabilized in the insulating orthorhombic phase rather than in the metallic tetragonal phase. The lattice distortion present in the orthorhombic phase corresponds to the $x^2 - z^2/y^2 - z^2$ hole-orbital ordering of the Ag^{2+} $4d^9$ ions, and this orbital ordering leads to the observed ferromagnetism, as confirmed by the present total-energy calculations. This picture holds in the presence of moderate $4d$-electron correlation. The results are compared with the picture of ferromagnetism based on the metallic tetragonal phase.

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I. INTRODUCTION

It is quite often that the $3d$ transition-metal oxides with orbital degeneracy display an orbital ordering associated with lattice distortions (of the Jahn-Teller type).[1,2] In contrast, $4d$ and $5d$ transition-metal compounds rarely show this,[3–7] mainly due to the delocalized character of the d electrons. It was therefore a surprise when the $4d$-orbital ordering and the orbitally driven spin-singlet dimerization were found in the ruthenate $La_4Ru_2O_{10}$.[7] Moreover, the fascinating superstructure of the spinel $CuIr_2S_4$ (Ref. 3) was explained in terms of the concept of orbitally-induced Peierls state (associated with the partially occupied Ir $5d$ orbitals).[4]

Very recently,[8,9] the magnetic behavior of the layered Cs_2AgF_4 was investigated, and the in-plane ferromagnetism (FM) of the S=1/2 Ag^{2+} ions was evidenced by magnetization and inelastic neutron scattering measurements, in sharp contrast to the structurally analogous high-T_c cuprates. Moreover, analysis of the structural data suggests that Cs_2AgF_4 is $4d$ orbitally-ordered, and it was proposed that such orbital ordering may be the origin of the observed FM.

Cs_2AgF_4 was first synthesized in 1974 by Odenthal, Paus, and Hoppe,[10] and it received, as well as other silver fluorides, attention due to pursuit of superconductivity in transition-metal compounds other than the cuprates.[11–13] Cs_2AgF_4 is a structural analog of the parent compound of cuprate superconductors, La_2CuO_4 (AgF_2 *vs* CuO_2 sheet), and both have the S=1/2 divalent transition-metal cations (Ag^{2+} $4d^9$ *vs* Cu^{2+} $3d^9$) and isoelectronic anions (F^- *vs* O^{2-}). It is well known that La_2CuO_4 is a Mott insulator of charge-transfer type with two-dimensional Heisenberg antiferromagnetism (AF). Upon hole doping (like Ba substitution for La) it is tuned into a superconductor, and, its high-temperature normal state being a paramagnetic metal, has the holes predominantly on the antibonding $pd\sigma$ band.[14] Silver fluorides have similar electronic band structure, namely the Ag-F $pd\sigma$ antibonding character in the vicinity of the Fermi level.[11] Moreover, the Ag-F bonding is substantially covalent in the Ag^{2+} and Ag^{3+} fluorides, and thus holes might be doped into the F $2p$ band, which is unprecedented in the chemistry of transition-metal compounds. As a result, an interesting new perspective is opened for the design of a novel family of metallic, perhaps even superconducting materials based on silver fluorides.[12]

Subsequent to the finding of FM in Cs_2AgF_4,[8] its electronic structure was studied by Kasinathan *et al.*[15] and Dai *et al.*,[16] both using density-functional theory (DFT). Kasinathan *et al.* found the FM, due to importance of the Ag-F covalency, to be itinerant in character, and substantial magnetic moment on the fluorine ions as result of a Stoner instability enhanced by Hund's coupling.[15] Dai *et al.* suggested that the FM originates from the spin polarization of the doubly occupied $x^2 - y^2$ band, which is induced by the $d_{z^2} - p - d_{x^2-y^2}$ orbital interaction through the Ag-F-Ag bridges.[16] Both groups of authors dealt with the tetragonal lattice[10] and obtained a nearly half-metallic solution in the FM state, and used it to explain the origin of FM in Cs_2AgF_4.[15,16] However, in reality Cs_2AgF_4 is an insulator with a relatively large energy gap (lilac color) and has a distorted orthorhombic lattice,[8] and thus the above studies of the FM are insufficient. More recently, Kan *et al.*[17] performed pseudopotential DFT calculations for the orthorhombic structure and they obtained an orbitally ordered solution (in contrast to Refs. 15 and 16). However, their calculations underestimated the in-plane distortion and strongly overestimated both the in-plane and out-of-plane magnetic coupling strengths. Moreover, they did not investigate the tetragonal structure. Therefore, their results do not allow to reach solid conclusions.

