

Ferromagnetism Induced by Orbital Order in the Charge-Transfer Insulator Cs_2AgF_4 : An Electronic Structure Study

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Cs_2AgF_4 was proposed to be an orbitally ordered ferromagnet based on recent neutron scattering data. Here, we report a detailed electronic structure study within the local spin density approximation also including strong Coulomb repulsion U . We investigate the influence of an orthorhombic distortion of the Ag environment and the importance of the on-site Coulomb repulsion. We find good quantitative agreement with both the experimentally observed exchange coupling and structural changes. Thus, our results strongly support that Cs_2AgF_4 is a strongly correlated charge-transfer insulator where the ferromagnetism is driven by orbital order.

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The layered perovskite system Cs_2AgF_4 containing the strongly oxidizing Ag(II) ion [1,2] is isostructural to the high- T_c cuprates. The possibility of observing superconductivity in other compounds with a structure similar to the cuprates is still very much an open topic. In contrast to the undoped two-dimensional cuprates that are antiferromagnetic (AFM) insulators at rather high temperatures, Cs_2AgF_4 was reported as a ferromagnet with $T_c \sim 15$ K [3], but the insulating nature of the system has not been studied yet.

Presently, Cs_2AgF_4 has become a focus of interest because of recent inelastic neutron scattering experiments [4] that propose orbital ordering (OO) as the origin of ferromagnetism (FM). Since the original refinement [3] of the structure to a tetragonal space group (SG) does not support the orbital ordering scenario, McLain *et al.* [4] re-refined the crystal structure to an orthorhombic SG, though not very decisively since the final goodness of fit (χ^2) differs by less than 0.04 for the tetragonal and orthorhombic solutions [4,5]. The re-refinement suggests that Cs_2AgF_4 is orbitally ordered both at room temperature and at 6 K (below the magnetic phase transition), implying no additional lattice distortion associated with the magnetic transition. From the neutron scattering data ($J_1 = -5.0$ meV) and susceptibility measurements ($J_1 = -3.8$ meV), the magnetic interactions were found to be very small. Thus, OO and ferromagnetism in Cs_2AgF_4 act on different energy scales with an OO independent of the FM.

Previous local spin density approximation (LSDA) calculations [2,6] have elucidated the strong covalency between the Ag d and F p states in this material. According to those results, the magnetism in Cs_2AgF_4 evolves via a Stoner-type itinerant mechanism, stabilized by Hund's coupling [6]. In this scenario, the system continues to remain metallic even in the ferromagnetically ordered state.

This contradiction raises again the question about the origin of the magnetism in Cs_2AgF_4 —is it itinerant and

metallic or OO and insulating? Here, we report band structure results of both scenarios to gain microscopic insight into the system and address the consequences: metallic vs insulating behavior, role of correlations, energy scales, structural changes. We show that, driven by strong Coulomb repulsion and exchange interaction (Hund's coupling), Cs_2AgF_4 is much more stable in the orthorhombic than the tetragonal symmetry. Orbital ordering does prevail up to large temperatures though the Coulomb repulsion U is reduced in comparison to undoped cuprates.

For our self-consistent calculations the full-potential local orbital (FPLO [7,8], version 6.00-24) band structure method was used. The core states are treated fully relativistically, while the valence states are treated scalar relativistically. We used a single numerical basis set for the core states and a double numerical basis set for the valence sector. Semicore states are treated as valence states with a single numerical radial function per nl shell. The Brillouin zone sampling was based on 100 k points in the irreducible wedge for both the tetragonal and orthorhombic structures. The exchange-correlation functional of Perdew and Wang [9] was used for both local density approximation (LDA) and LSDA. The double-counting correction for the LSDA + U calculations followed the around mean field approximation. The Coulomb repulsion U was varied from 4 to 8 eV while J was kept fixed at 1 eV [10]. Different initial occupation matrices for the Ag d electrons were prepared to obtain the various solutions. We cross-checked our FPLO results with linearized augmented-plane-wave calculations using WIEN2K [11].

