Magnetism in the high-$T_c$ analogue Cs$_2$AgF$_4$ studied with muon-spin relaxation

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We present the results of a muon-spin relaxation study of the high-$T_c$ analogue material Cs$_2$AgF$_4$. We find unambiguous evidence for magnetic order, intrinsic to the material, below $T_C = 13.95(3)$ K. The ratio of inter- to intraplane coupling is estimated to be $|J'/J| = 1.9 \times 10^{-2}$, while fits of the temperature dependence of the order parameter reveal a critical exponent $\beta = 0.292(3)$, implying an intermediate character between pure two- and three-dimensional magnetism in the critical regime. Above $T_C$ we observe a signal characteristic of dipolar interactions due to linear $F^-\mu^+\cdot F$ bonds, allowing the muon stopping sites in this compound to be characterized.

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Twenty years after its discovery, high-$T_c$ superconductivity remains one of the most pressing problems in condensed matter physics. High-$T_C$ cuprates share a layered structure of $[CuO_2]$ planes with strong antiferromagnetic (AFM) interactions between $S = 1/2$ $3d^9$ $Cu^{2+}$ ions$^1,2$. However, analogous materials based upon $3d$ transition metal systems such as manganites$^3$ and nickelates$^4$ share neither the magnetic nor the superconducting properties of the high-$T_C$ cuprates, leading to speculation that the spin-$1/2$ character of $Cu^{2+}$ is unique in this context. A natural extension to this line of inquiry is to explore compounds based on the $4d$ analogue of $Cu^{2+}$, namely $S = 1/2$ $4d^9$ $Ag^{2+}$, which contain silver in the unusual divalent oxidation state $[AgF_2]$. This material possesses several structural similarities with the superconducting parent compound La$_2$CuO$_4$; it is comprised of planes of $[AgF_2]$ instead of $[CuO_2]$ separated by planes of $[CsF]$ instead of $[LaO]$ (Fig. 1).

Magnetic measurements$^5$ suggest that in contrast to the antiferromagnetism of La$_2$CuO$_4$, Cs$_2$AgF$_4$ is well modelled as a two-dimensional (2D) Heisenberg ferromagnet (described by the Hamiltonian $\mathcal{H} = J \sum_{ij} \mathbf{S}_i \cdot \mathbf{S}_j$) with intralayer coupling $J/k_B = 44.0$ K. The observation of a magnetic transition below $T_C \approx 15$ K with no spontaneous magnetization in zero applied field (ZF) and a small saturation magnetization ($\sim 40$ mT), suggests the existence of a weak, AFM interlayer coupling. This behavior is reminiscent of the 2D ferromagnet K$_2$CuF$_4$$^6$, where ferromagnetic (FM) exchange results from orbital ordering driven by a Jahn-Teller distortion$^7$. On this basis, it has been suggested that in Cs$_2$AgF$_4$ a staggered ordering of $d_{x^2-y^2}$ and $d_{z^2-y^2}$ hole-containing orbitals on the Ag$^{2+}$ ions gives rise to the FM superexchange$^8$. An alternative scenario has also been advanced on the basis of density functional calculations in which a $d_{3z^2-r^2} - p - d_{x^2-y^2}$ orbital interaction through the Ag--F--Ag bridges causes spin polarization of the $d_{x^2-y^2}$ band$^9$. Although inelastic neutron scattering measurements have been carried out on this material$^{10}$, both Cs and Ag strongly absorb neutrons, resulting in limited resolution and a poor signal-to-noise ratio. In contrast, spin-polarized muons, which are very sensitive probes of local magnetic fields, suffer no such impediments and, as we shall see, are ideally suited to investigations of the magnetism in fluoride materials.

In this paper we present the results of a ZF muon-spin relaxation ($\mu^+\cdot$SR) investigation of Cs$_2$AgF$_4$. We are able to confirm that the material is uniformly ordered throughout its bulk below $T_C$ and show that the critical behavior associated with the magnetic phase transition is intermediate in character between 2D and 3D. In addition, strong coupling between the muon and $F^-$ ions allows us to characterise the muon stopping states in this material.

