Orbital ordering in the ferromagnetic insulator Cs$_2$AgF$_4$ from first principles

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We found, using density-functional theory calculations within the generalized gradient approximation, that Cs$_2$AgF$_4$ 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 $z^2$ hole-orbital ordering of the Ag$^{2+}$ $4d^0$ 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 4$d$-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 3$d$ transition-metal oxides with orbital degeneracy display an orbital ordering associated with lattice distortions (of the Jahn-Teller type)\textsuperscript{11,12,13} In contrast, 4$d$ and 5$d$ transition-metal compounds rarely show this, mainly due to the delocalized character of the $d$ electrons. It was therefore a surprise when the 4$d$-orbital ordering and the orbitally driven spin-singlet dimerization were found in the ruthe- nate La$_4$Ru$_2$O$_{10}$\textsuperscript{14}. Moreover, the fascinating superstructure of the spinel CuIr$_2$S$_4$ (Ref. 2) was explained in terms of the concept of orbitally-induced Peierls state (associated with the partially occupied Ir 5$d$ orbitals)\textsuperscript{2}.

Very recently,\textsuperscript{8,9} the magnetic behavior of the layered Cs$_2$AgF$_4$ 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$_2$AgF$_4$ is 4$d$ orbitally-ordered, and it was proposed that such orbital ordering may be the origin of the observed FM.

Cs$_2$AgF$_4$ was first synthesized in 1974 by Odenthal, Paus, and Hoppe\textsuperscript{10} and it received, as well as other silver fluorides, attention due to pursuit of superconductivity in transition-metal compounds other than the cuprates.\textsuperscript{11,12,13} Cs$_2$AgF$_4$ is a structural analog of the parent compound of cuprate superconductors, La$_2$CuO$_4$ (AgF$_2$ vs CuO$_2$ sheet), and both have the $S=1/2$ divalent transition-metal cations (Ag$^{2+}$ $4d^0$ vs Cu$^{2+}$ $3d^9$) and isoelectronic anions (F$^-$ vs O$^{2-}$). It is well known that La$_2$CuO$_4$ 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.\textsuperscript{14} Silver fluorides have similar electronic band structure, namely the Ag-F $pd\sigma$ antibonding character in the vicinity of the Fermi level.\textsuperscript{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 2$p$ band, which is unprece-
Cs₂AgF₄ is thus very similar to that of an isoelectronic and isostructural compound K₂CuF₄.₁¹⁰

II. RESULTS AND DISCUSSION

Our electronic structure calculations are performed by using the all-electron full-potential augmented plane wave plus local orbital method.₂² The generalized gradient approximation (GGA) to density-functional theory is adopted.²² We took the neutron diffraction structure data measured at 6 K. As seen below, the electronic structure and magnetic properties of Cs₂AgF₄ are determined by an orbital ordering, and the orbital ordering is the most relevant to the local distortion of the AgF₆ octahedra. To account for a possible lattice distortion connected with an orbital ordering, we carried out an 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. 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 Cs₂AgF₄ 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 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 t₂g (xz, yz, and xy) orbitals and even a larger one for the e_g orbitals. The t₂g 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⁺⁺ (4d⁰) ions. Actually, the one hole spreads, due to the strong Ag–F covalency, over the six fluorine atoms of the AgF₆ 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 Cs₂AgF₄.²³ 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 \( x^2 - y^2 \) and \( y^2 - z^2 \) symmetry shown in Figs. 1 and 2.

Thus, even the GGA calculations, not including correlation effects, already give an orbital ordering of the same type as that in K₂CuF₄, 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) which leads to a pronounced crystal-field splitting and suppressed band-widths. 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 AgF₂ basal plane, giving the observed FM. Also, our GGA calculations confirm this by showing that the in-plane (intralayer) FM state is in-

![FIG. 1: (Color online) Density of states (DOS) of Cs₂AgF₄ 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⁺⁺ \( x^2 - z^2 \) hole state, and the corresponding \( y^2 - z^2 \) hole state of the nearest neighbor Ag⁺⁺ ions form the in-plane orbital ordering (see also Fig. 2).](image-url)
TABLE I: Electronic structure of the in-plane FM and AF states of Cs$_2$AgF$_4$ in the orthorhombic and tetragonal phases calculated by GGA and GGA+U with $U$=3 eV. Energy difference ($\Delta E$, meV/f.u.), gap size (eV), and local spin moments ($\mu_B$) 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       |
|----------------|-------------|-------------|
|                | $\Delta E$ | gap | $F_{ap}$ | $F_{pl}$ | $\Delta E$ | gap | $F_{ap}$ | $F_{pl}$ |
| orthorhombic   | 0           | 0.2 | 0.560    | 0.105    | 0.112     | 0    | 1.0       | 0.600    | 0.099    | 0.097    |
| AF             | 34          | 0.2 | $\pm 0.457$ | $\pm 0.098$ | $\pm 0.102$ | 13   | 1.0       | $\pm 0.560$ | $\pm 0.094$ | $\pm 0.092$ |
| tetragonal     | 27          | 0.2 | 0.558    | 0.103    | 0.117     | 83   | 0.4       | 0.547    | 0.102    | 0.084    |
| AF (NM)        | 39 (36)     | 0.537 | $\pm 0.015$ | $\pm 0.053$ | 0.905     | 42   | 0.560     | 0.099    | 0.092    | 0.097    |

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$_2$AgF$_4$ in the FM insulating orthorhombic phase obtained by GGA. It evidences the $x^2 - y^2$ 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$_2$AgF$_4$ 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.
also that the compressed octahedron is extremely rare in Jahn-Teller insulators with $e_g$ degeneracy. 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 $\mu_B$/f.u. (close to integer 1 $\mu_B$), in the tetragonal phase would spread over Ag (0.558 $\mu_B$), $F_{ap}$ (0.103 $\mu_B$ each), and $F_{pl}$ (0.117 $\mu_B$ each).

Fig. 4: (Color online) Density of states (DOS) of Cs$_2$AgF$_4$ 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$_2$AgF$_4$ is insulating in the FM-ordered orthorhombic phase, even in GGA, see Fig. 1. A moderate electron correlation may be present for the Ag$^{2+}$ 4$d$ electrons, and thus we also carried out calculations using GGA+$U$ method 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$^{2+}$ 4$d$ electrons. The insulating gap is increased up to 1.0 eV (1.4 eV when $U=4$ eV). The Hubbard $U$ pushes the occupied 4$d$ levels downwards so that their center of gravity is now lower in energy than the F 2$p$ levels. As a result, the lower-lying bonding states have larger Ag 4$d$ 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 $\mu_B$/Ag, 0.099 $\mu_B$/F$_{ap}$, and 0.097 $\mu_B$/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, $H = -J \sum_{(i,j)} S_i S_j$ (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.

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$_2$AgF$_4$ is indeed stabilized in the insulating orthorhombic phase.

III. CONCLUSION

Summarizing, by means of GGA and GGA+$U$ band structure calculations, we find that the layered Cs$_2$AgF$_4$, 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 and lead us to the conclusion that Cs$_2$AgF$_4$ 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$_2$CuF$_4$.

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Our calculations within the local-spin-density approximation (LSDA) reach the same conclusion as reported in the main text by using the GGA calculations.

Note that the F 2p content of the hole state would be even larger if one would count the number of holes within the volumes with the effective ionic radii of F\(^-\) (1.3 Å) and Ag\(^{2+}\) (0.94 Å) [R. D. Shannon, Acta Cryst. A32, 751 (1976)] instead of the present set of the muffin-tin sphere radii.

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