The calculations were performed for both the originally proposed tetragonal structure by Odenthal *et al.* [3], SG: $I4/mmm$ (No. 139), $a_{\text{tet}} = 4.58$ Å, $c_{\text{tet}} = 14.19$ Å, with $Z_{\text{Cs}} = 0.36$, $Z_{\text{F1}} = 0.15$ and the recently proposed orthorhombic structure by McLain *et al.* [4] The orthorhombic lattice (SG: $Bbcm$, No. 64) is related to the associated tetragonal lattice via $a_{\text{ortho}} = \sqrt{2}a_{\text{tet}}$; $b_{\text{ortho}} = \sqrt{2}b_{\text{tet}}$. In our calculations we used $a_{\text{ortho}} = b_{\text{ortho}} = 6.4764$ Å, and

$c_{\text{ortho}} = 14.19 \text{ \AA}$, with $Z_{\text{Cs}} = 0.356$ and $Z_{\text{F1}} = 0.1488$. This symmetry has internal degrees of freedom for the in-plane fluorines, whose positions are most important in determining the possibility of OO. These parameters X_{F2} and Y_{F2} were varied between 0.25 and 0.20 [12].

Starting with the first scenario (itinerant, metallic FM), Figs. 1(a) and 1(b) display the LDA and LSDA band structures of the tetragonal structure, respectively. They are in accordance with previously published work [6], but have been calculated and displayed along the high-symmetry lines of the orthorhombic unit cell (2 Ag per formula unit \rightarrow 2 bands for every orbital) to facilitate comparison with the results shown later. In the LDA, both the Ag $d_{x^2-y^2}$ (in-plane) and $d_{3z^2-r^2}$ (out-of-plane) bands are partially occupied (Fig. 5, left panel) and have strong covalency with the F orbitals. The band center of the $d_{x^2-y^2}$ is deeper in energy than that of the $d_{3z^2-r^2}$ orbital. Within LSDA we get a FM metallic solution close to half-metallicity.

Going from tetragonal to the orthorhombic crystal structure, the main change is in the position of the fluorine atoms in the basal plane. It has been shown that the orthorhombic fluorine positions can be obtained in three consecutive steps [13]. These distortions are rather small and lead to alternating short and long Ag-F bonds in the

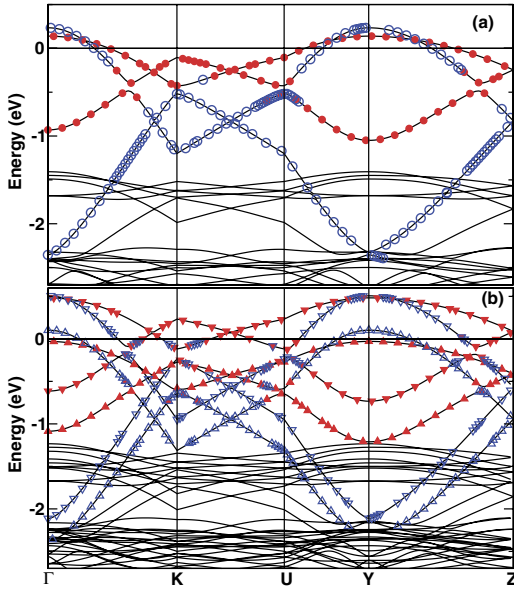


FIG. 1 (color online). LDA (a) and LSDA (b) band structures of the tetragonal Cs_2AgF_4 along the high-symmetry points: $\Gamma(0\ 0\ 0) \rightarrow K(0\ 0.604\ 0)\frac{2\pi}{a} \rightarrow U(1\ 0.396\ 0)\frac{2\pi}{a} \rightarrow Y(1\ 0\ 0) \times \frac{2\pi}{a} \rightarrow Z(0\ 0\ 0.5)\frac{2\pi}{c}$. For clarity, the in-plane $d_{x^2-y^2}$ and out-of-plane $d_{3z^2-r^2}$ bands are highlighted using open (blue) and closed (red) symbols, respectively. The calculations were done constraining the atom positions to that of a tetragonal symmetry but placed in an orthorhombic unit cell. This leads to 2 Ag per formula unit \rightarrow 2 bands for every orbital. The majority and minority spin channels are distinguishable via the up and down triangles.

a - b plane. Hence connecting the four shortest Ag-F bonds creates a plaquette in the x - z plane for one Ag site and in the y - z plane for the other Ag site (Fig. 5, right panel). In the remainder of this Letter, the notation for the orbitals are as follows: Ag1 $d_{z^2-x^2}$ (in-plane), Ag1 $d_{3y^2-r^2}$ (out-of-plane), Ag2 $d_{z^2-y^2}$ (in-plane), Ag2 $d_{3x^2-r^2}$ (out-of-plane).