![FIG. 1: (Color online.) Structure of Cs$_2$AgF$_4$ showing a possible magnetic structure. Candidate muon sites occur in both the [CsF] and [AgF$_2$] planes.](image-url)
compound.

ZF µ+SR measurements were made on the MuSR instrument at the ISIS facility, using an Oxford Instruments Variox 4He cryostat. In a µ+SR experiment spin-polarized positive muons are stopped in a target sample, where the muon usually occupies an interstitial position in the crystal. The observed property in the experiment is the time evolution of the muon spin polarization, the behavior of which depends on the local magnetic field \( B \) at the muon site [12]. Polycrystalline Cs₂AgF₄ was synthesized as previously reported [7]. Due to its chemical reactivity, the sample was mounted under an Ar atmosphere in a gold plated Ti sample holder with a cylindrical sample space of diameter 2.5 cm and depth 2 mm. A 25 µm thick window was screw-clamped onto a gold o-ring on the main body of the sample holder resulting in an airtight seal.

Example ZF µ+SR spectra measured on Cs₂AgF₄ are shown in Fig. 2(a). Below \( T_C \) (Fig. 2(c)) we observe oscillations in the time dependence of the muon polarization (the “asymmetry” \( A(t) \)) which are characteristic of a quasi-static local magnetic field at the muon stopping site. This local field causes a coherent precession of the spins of those muons for which a component of their spin polarization lies perpendicular to this local field (expected to be 2/3 of the total spin polarization for a powder sample). The frequency of the oscillations is given by \( \nu_i = \gamma_\mu |B_i|/2\pi \), where \( \gamma_\mu \) is the muon gyromagnetic ratio (= 2\( \pi \times 135.5 \) MHz T⁻¹) and \( B_i \) is the average magnitude of the local magnetic field at the \( i \)th muon site. Any fluctuation in magnitude of these local fields will result in a relaxation of the oscillating signal [12], described by relaxation rates \( \lambda_i \).

Maximum entropy analysis (inset, Fig. 2(c)) reveals two separate frequencies in the spectra measured below \( T_C \), corresponding to two magnetically inequivalent muon stopping sites in the material. The precession frequencies, which are proportional to the internal magnetic field experienced by the muon, may be viewed as an effective order parameter for these systems [12]. In order to extract the temperature dependence of the frequencies, the low temperature data were fitted to the function

\[
A(t) = \sum_{i=1}^{2} A_i \exp(-\lambda_i t) \cos(2\pi \nu_i t) + A_3 \exp(-\lambda_3 t) + A_{bg},
\]

where \( A_1 \) and \( A_2 \) are the amplitudes of the precession signals and \( A_3 \) accounts for the contribution from those muons with a spin component parallel to the local magnetic field. The term \( A_{bg} \) reflects the non-relaxing signal from those muons which stop in the sample holder or cryostat tail.

The ratio of the two precession frequencies was found to be \( \nu_2/\nu_1 = 0.83 \) across the temperature range \( T < T_C \) and this ratio was fixed in the fitting procedure. The amplitudes \( A_i \) were found to be constant across the temperature range and were fixed at values \( A_1 = 1.66\% \), \( A_2 = 3.74\% \) and \( A_3 = 5.54\% \). This shows that the probability of a muon stopping in a site that gives rise to frequency \( \nu_1 \) is approximately half that of a muon stopping in a site that corresponds to \( \nu_2 \). We note also that \( A_3 \) is in excess of the expected ratio of \( A_3/(A_1 + A_2) = 1/2 \). The unambiguous assignment of amplitudes is made difficult by the resolution limitations that a pulsed muon source places on the measurement. The initial muon pulse at ISIS has FWHM \( \tau_{mp} \sim 80 \) ns, limiting the response for frequencies above \( \sim \tau_{mp}^{-1} \) [12]. We should expect, therefore, slightly reduced amplitudes or increased relaxation (see below) for the oscillating components in our spectra for which \( \nu_{1,2} \gg 5 \) MHz. The amplitudes of the oscillations are large enough, however, for us to conclude that the magnetic order in this material is an intrinsic property of the bulk compound. Moreover, above \( T_C \) there is a complete recovery of the total expected muon asymmetry. This observation, along with the constancy of \( A_{1,2,3} \) below \( T_C \), leads us to believe that Cs₂AgF₄ is completely ordered throughout its bulk below \( T_C \).