In the present work, we re-investigate theoretically the electronic structure of Cs_2AgF_4 and the origin of its FM, by carrying out a comparative study of the orthorhombic and tetragonal lattices of Cs_2AgF_4 using DFT total-energy calculations. We find that the orthorhombic phase is more stable and it is insulating with suppressed Ag-F bandwidths. The inherent lattice distortion is accompanied by the Ag $4d$-orbital ordering, and this orbital ordering readily accounts for the observed FM (similar results were also obtained recently by Hao *et al.*[18]). This picture holds in the presence of a moderate correlation of the Ag $4d$ electrons. The resulting picture of an orbital ordering and of a ferromagnetic insulating state of

Cs_2AgF_4 is thus very similar to that of an isoelectronic and isostructural compound K_2CuF_4.[1,19]

II. RESULTS AND DISCUSSION

Our electronic structure calculations are performed by using the all-electron full-potential augmented plane wave plus local orbital method.[20] The generalized gradient approximation[21] (GGA) to density-functional theory is adopted.[22] We took the neutron diffraction structure data measured at 6 K.[8] As seen below, the electronic structure and magnetic properties of Cs_2AgF_4 are determined by an orbital ordering, and the orbital ordering is the most relevant to the local distortion of the AgF_6 octahedra. To account for a possible lattice distortion connected with an orbital ordering, we carried out the optimization of the atomic positions, keeping the unit-cell parameters fixed and relaxing the atomic coordinates. The obtained values of atomic positions and bond-lengths are in good agreement with the experimentally determined values, see below. Based on that, in the further calculations we use the experimental structure data. The Cs $5p5d6s$ ($4d5s$), Ag $4d5s5p$ ($4s4p$), and F $2p3s$ ($2s$) are treated as valence (semicore) states. The muffin-tin sphere radii are chosen to be 2.8, 2.2, and 1.7 Bohr for Cs, Ag, and F atoms, respectively. The cut-off energy of 16 Ryd is set for the plane-wave expansion of the interstitial wave functions. The sufficiently dense **k** mesh, e.g., 10×10×4 is used for integration over the Brillouin zone of the primitive cell with the experimental orthorhombic lattice constant a=6.4345 Å , b=6.4390 Å , and c=14.1495 Å .[8] The present set-up ensures a sufficient accuracy of the calculations.

Fig. 1 shows the total and the orbital-resolved density of states (DOS) for the FM orthorhombic phase of Cs_2AgF_4 obtained in GGA. It is an insulator with a gap of about 0.2 eV, but neither a metal (nor a half-metal) as predicted before for the tetragonal phase[15,16] (see also below) nor a semimetal as obtained for the orthorhombic phase.[17] The strong hybridization between Ag $4d$ and F $2p$ levels (apical F_{ap} and planar F_{pl}), both centered around 3 eV below the Fermi level, is obvious in both the valence and the conduction bands, and this gives rise to the large bonding–antibonding splitting of about 2 eV for the Ag t_{2g} (xz, yz, and xy) orbitals and even a larger one for the e_g orbitals. The t_{2g} bands are fully occupied and the e_g bands are three-fourth occupied (with one hole left on them) as expected for the formal Ag^{2+} ($4d^9$) ions. Actually, the one hole spreads, due to the strong Ag–F covalency, over the six fluorine atoms of the AgF_6 octahedron. As a result, the hole state consists of approximately 60% of the Ag $4d$ and 40% of the $2p$ of the four F atoms (see the DOSs above the Fermi level in the second, third, and fourth panels of Fig. 1), according to the stoichiometry of Cs_2AgF_4.[23] This is also reflected by the magnitude of local spin magnetic moments within each muffin-tin sphere, 0.560 μ_B/Ag, 0.105 μ_B/F_{ap}, and 0.112 μ_B/F_{pl}, see also Table I. The hole states have alternating x^2-z^2 and y^2-z^2 symmetry shown in Figs. 1 and 2.