The changes in the total energy as we reduce the symmetry and move from the tetragonal to orthorhombic fluorine positions are displayed in Fig. 2 as a function of the internal parameter of the in-plane fluorine atom. In LDA, the orthorhombic distortion is energetically disfavored by about 50 meV/Ag for the refined F2 position [14]. Allowing spin polarization within the LSDA makes the tetragonal structure metastable, gaining energy when the distortions to the in-plane fluorine atoms are introduced, thereby favoring the orthorhombic over the tetragonal structure by 25 meV/Ag. The optimized Ag-F in-plane bonds are slightly longer ($\sim 0.02 \text{ \AA}$) than in the experiment [14]. The orthorhombic symmetry along with the exchange makes Cs_2AgF_4 to orbitally order, but the energy scale of 25 meV ($\approx 290 \text{ K}$) is too small for OO at room temperature.

As for the electronic structure, the new ligand field changes the band energies considerably when reducing the symmetry from tetragonal to orthorhombic [Fig. 3(a)]. Contrary to the tetragonal band structure [Fig. 1(a)], which has both the e_g orbitals partially occupied with a splitting of about 0.2 eV, in the orthorhombic structure only the in-plane orbitals remain partially occupied while the out-of-plane orbitals are fully filled with a split of about 1.5 eV for the re-refined fluorine positions. Since the distortion alone already separates the e_g band complexes and places only one orbital at the Fermi energy, the LDA result already seems to act as a “precursor” to the orbitally ordered solution, but presently metallic. Also, the bandwidth of the in-plane orbitals are extremely reduced (0.35 eV) as compared to the tetragonal structure due to the change in

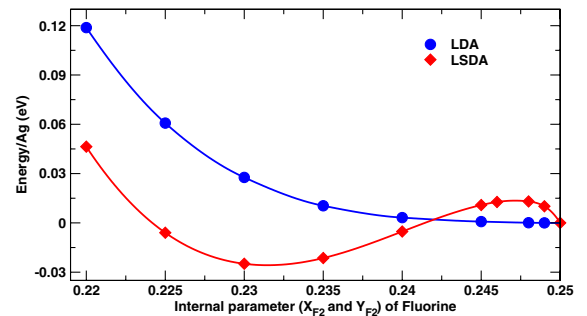


FIG. 2 (color online). Energy vs position of F2 atoms for LDA and LSDA calculations. The rightmost point on the graph corresponds to the tetragonal unit cell, and, as we move away from it, the symmetry reduces to orthorhombic. Within LDA, distortions of the fluorine positions does not favor orbital ordering, but allowing spin polarization in addition (LSDA) favors orbital ordering, though only for very low temperatures.

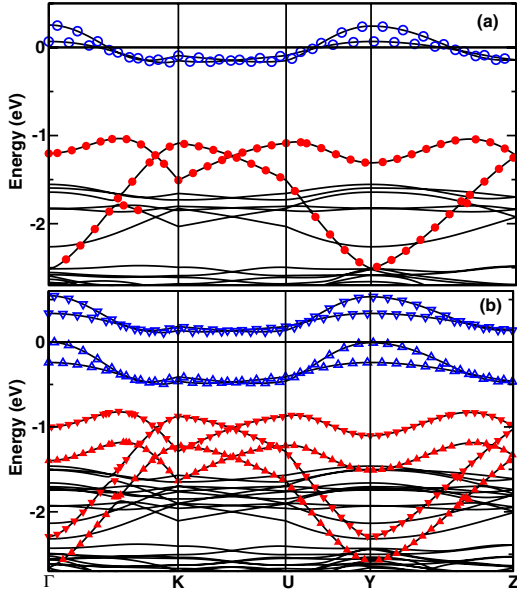


FIG. 3 (color online). LDA (a) and LSDA (b) energy bands for the orthorhombic Cs_2AgF_4 . The open (blue) symbols highlight the in-plane $\text{Ag}1-d_{z^2-x^2}$ and $\text{Ag}2-d_{z^2-y^2}$ bands, while the filled (red) symbols highlight out-of-plane $\text{Ag}1-d_{3y^2-r^2}$ and $\text{Ag}2-d_{3x^2-r^2}$ bands. The distortion of the F atoms from the ideal tetragonal positions lead to a strong ligand field splitting of about 1.5 eV. Spin polarization (LSDA) opens a gap of about 0.2 eV. The majority and minority spin channels are distinguishable via the up and down triangles.

the orientation of the nearest neighbor AgF_4 plaquettes (Fig. 5) by 90° . Because of this reduced bandwidth, just the atomic exchange is strong enough to split the in-plane $\text{Ag}1-d_{z^2-x^2}$ and $\text{Ag}2-d_{z^2-y^2}$ bands and to open up a gap of about 0.2 eV [Fig. 3(b)]. In consequence, this would lead to an exchange induced metal-insulator phase transition in orthorhombic Cs_2AgF_4 connected to the magnetic phase transition.