Fig. 3(a) shows the evolution of the precession frequen-
Our measurements probe the behavior of Cs$_2$AgF$_4$. More 2D-like behavior at temperatures lower than expected for 2D models ($\beta = 0.367$ for 3D Heisenberg), but larger than expected for 2D models ($\beta = 0.23$ for 2D XY or $\beta = 0.125$ for 2D Ising) \cite{14, 15}. This suggests that in the critical regime the behavior is intermediate in character between 2D and 3D; this contrasts with the magnetic properties of K$_2$CuF$_4$ where $\beta = 0.33$, typical of a 3D system, is observed in the reduced temperature region $t_r = (T_C - T)/T_C > 7 \times 10^{-2}$, with a crossover to more 2D-like behavior at $t_r < 7 \times 10^{-2}$, where $\beta = 0.22$ \cite{16, 17, 18}. Our measurements probe the behavior of Cs$_2$AgF$_4$ for $t_r \geq 5.5 \times 10^{-3}$, for which we do not observe any crossover.

A knowledge of $T_C$ and the intraplane coupling $J$, allows us to estimate the interplane coupling $J'$. Recent studies of layered $S = 1/2$ Heisenberg ferromagnets using the spin-rotation invariant Green’s function method \cite{19}, show that the interlayer coupling may be described by an empirical formula

$$|\frac{J'}{J}| = \exp\left(b - a|\frac{J}{J_C}|^\gamma\right)$$

(2)

with $a = 2.414$ and $b = 2.506$. Substituting our value of $T_C = 13.95$ K and using $|J|/k_B = 44.0$ K \cite{2}, we obtain $|J'|/k_B = 0.266$ K and $|J'|/J = 1.9 \times 10^{-2}$. The application of this procedure to K$_2$CuF$_4$ (for which $T_C = 6.25$ K and $|J|/k_B = 20.0$ K \cite{3}) results in $|J'|/k_B = 0.078$ K and $|J'|/J = 3.9 \times 10^{-3}$. This suggests that, although highly anisotropic, the interlayer coupling is stronger in Cs$_2$AgF$_4$ than in K$_2$CuF$_4$. This may account for the lack of dimensional crossover in Cs$_2$AgF$_4$ down to $t_r = 5.5 \times 10^{-3}$.

Both transverse depolarization rates $\lambda_1$ and $\lambda_2$ are seen to decrease with increasing temperature (Fig. 3(b)) except close to $T_C$ where they rapidly increase. The large values of $\lambda_{1,2}$ at low temperatures may reflect the reduced frequency response of the signal due to the muon pulse width described above. The large upturn in the depolarization rate close to $T_C$, which is also seen in the longitudinal relaxation rate $\lambda_3$ (which is small and nearly constant except on approach to $T_C$), may be attributed to the onset of critical fluctuations close to $T_C$. The component in the spectra with the larger precession frequency $\nu_1$ has the smaller depolarization rate $\lambda_1$ at all temperatures. These features provide further evidence for a magnetic phase transition at $T_C = 13.95$ K.

