2D Ferromagnetism in the High-\(T_c\) Analogue Cs\(_2\)AgF\(_4\)

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Although the precise mechanism of high-\(T_c\) superconductivity in the layered cuprates remains unknown, it is generally thought that strong 2D Heisenberg antiferromagnetism combined with disruptive hole doping is an essential aspect of the phenomenon. Intensive studies of other layered 3d transition metal systems have greatly extended our understanding of strongly correlated electron states, but to date have failed to show strong 2D antiferromagnetism or high-\(T_c\) superconductivity. For this reason the largely unexplored 4d electrons, which are structurally and perhaps magnetically similar to the 3d \(\text{Cu}^{\text{II}}\) cuprates, merit close study. Here we present a comprehensive study of magnetism in the layered \(\text{Ag}^{\text{II}}\) fluoride Cs\(_2\)AgF\(_4\), using magnetic susceptometry, neutron diffraction and inelastic neutron scattering techniques. We find that this material is well described as a 2D Heisenberg ferromagnet, in sharp contrast to the high-\(T_c\) cuprates. The exchange constant \(J\) is the largest known for any material of this type. We suggest that orbital ordering may be the origin of the ferromagnetism we observe in this material.

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High-\(T_c\) cuprates are distinctive in having \([\text{CuO}_2]\) planes with very strong antiferromagnetic interactions between the spin-1/2 3d\(^9\) \(\text{Cu}^{\text{II}}\) ions. Searches for antiferromagnetism with similarly large interactions in magnetic insulators containing other 3d spin-1/2 transition metal ions have not been successful to date. It may be instructive to extend the studies of magnetism in high-\(T_c\) analogues in another direction, to materials possessing spin-1/2 4d electrons. The spin-1/2 4d\(^9\) \(\text{Ag}^{\text{II}}\) ion is an obvious first choice for this research program, as it is the heavier congener of \(\text{Cu}^{\text{II}}\). Cuprates also show charge-transfer character, and it is known that doped holes preferentially reside on the oxygen sites in the \([\text{CuO}_2]\) planes rather than forming \(\text{Cu}^{\text{III}}\) ions. In silver fluorides analogous charge-transfer is anticipated for fluorine sites in \([\text{AgF}_2]\) planes.

Despite having common formal oxidation states, Cu and Ag show marked differences in oxidation-state stability: although \(\text{Cu}^{\text{I}}\), \(\text{Cu}^{\text{II}}\) and \(\text{Cu}^{\text{III}}\) are all well-represented in Cu chemistry, \(\text{Ag}^{\text{I}}\) and \(\text{Ag}^{\text{II}}\) dominate the solid-state and coordination chemistry of Ag. To our knowledge, no oxide phases with \([\text{Ag}^{\text{II}}\text{O}_2]\) planes that are analogous to the cuprates exist, and AgO itself is best formulated as \([\text{Ag}^{\text{I}}\text{Ag}^{\text{II}}\text{O}_2]\). \(\text{Ag}^{\text{II}}\) is an unusual oxidation state for Ag, although materials containing this ion in a fluoride lattice are known.

\(\text{Ag}^{\text{II}}\) is a powerful oxidizer, which presents practical difficulties and requires the use of reagents and solvents such as F\(_2\) or HF. However, using appropriate synthetic techniques, compounds containing \(\text{Ag}^{\text{II}}\text{F}_2\) square lattices can be prepared. In particular, ternary fluorides including Cs\(_2\)AgF\(_4\) and Rb\(_2\)AgF\(_4\) are known. These compounds appear especially interesting as high-\(T_c\) analogues, since they are structurally very similar to K\(_2\)NiF\(_4\) and are related to the high-\(T_c\) precursor La\(_2\)CuO\(_4\): both families contain planes of \([\text{AgF}_2]\) or \([\text{CuO}_2]\) separated by planes of Cs/RbF or LaO. Few studies of these \(\text{Ag}^{\text{II}}\) compounds have been reported to date, and their magnetic properties are not well understood. Here we report detailed measurements of the magnetic properties of Cs\(_2\)AgF\(_4\), and compare with results for related materials.

The inverse of the measured molar static magnetic susceptibility of polycrystalline Cs\(_2\)AgF\(_4\) (Methods) is shown in Figure 1. Our results are consistent with and extend the earlier data of Odenthal et al. \(\text{La}_2\text{CuO}_4\) is an unusual oxida-
FIG. 1: Figure 1: The inverse of our measured molar susceptibility of Cs$_2$AgF$_4$ (points) after background subtraction. A fit to the theoretical susceptibility of the 2D spin-1/2 Heisenberg ferromagnet (the 10th order series of Baker et al. [6]) is shown as a solid line, and gives $g = 1.832$ and $J = -3.793$ meV. The insert shows the 15 K Curie transition and the low-temperature magnetic moment (with a simple interpolating curve).