The energy difference between an FM and an AFM ordered spin configuration can be mapped onto a nearest neighbor (NN) 2D-Heisenberg model, and thereby an effective exchange constant J_{NN} can be estimated, $H = \sum_{i,j} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j$, which leads to $E_{\text{AFM}} - E_{\text{FM}} = J_{\text{NN}}$. Within the LSDA, we obtain a $J_{\text{NN}}^{\text{LSDA}}$ of -38 meV, rather large compared to the experimental findings ($J_{\text{expt}} = -3.8$ to -5 meV). The too small energy scale for the orbital ordering and the too large resulting exchange constant of the LSDA calculations do not sufficiently describe an OO scenario for orthorhombic Cs_2AgF_4 .

Though it is immediately obvious that Coulomb correlations beyond the LSDA will increase the size of the insulating gap, it is not clear for the energy gain due to the OO and also for the resulting exchange constant. In general, strong Coulomb repulsion favors orbital ordering and/or magnetic order. The size of the correlations for an Ag^{2+} ion is not known. The commonly used value of the Coulomb parameter U for a Cu^{2+} ion is about 8 eV. Since

the $4d$ orbitals of an Ag^{2+} ion are less localized than the $3d$ orbitals of a Cu^{2+} ion, it should be appropriate to use 8 eV for Ag as an upper limit. The changes of the total energies as a function of the F displacement for different U values are collected in the lower panel of Fig. 4. We find a strong gain in energy with the inclusion of correlations when the system transforms from tetragonal to the orthorhombic structure, of the order of 0.2 eV/Ag for U ranging from 5 to 8 eV. The position of the minimum seems to be rather independent of U , but the shape of the curve has changed compared to LSDA (Fig. 2). The energy gain of 0.2 eV (≈ 2300 K) according to the LSDA + U calculations favors OO at all temperatures consistent with the experimental findings [4].

By manipulating the initial density matrix in LSDA + U calculations, it is also possible to stabilize a solution with the in-plane $\text{Ag}1-d_{z^2-x^2}$, $\text{Ag}2-d_{z^2-y^2}$ orbitals fully occupied while the out-of-plane $\text{Ag}1-d_{3y^2-r^2}$, $\text{Ag}2-d_{3x^2-r^2}$ orbitals are half filled. Such a solution is much higher in energy, larger than 1 eV (per Ag atom) depending upon the position of the F atoms. The energies of such a solution for $U = 8$ eV are displayed in the middle panel of Fig. 4.

From FM and AFM spin configurations we evaluated the exchange constant J_{NN} . The results are collected in Fig. 4 (upper panel) for various values of the Coulomb repulsion U . Notice that the FM exchange constant starts to increase as we move away from the tetragonal symmetry and the

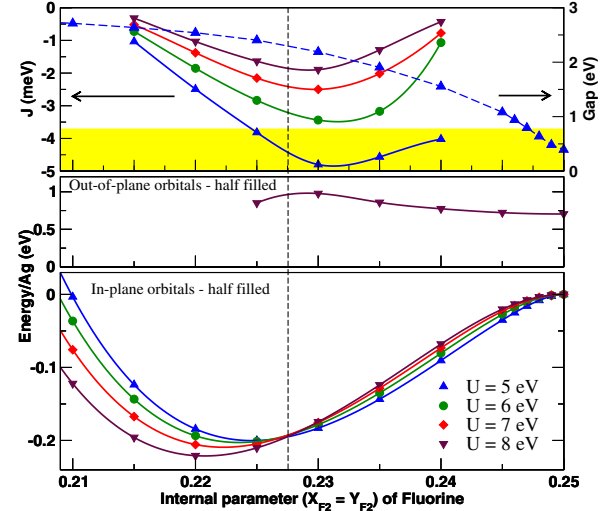


FIG. 4 (color online). Lower panel: Total energy vs $F2$ position for various choices of the Coulomb repulsion U . In all these calculations, in-plane orbitals are half filled while the out-of-plane orbitals are fully occupied. Middle panel: Total energy vs $F2$ position for $U = 8$ eV. The ground state of these calculations have in-plane orbitals fully occupied while the out-of-plane orbitals are half filled. Upper panel: Ferromagnetic exchange constant vs $F2$ position for various U values. The experimental range for J is highlighted. The “direct” band gap ($U = 5$ eV) vs $F2$ position is displayed by the dashed curve. The dashed vertical line corresponds to the averaged experimental position of the $F2$ sites.