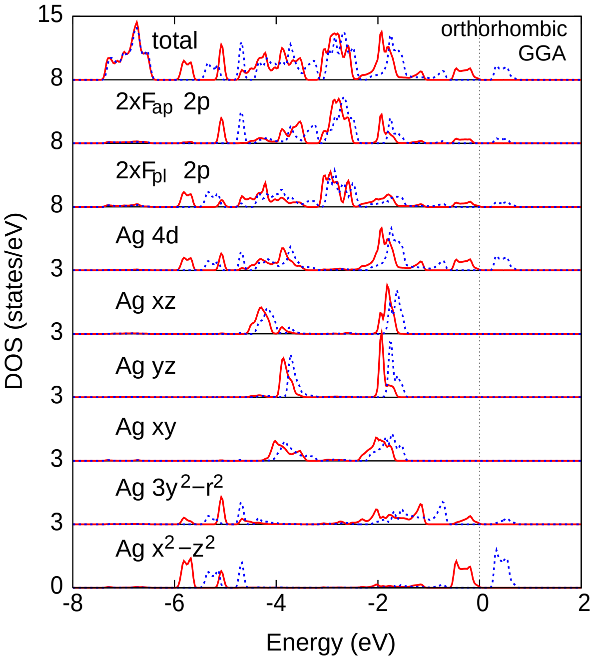

FIG. 1: (Color online) Density of states (DOS) of Cs_2AgF_4 in the FM orthorhombic phase from GGA. This insulating solution has a small band gap of 0.2 eV. The Fermi level is set at zero energy. Solid red (dashed blue) lines depict the spin-up (down) states. The panels show, from top to bottom, the total DOS per formula unit and orbital-resolved DOS. The state around –7 eV comes from the Cs $5p$ orbital. For the Ag $4d$-resolved DOS, the local coordinate system is chosen in such a way that the y (x)-axis is along the in-plane longer (shorter) Ag-F bond. The Ag^{2+} x^2-z^2 hole state, and the corresponding y^2-z^2 hole state of the nearest neighbor Ag^{2+} ions form the in-plane orbital ordering (see also Fig.2).

Thus, even the GGA calculations, not including correlation effects, already give an orbital ordering of the same type as that in K_2CuF_4,[19] which in a picture of localized electrons would immediately give in-plane ferromagnetism, according to Goodenough-Kanamori-Anderson rules. This orbitally-polarized hole state in the insulating solution is associated with the large distortion of the Ag-F bonds of 0.33 Å (2.44 Å along the y-axis versus 2.11 Å along the x-axis, and 2.11 Å along the z-axis, all in a local coordinate system),[8] which leads to a pronounced crystal-field splitting and suppressed bandwidths. As a result, the antibonding x^2-z^2 band lies about 1 eV above the antibonding $3y^2-r^2$ band, and then an exchange splitting of the x^2-z^2 band gives rise to the small band gap and the x^2-z^2 hole state. Thus, such a cooperative distortion accommodates the x^2-z^2/y^2-z^2 hole-orbital ordering in the AgF_2 basal plane, giving the observed FM. Also, our GGA calculations confirm this by showing that the in-plane (intralayer) FM state is in-

TABLE I: Electronic structure of the in-plane FM and AF states of Cs_2AgF_4 in the orthorhombic and tetragonal phases calculated by GGA and GGA+U with U=3 eV. Energy difference (ΔE, meV/f.u.), gap size (eV), and local spin moments (μ_B) of each Ag, apical F (F_{ap}) and planar F (F_{pl}) atom are shown. The AF solution of the tetragonal phase by GGA is close to a nonmagnetic (NM) solution indicated in the bracket. Note that the orthorhombic FM insulating solution is the ground state.

		GGA					GGA+U				
		ΔE	gap	Ag	F_{ap}	F_{pl}	ΔE	gap	Ag	F_{ap}	F_{pl}
orthorhombic	FM	0	0.2	0.560	0.105	0.112	0	1.0	0.600	0.099	0.097
	AF	34	0.2	±0.457	±0.098	±0.102	13	1.0	±0.560	±0.094	±0.092
tetragonal	FM	27	. . .	0.558	0.103	0.117	83	. . .	0.584	0.102	0.084
	AF (NM)	39 (36)	. . .	±0.053	±0.015	0	90	0.4	±0.547	±0.111	0

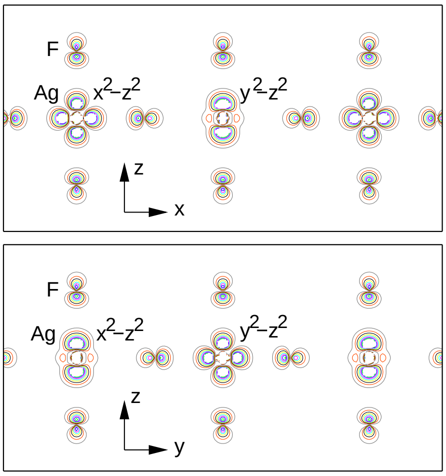

FIG. 2: (Color online) Contour plot (0.1–0.8 $e/Å^3$) of the spin density in the the xz (upper panel) and yz (lower panel) planes, through the AgF_6 octahedra of Cs_2AgF_4 in the FM insulating orthorhombic phase obtained by GGA. It evidences the x^2-z^2/y^2-z^2 hole-orbital ordering of the Ag^{2+} ions in the xy basal plane. See also Fig. 1. Note also a relatively strong spin polarization of the F atoms (see more in the text).