Our fit to the susceptibility is shown in Figure 1; this gave the parameters $g = 1.832$ and $J = -3.793$ meV. We also considered 1D and 3D Heisenberg models, but these were found to be in clear disagreement with the measured susceptibility.

The Ag$^{II}$ ion moment was estimated from a field-magnetization scan to be 0.8 $\mu_B$ at 5 K, corresponding to $g = 1.6$; a value of 1.0 $\mu_B$ would be expected for an isolated, isotropic spin-1/2 ion. Note that in a magnetization measurement the extracted ionic moment would be lowered by the presence of non-magnetic impurity phases. Covalency effects may also have lowered the moment in the pure material.

The predominant difference between Ag$^{II}$ and Cu$^{II}$ is the increase in the principle quantum number of the valence orbitals. In this ternary silver fluoride, the combination of lower Coulomb repulsion of 4$d^9$ compared to 3$d^9$ electrons and charge transfer properties anticipated for Ag$^{II}$F$_2$, which should differ from those of Cu$^{II}$F$_2$, may lead to new effects due to orbital fluctuations. The reduced $g$-value may be evidence for fluctuation or hybridization phenomena.

A ferromagnetic ordering (Curie) transition was observed in Cs$_2$AgF$_4$ near 15 K (see Figure 1 insert). Since an ideal 2D Heisenberg magnet only undergoes ordering at absolute zero [7], this 15 K transition signifies the presence of additional interactions such as anisotropies or interlayer coupling.

Although the bulk susceptibility is useful for characterizing the general magnetic behaviour of a material, establishing the nature of these interactions at the atomic scale requires a local probe. Inelastic neutron scattering is ideal for this purpose, as the magnetic interaction strengths and pathways can be inferred from the energy and momentum transfer to the sample. As the impurities in the sample have very different magnetic properties than Cs$_2$AgF$_4$, it is reasonable to assume that they will not interfere with the interpretation of the inelastic neutron scattering signal.

Figure 2 shows the results of our inelastic neutron scattering measurements. Figure 2(a) shows the scattering from Cs$_2$AgF$_4$ over the wavevector range $Q = 0.2 - 1.2$ Å$^{-1}$ at $T = 8$ K after background subtraction. Production of magnetic excitations is clearly observed above 6 meV. The magnetic nature of these excitations was confirmed by a decrease in intensity and broadening of the signal upon heating to 35 K. For comparison, Figure 2(b) shows the scattering predicted by the ferromagnetic 2D spin-1/2 Heisenberg model with $J = -5.0$ meV.

To determine $J$, scans in energy at constant wavevector were extracted and the peak positions were determined.
by fitting Gaussian profiles to these data. The data and fits are shown in Figure 3 (main panel). The dispersion relation for ferromagnons in the 2D Heisenberg model was fitted to this data after correcting for instrumental effects, yielding \( J = -5.0(4) \text{ meV} \) for the exchange constant in Cs₂AgF₄. (Recall that the fit to the susceptibility gave a somewhat lower value of \( J = -3.8 \text{ meV} \).)

For wavevectors above \( \sim 1 \text{Å}^{-1} \), scattering from phonons becomes dominant, so the higher-\( Q \) data was not fitted. Below 6 meV, quasi-elastic incoherent scattering masks any magnetic signal that may be present.

The ferromagnetism we observe in Cs₂AgF₄ is in striking contrast to the antiferromagnetism in La₂CuO₄, and is instead reminiscent of K₂CuF₄. This material is one of the few known 2D spin-1/2 ferromagnetic insulators and, like Cs₂AgF₄, is a Heisenberg ferromagnet, with \( J = -1.0 \text{ meV} \) and \( T_{\text{Curie}} = 6.25 \text{ K} \). The ferromagnetism in K₂CuF₄ has been attributed to a cooperative Jahn-Teller distortion and associated orbital ordering, as depicted in Figure 4(c).

According to the Jahn-Teller theorem, the stereochemistry of a \( d^{9} \) metal ion should distort so as to lower both the symmetry and the energy of the system. For a hypothetical \( \text{Ag}^{II} \text{F}_{6} \) octahedron, in which the \( \text{Ag}^{II} \) ion is in a \( t_{2g}^{6}e_{g}^{3} \) electronic state, two structural pathways are commonly observed for this distortion \[ [8, 9], as depicted in Figure 4(c). \]

Axial compression of the octahedron results in a partially filled \( a_{1g} \) (\( \sim 3z^{2} - r^{2} \)) ground state orbital, whereas axial elongation results in a \( b_{1g} \) (\( \sim x^{2} - y^{2} \)) ground state \[ [13, 14]. \]

Both distortions give rise to the same \( D_{4h} \) local point group, which is the local symmetry of the \( \text{Ag}^{II} \) ion in the space group \( I4/mmm \).

