Ferromagnetism Induced by Orbital Order in the Charge-Transfer Insulator Cs$_2$AgF$_4$: An Electronic Structure Study

Deepa Kasinathan,$^1$ Klaus Koepernik,$^{1,2}$ Ulrike Nitzsche,$^2$ and Helge Rosner$^1$

$^1$Max-Planck-Institut für ChemischePhysik fester Stoffe Dresden, D-01187 Dresden, Germany
$^2$IFW Dresden, P.O. Box 270116, D-01171 Dresden, Germany

(Received 23 July 2007; published 14 December 2007)

Cs$_2$AgF$_4$ 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$_2$AgF$_4$ is a strongly correlated charge-transfer insulator where the ferromagnetism is driven by orbital order.

DOI: 10.1103/PhysRevLett.99.247210

PACS numbers: 75.10.Lp, 71.15.Nc, 75.50.Dd

The layered perovskite system Cs$_2$AgF$_4$ 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$_2$AgF$_4$ 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$_2$AgF$_4$ 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 ($\chi^2$) differs by less than 0.04 for the tetragonal and orthorhombic solutions [4,5]. The re-refinement suggests that Cs$_2$AgF$_4$ 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$_2$AgF$_4$ 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$_2$AgF$_4$ 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$_2$AgF$_4$—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$_2$AgF$_4$ 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 WEN2K [11].

The calculations were performed for both the originally proposed tetragonal structure by Odenthal et al. [3], SG: $I4/mmm$ (No. 139), $a_{tet} = 4.58$ Å, $c_{tet} = 14.19$ Å, with $Z_{Cs} = 0.36$, $Z_{F1} = 0.15$ and the recently proposed orthorhombic structure by McLain et al. [4] The orthorhombic lattice (SG: $Bbam$, No. 64) is related to the associated tetragonal lattice via $a_{ortho} = \sqrt{2}a_{tet}$; $b_{ortho} = \sqrt{2}b_{tet}$. In our calculations we used $a_{ortho} = b_{ortho} = 6.4764$ Å, and...
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 (~0.02 Å) than in the experiment [14]. The orthorhombic symmetry along with the exchange makes Cs2AgF4 to orbitally order, but the energy scale of 25 meV (=290 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 eg 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 eg 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. 1 (color online). LDA (a) and LSDA (b) band structures of the tetragonal Cs2AgF4 along the high-symmetry points: Γ(0 0 0) → K(0 0.604 0) → L(0 1.096 0) → Z(1 0 0) × \( \frac{2\pi}{a} \rightarrow \frac{2\pi}{a} \rightarrow Z(0 0 0.5) \frac{2\pi}{a} \). For clarity, the in-plane \( d_{x^2-y^2} \) and out-of-plane \( d_{x^2-z^2} \) 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 → 2 bands for every orbital. The majority and minority spin channels are distinguishable via the up and down triangles.](image)

![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.](image)
scenario for orthorhombic LSDA calculations do not sufficiently describe an OO and the too large resulting exchange constant of the /0.255
the in-plane Ag1-dz2 orbitals, while the filled (red) symbols highlight out-of-plane Ag1-dz2 and Ag2-dz2 orbitals. 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.

FIG. 3 (color online). LDA (a) and LSDA (b) energy bands for the orthorhombic Cs2AgF4. The open (blue) symbols highlight the in-plane Ag1-dz2 and Ag2-dz2 orbitals, while the filled (red) symbols highlight out-of-plane Ag1-dz2 and Ag2-dz2 orbitals. 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 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 JNN can be estimated, $H = \sum_{i,j} J_{ij} S_i \cdot S_j$, which leads to $E_{AFM} - E_{FM} = J_{NN}$. Within the LSDA, we obtain a $J_{NN}^{LSDA}$ of $-38$ meV, rather large compared to the experimental findings ($J_{exp} = -3.8$ 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 Cs2AgF4.

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 Ag2+ ion is not known. The commonly used value of the Coulomb parameter $U$ for a Cu2+ ion is about 8 eV. Since the 4d orbitals of an Ag2+ ion are less localized than the 3d orbitals of a Cu2+ 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 ($\approx 2300$ 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 Ag1-dz2, Ag2-dz2 orbitals fully occupied while the out-of-plane Ag1-dz2, Ag2-dz2 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.
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 $J_{NN}^{LSDA} + U = -4.2$ meV. This is perfectly consistent with the observations from the neutron scattering experiment [4] ($J_{exp} = -3.8$ to $-5$ meV) and also clarifies the choice of a smaller $U$ value for Cs$_2$AgF$_4$.

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 ($\approx 2.5$ eV) that is consistent with this sample color. More grave, OO in Cs$_2$AgF$_4$ 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$_2$AgF$_4$ 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$_2$AgF$_4$ 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$_2$AgF$_4$. 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$_2$AgF$_4$, 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$_2$AgF$_4$ belongs to the family of strongly correlated charge-transfer insulators rather than to the itinerant magnets.

We kindly acknowledge the use of supercomputing facilities at ZIH Dresden and financial support by the GIF and the “Emmy-Noether-Programm” of the DFG.

[10] The results were insensitive to the choice of $J$ (0 to 1 eV).
[12] $X_{F_2}$ and $Y_{F_2}$ that are in principle independent were set equal to each other, because the small differences cause no significant changes in the results. $X_{F_2} = Y_{F_2} = 0.25$ re-instates the tetragonal symmetry, while any other value creates the orthorhombic symmetry.
[14] $X_{exp}^{F_2}$ and $Y_{exp}^{F_2}$ are 0.226 and 0.229, respectively, at 300 K, while $X_{LSDA}^{F_2} = Y_{LSDA}^{F_2} = 0.231$.