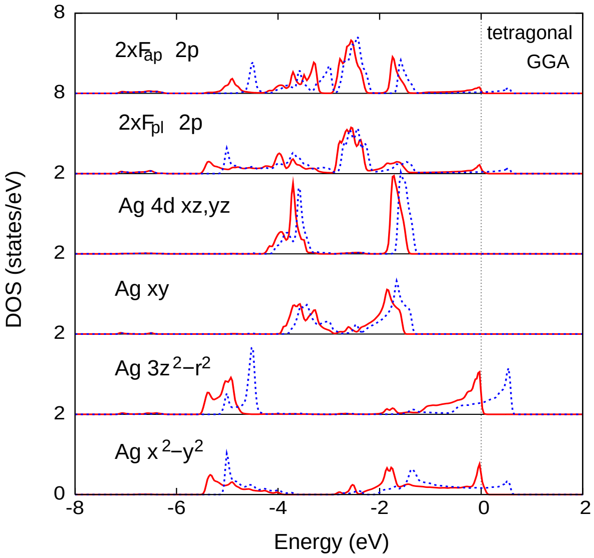

FIG. 3: (Color online) Orbital-resolved density of states (DOS) of Cs_2AgF_4 in the FM tetragonal phase from GGA. It is nearly half-metallic, and the wide in-plane x^2-y^2 band and the small e_g-level splitting are obvious.

deed more stable than the in-plane AF state by 34 meV per formula unit (f.u.), see Table I. We note that the interlayer magnetic coupling is too weak (0.004 meV in energy scale[8]) to be captured by the present calculations, which show practically degenerate interlayer FM and AF states within the error bar of 1 meV/f.u.

Actually, the experimental distorted lattice turns out to be in the vicinity of the theoretical equilibrium state after atomic relaxation. The structural optimization shows that Cs would shift by only 0.005 Å and the Ag–F_{ap} bond would be elongated by 0.041 Å and the in-plane longer (shorter) Ag–F_{pl} bond would be shortened (elongated) by 0.018 Å , as compared with the experimentally observed structure. As a result, the large in-plane distortion of about 0.3 Å , found experimentally,[8] is well reproduced theoretically. Moreover, the FM orthorhombic phase turns out to be more stable than a FM tetragonal phase by 27 meV/f.u. (which, as well as the following GGA+U result, implies a stability of the orthorhombic phase above room temperature as observed[8]). We checked it by performing the calculations for the average tetragonal structure.

The tetragonal phase is constructed in such a way that the lattice volume, c-axis constant, and positions of Cs and F_{ap} atoms are the same as in the orthorhombic phase we calculated above, and that the basal plane is a regular AgF_2 square lattice. This FM tetragonal phase shows the same electronic-structure features (see, e.g., near half-metallicity in Fig. 3) as previously found,[15,16] since the structural parameters used in Refs. 15 and 16 are very close to what we used for this hypothetical phase. The regular AgF_2 square sheet would produce a wide x^2-y^2 band with a bandwidth of about 3 eV, and the compressed distortion of the AgF_6 octahedron (out-of-plane Ag–F bond length of 2.12 Å vs in-plane one of 2.29 Å) is not large enough to generate a crystal-field splitting in excess of the bandwidths to open a gap. (Note also that the compressed octahedron is extremely rare in Jahn-Teller insulators with e_g degeneracy.[24]) Actually, the crystal field splitting would make the x^2-y^2 level lie below $3z^2-r^2$ by only about 0.2 eV. As a result, both the minority-spin x^2-y^2 and $3z^2-r^2$ bands cross the Fermi level. The total spin moment of 0.98 μ_B/f.u. (close to integer 1 μ_B), in the tetragonal phase would spread over Ag (0.558 μ_B), F$_{ap}$ (0.103 μ_B each), and F$_{pl}$ (0.117 μ_B each).