There is, however, no known example of a system in which the electronic ground state is \( a_{1g} \) (\( \sim 3z^{2} - r^{2} \)) \[ [12] \); rather, systems that show axial compression are better described using a partially filled (\( z^{2} - x^{2} \)) and (\( z^{2} - y^{2} \)) basis on the metal center \[ [11, 13]. \] The magnitude and precise nature of the distortion will depend, \emph{inter alia}, on the axial electrostatic potential and anisotropic elastic constants for axial \emph{versus} equatorial ligand displacement \[ [10] \), but the orbital occupancies and symmetries themselves will conform to this general model. In the square lattice copper halides K₂CuF₄ \[ 8 \] and (\( \text{C}_{2}H_{5}NH_{3})_{2}\text{CuCl}_{4} \[ 17 \), \( a_{1g} \) and \( b_{1g} \) orbital states couple to each other and to the electron spin and lattice degrees of freedom, producing a complex nonlinear Hamiltonian that involves all these degrees of freedom \[ [13]. \]

An antiferrodistortive pattern of (\( \sim z^{2} - x^{2} \)) and (\( \sim z^{2} - y^{2} \)) hole orbitals results, giving a strong ferromagnetic state. In this state, the fluorine atoms are displaced from their symmetric \( I4/mmm \) positions, lowering the symmetry to \( Bbcm \). We suggest that a similar mechanism is responsible for the observed ferromagnetism in Cs₂AgF₄. If the difference in the exchange constant \( J \) measured above and below \( T_{c} \) is significant (\( \sim -5 \text{ meV} \)) from neutron scattering versus \( -3.8 \text{ meV} \) from the susceptibility), it may be associated with this orbital ordering transition.

Orbital ordering has been observed in other systems; cooperative orbital order in pseudo-cubic K₃CuF₃ leads to strong 1D antiferromagnetism, and strong antiferromagnetism has also been reported in KAgF₃, in which evidence for conduction above 50 K has been reported \[ [19]. \] However the absence of strong 2D antiferromagnetism among the copper halides in general suggests that the arrangement of pseudo-octahedra in the perovskites or associated Ruddlesden-Popper phases is important.

In a search for evidence of this structural distortion in Cs₂AgF₄, we carried out neutron diffraction measurements on Cs₂AgF₄ at 6 K and 298 K. The data were fit using the Rietveld method assuming the space groups \( I4/mmm \) and \( Bbcm \), the latter being the space group of the orbitally ordered phase of K₂CuF₄ \[ [10] \]. As no significant difference in the quality of fit was observed between the \( I4/mmm \) - and \( Bbcm \)-symmetry models, our results are consistent with either space group. However, we note that the atomic displacement parameters for the equatorial fluorine atoms in the AgF₆ pseudo-octahedra are large, which may be a signature of disorder in the plane; the resolution of our diffraction experiments does not allow discrimination of this disorder. This may be due to the limitation of statistics for a highly absorbing sample, in which small shifts in position may not be easily detectable. These diffraction measurements showed that...
the AgF$_6$ pseudo-octahedra in Cs$_2$AgF$_4$ are compressed, which is inconsistent with the $b_{1g}$ ground state familiar in La$_2$CuO$_4$; in that case the CuO$_6$ pseudo-octahedra show axial extension (see Figure 4(a)). Future investigations are planned, using high resolution neutron diffraction and resonant X-ray diffraction \cite{20, 21}, which should clarify the precise nature of the orbital ordering.

The structural similarity to the high-$T_c$ precursor La$_2$CuO$_4$, combined with our confirmation of strong magnetic interactions between the Ag$^{II}$ ions in Cs$_2$AgF$_4$, suggests the possibility of a rich variety of magnetic phases in Ag$^{II}$ fluorides \cite{1}. Given the oxidizing power of Ag$^{II}$, it is unlikely that other non-fluoride anion lattices will accommodate this species; accordingly, we are currently exploring ternary and quaternary Ag$^{II}$-fluoride Ruddlesden-Popper phases \cite{22}. High pressure experiments, which have proved fruitful in other systems \cite{17}, may also be particularly interesting.