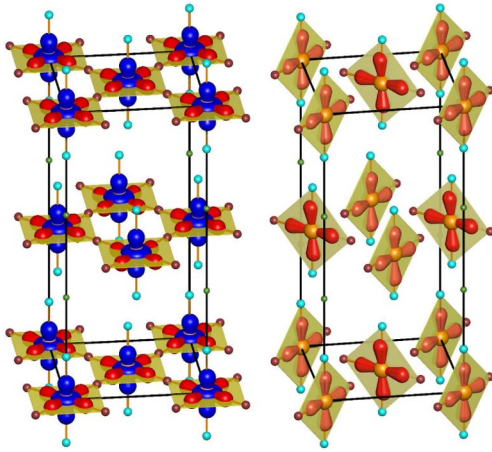


FIG. 5 (color online). Left panel: Itinerant scenario for the tetragonal Cs_2AgF_4 with both e_g orbitals partially occupied. Right panel: Orbitally ordered scenario wherein the distortions along with the exchange lower one of the e_g orbitals, leaving half filled only the plaquette orbitals shown.

shape of the J_{NN} curves tends to follow that of the LSDA + U total energies (Fig. 4, lower panel). For $U = 5$ eV and for the calculated minimum total energy, we obtain $J_{\text{NN}}^{\text{LSDA}+U} \approx -4.2$ meV. This is perfectly consistent with the observations from the neutron scattering experiment [4] ($J_{\text{expt}} \approx -3.8$ to -5 meV) and also clarifies the choice of a smaller U value for Cs_2AgF_4 .

Considering only the strong correlations without the orthorhombic distortion, we find insulating behavior, but with a small gap size of about 0.4 eV ($U = 5$ eV; see Fig. 4) that is inconsistent with the “lilac” color of the sample. Only an unlikely large U ($U > 8$ eV) can force a gap (≈ 2.5 eV) that is consistent with this sample color. More grave, OO in Cs_2AgF_4 cannot be obtained without orthorhombic distortion, and then the corresponding exchange integrals are AFM and therefore inconsistent with all measurements. The tendency towards AFM coupling in the tetragonal SG is visible in the shape of the exchange constant curves (Fig. 4), moving towards positive values closer to the undistorted structure. Altogether, the scenario in Cs_2AgF_4 is different from KCuF_3 wherein a “preexisting” electronically driven orbital polarization was observed even in the undistorted phase itself [15,16].

Figure 5 illustrates the two scenarios, itinerant and OO, for the tetragonal and orthorhombic SG, respectively. In the itinerant scenario Cs_2AgF_4 has short apical bonds of length 2.1 Å, and the AgF_4 plaquettes are similar to that of the cuprates, but with a much larger bond length (2.3 Å). This in turn results in the partial occupation of both the Ag e_g bands. Ferromagnetism is stabilized due to the strong covalency between the Ag and F atoms in this scenario, leading to a high density of states at the Fermi level and a Stoner-type magnetism. In the OO scenario, one of the in-plane bonds becomes much shorter, essentially the same length (2.08 Å) as the apical bond in the itinerant picture.

Simultaneously, the other in-plane Ag-F connection increases to 2.47 Å and ceases to be a covalent bond. This restores the old plaquette picture as in the cuprates (quadratic oxygen coordination, plaquettes in the x - y plane), now with plaquettes lying in the x - z and y - z planes and showing OO. Our pattern of the OO orbitals is identical with the suggestion of the experiment [4] and provides a natural explanation for the observed FM [16].

In conclusion, from band structure calculations it is evident that distortions of the F atoms along with spin polarization can introduce OO in Cs_2AgF_4 . OO could be stabilized without the introduction of strong correlations, though only for low temperatures. Adding correlations allows for OO at all temperatures. The corresponding structural parameters are consistent with recent neutron scattering experiments. From the OO picture, we predict an insulating behavior for Cs_2AgF_4 , which is yet to be verified. According to our calculations, the size of the insulating direct gap should be about 2.5 eV ($U \sim 5$ eV; see Fig. 4), consistent with the observed lilac sample color. Further structural studies of this system are desirable. According to our theoretical study, Cs_2AgF_4 belongs to the family of strongly correlated charge-transfer insulators rather than to the itinerant magnets.

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