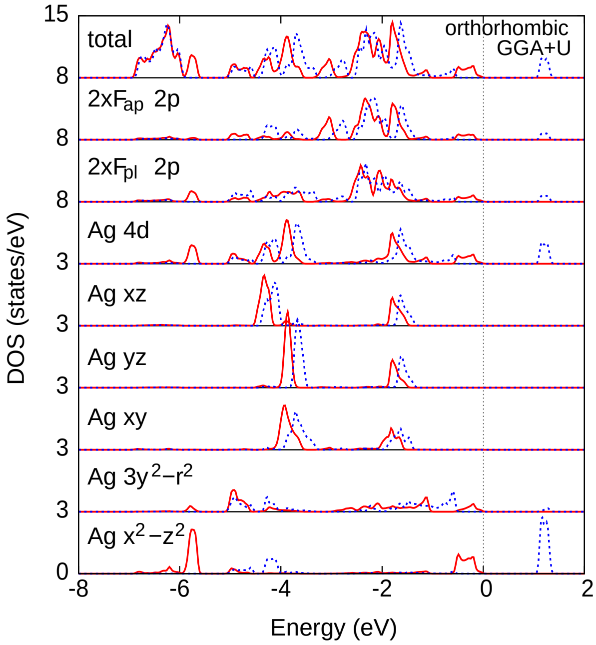

FIG. 4: (Color online) Density of states (DOS) of Cs_2AgF_4 in the FM orthorhombic phase from GGA+U with U=3 eV. The insulating gap is increased up to 1.0 eV, compared with GGA (see Fig. 1). See other notes in Fig. 1 caption.

As we saw above, Cs_2AgF_4 is insulating in the FM-ordered orthorhombic phase, even in GGA, see Fig. 1. A moderate electron correlation may be present for the Ag^{2+} $4d$ electrons, and thus we also carried out calculations using GGA+U method[25] to include the on-site Coulomb interaction for both the orthorhombic and tetragonal phases. In Fig. 4 we show the DOS results for the actual FM orthorhombic structure, given by the GGA+U calculation with an effective U=3 eV for the Ag^{2+} $4d$ electrons. The insulating gap is increased up to 1.0 eV (1.4 eV when U=4 eV). The Hubbard U pushes the occupied $4d$ levels downwards so that their center of gravity is now lower in energy than the F $2p$ levels. As a result, the lower-lying bonding states have larger Ag $4d$ character than the higher-lying antibonding states, in contrast to the GGA results shown in Fig. 1. Again, the x^2-z^2/y^2-z^2 hole-orbital ordering is obvious, and the orbital polarization of the e_g states is enhanced. The local spin moments are 0.600 μ_B/Ag, 0.099 μ_B/F$_{ap}$, and 0.097 μ_B/F$_{pl}$. Note that in the GGA+U with U=3 eV (U=4 eV), the in-plane FM state is more stable than the in-plane AF state by 13 meV (10 meV) per formula unit. Using a simple Heisenberg model for the spin-1/2 square lattice, $H=-J\sum_{(i,j)} S_iS_j$ (counting twice the magnetic exchange per spin pair), the nearest-neighbor intersite FM exchange integral is estimated to be 6.5 meV (5 meV) when U=3 eV (U=4 eV). This value, reduced from the GGA estimate of 17 meV, is well comparable to the experimental one of 3.8–5 meV.[8]

The GGA+U (U=3–4 eV) calculations for the tetragonal structure still give a metallic solution for the in-plane FM state with the broad e_g bands, but open an insulating gap of 0.4–0.7 eV for the in-plane AF state with suppressed bandwidths (not shown). With the gap opening, this insulating AF state becomes stable with a large Ag spin moment, in contrast to the GGA results (see Table I). Note however that also in GGA+U both the AF and FM tetragonal phases have much higher energy than the orthorhombic phases, by more than 80 meV/f.u.. Thus, once again these calculations show that the orthorhombic phase is indeed more stable than the tetragonal phase, with the orbitally ordered FM state being the ground state. All this confirms the recent experimental finding that the layered Cs_2AgF_4 is indeed stabilized in the insulating orthorhombic phase.[8]

III. CONCLUSION

Summarizing, by means of GGA and GGA+U band structure calculations, we find that the layered Cs_2AgF_4, a structural analog of cuprates, is stabilized in an insulating orthorhombic phase rather than in a metallic tetragonal phase. The intrinsic lattice distortion of the orthorhombic phase is accompanied by the x^2-z^2/y^2-z^2 hole orbital ordering, which readily accounts for the observed in-plane ferromagnetism. The present calculations confirm the recent experiments[8] and lead us to the conclusion that Cs_2AgF_4 is indeed an orbitally-ordered ferromagnetic insulator, in strong contrast to the antiferromagnetic nature of the parent high-T_c cuprates, but in close analogy to K_2CuF_4.

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