The different d-orbital orientations proposed for Cs$_2$AgF$_4$ and La$_2$CuO$_4$ may have a simple origin in the electrostatics of these materials. In the cuprates, the [CuO$_2$] layers possess a net negative charge, having two electrons per formula unit. For this reason it is energetically favourable for the positively charged holes to lie in the $ab$ plane, localized in $b_{1g}$ orbitals. In contrast the [AgF$_2$] layers in Cs$_2$AgF$_4$ are charge neutral, so there is no strong electrostatic orientation preference. ($a_{1g}$ states are expected to be slightly preferred \cite{16}.) To test the stability of the assumed $a_{1g}$ configuration of Cs$_2$AgF$_4$, we have also synthesized the isostructural Rb$_2$AgF$_4$ \cite{16}. This material shows magnetic properties very similar to Cs$_2$AgF$_4$, demonstrating that this magneto-orbital configuration is robust. We speculate that charge-doping of Ag$^{II}$ fluorides may alter the electrostatic forces sufficiently to allow in-plane holes and stabilize a strong antiferromagnetic state. Our initial investigation of electron-doped Cs$_{2-x}$Ba$_x$AgF$_4$ for $0 < x < 0.3$ however has not identified an antiferromagnetic state \cite{22}.

In summary, we have found that the layered silver fluoride Cs$_2$AgF$_4$ is well described magnetically as a 2D spin-1/2 Heisenberg ferromagnet, and the exchange constant $J$ is the largest known for any magnetic material of this type. These conclusions followed from measurements of both static (susceptibility) and dynamic (inelastic neutron scattering) magnetic properties of polycrystalline Cs$_2$AgF$_4$.

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**METHODS**

Cs$_2$AgF$_4$ was prepared through a solid state reaction between AgF$_2$ and CsF (Flurochem USA). In a typical preparation, 0.0178 mol of AgF$_2$ and 0.0356 mol of CsF were ground together in a dry box in an inert atmosphere of argon or N$_2$ using an agate mortar and pestle until they formed a visually homogenous mixture. The mixture was then transferred to a pure gold reaction tube.
(height 9 cm, i.d. 1.5 cm) and placed inside a Schlenk flask and subsequently heated to 270°C under a flow of argon for 24 hours. The resulting lilac coloured solid was stored in an N₂-filled glove box in a desiccator over NaK₃ alloy. Sample purity was checked by X-ray powder diffraction using a Bruker AXS Smart 1000 diffractometer equipped with a graphite monochromatized Mo-Kα source. The observed pattern and positions of diffraction rings corresponded to the Cs₂AgF₄ unit cell parameters reported previously. X-ray diffraction experiments at NSLS also confirmed the nature of the phases.

For the SQUID measurements, approximately 100 mg of Cs₂AgF₄ powder was loaded into prefluorinated PTFE sample holders under an argon atmosphere. Measurements were made using a Quantum Design SQUID magnetometer, under a weak applied field of 100 Oe. For the neutron diffraction measurements, approximately 0.5 g of Cs₂AgF₄ powder was loaded into flame-dried quartz tubing (o.d. 0.4 cm, i.d. 0.30 cm), also under an argon atmosphere and subsequently flame-sealed under vacuum (ca. 10⁻³ mbar). Measurements were performed using the Neutron Powder Diffractometer (NPDF) at the Manuel Lujan Neutron Scattering Center at Los Alamos National Laboratory. All diffraction data were corrected for background scattering, incident neutron flux, multiple scattering and absorption effects, using the PDFgetN analysis procedures. The data were analysed using reciprocal space Rietveld refinements, performed with the GSAS package, and yielded the tetragonal lattice parameters a = b = 4.5573(14) Å and c = 14.166(6) Å at 6 K, and a = b = 4.5905(18) Å and c = 14.213(6) Å at 295 K, consistent with previous reports. Multiphase Rietveld refinement of these data showed the presence of small quantities of AgF and CsF at the level of a few mole percent.

For the inelastic neutron scattering measurements, approximately 10 g of Cs₂AgF₄ powder were loaded into scattering cells under an argon atmosphere. As the neutron absorption cross-section for Ag is quite large (63.3 barns), a thin plate Al sample cell (3 mm thickness) was utilized. The sample was initially placed in an envelope of prefluorinated PTFE sheet (5 cm x 5 cm x 0.01 mm) to prevent a chemical reaction with the aluminium sample cell. Measurements were performed using the High Energy Transfer (HET) time-of-flight spectrometer at the ISIS pulsed neutron source, Rutherford Appleton Laboratory, UK. HET is a direct geometry chopper spectrometer with large angular ³He detector coverage, from scattering angles of φ = 3° to 7° (4 m) and φ = 9° to 29° (2.5 m) in two separate banks, which makes it especially effective for the study of neutron scattering from powders. Incident energies of 50 and 100 meV were selected and measurements made at temperatures of 8 K, 35 K and 295 K. Typical measurement times were 10 hours per run at an average proton current of 1700 µA. Empty cell runs were also performed at the same energies and temperatures. All data were corrected individually for incident neutron flux and detector efficiencies. Empty cell runs were then corrected for sample absorption effects before being subtracted from the data sets obtained from the powder sample itself. This subtraction was necessary because scattering from PTFE remains significant at the low wave-vectors associated with magnetic excitations.