Above $T_C$ the character of the measured spectra changes considerably (Fig 2(a) and (b)) and we observe lower frequency oscillations characteristic of the dipole-dipole interaction of the muon and the $^{19}$F nucleus \cite{21}. The Ag$^{2+}$ electronic moments, which dominate the spectra for $T < T_C$, are no longer ordered in the paramagnetic regime, and fluctuate very rapidly on the muon time scale. They are therefore motionally narrowed from the spectra, leaving the muon sensitive to the quasistatic nuclear magnetic moments. This interpretation is supported by $\mu^+\text{SR}$ measurements of K$_2$CuF$_4$ where similar behavior was observed \cite{21}. In many materials containing fluorine, the muon and two fluorine ions form a strong hydrogen bond usually separated by approximately twice the F$^-$ ionic radius. The linear F$^-\mu^+\text{F}$ spin system consists of four distinct energy levels with three allowed transitions between them (inset, Fig. 2(b)) giving rise to the distinctive three-frequency oscillations observed. The signal is described by a polarization function \cite{20} $D(\omega t) = \frac{1}{3} \left[ 3 + \sum_{j=1}^{3} u_j \cos(\omega_j t) \right]$, where $u_1 = 1$, $u_2 = (1 + 1/\sqrt{3})$ and $u_3 = (1 - 1/\sqrt{3})$. The transition frequencies (shown in Fig. 2(b)) are given by $\omega_j = 3u_j \omega_d/2$ where $\omega_d = \mu_0 \gamma_\mu \gamma_F / 4\pi r^3$, $\gamma_F$ is the $^{19}$F nuclear magnetic moment. This interpretation is supported by $\mu^+\text{SR}$ measurements of K$_2$CuF$_4$ where similar behavior was observed \cite{21}. In many materials containing fluorine, the muon and two fluorine ions form a strong hydrogen bond usually separated by approximately twice the F$^-$ ionic radius. The linear F$^-\mu^+\text{F}$ spin system consists of four distinct energy levels with three allowed transitions between them (inset, Fig. 2(b)) giving rise to the distinctive three-frequency oscillations observed. The signal is described by a polarization function \cite{20} $D(\omega t) = \frac{1}{3} \left[ 3 + \sum_{j=1}^{3} u_j \cos(\omega_j t) \right]$, where $u_1 = 1$, $u_2 = (1 + 1/\sqrt{3})$ and $u_3 = (1 - 1/\sqrt{3})$. The transition frequencies (shown in Fig. 2(b)) are given by $\omega_j = 3u_j \omega_d/2$ where $\omega_d = \mu_0 \gamma_\mu \gamma_F / 4\pi r^3$, $\gamma_F$ is the $^{19}$F nuclear magnetic moment. This interpretation is supported by $\mu^+\text{SR}$ measurements of K$_2$CuF$_4$ where similar behavior was observed \cite{21}. In many materials containing fluorine, the muon and two fluorine ions form a strong hydrogen bond usually separated by approximately twice the F$^-$ ionic radius. The linear F$^-\mu^+\text{F}$ spin system consists of four distinct energy levels with three allowed transitions between them (inset, Fig. 2(b)) giving rise to the distinctive three-frequency oscillations observed. The signal is described by a polarization function \cite{20} $D(\omega t) = \frac{1}{3} \left[ 3 + \sum_{j=1}^{3} u_j \cos(\omega_j t) \right]$, where $u_1 = 1$, $u_2 = (1 + 1/\sqrt{3})$ and $u_3 = (1 - 1/\sqrt{3})$. The transition frequencies (shown in Fig. 2(b)) are given by $\omega_j = 3u_j \omega_d/2$ where $\omega_d = \mu_0 \gamma_\mu \gamma_F / 4\pi r^3$, $\gamma_F$ is the $^{19}$F nuclear magnetic moment.
nuclear gyromagnetic ratio and \( r \) is the \( \mu^+ - \text{F} \) separation. This function accounts for the observed frequencies very well, leading us to conclude that the F–\( \mu^+ \)–F bonds are highly linear.

A successful fit of our data required the multiplication of \( D(\omega_d t) \) by an exponential function with a small relaxation rate \( \lambda_3 \), crudely modelling fluctuations close to \( T_C \). The addition of a further exponential component \( A_2 \exp(-\lambda_2 t) \) was also required in order to account for those muon sites not strongly dipole coupled to fluorine nuclei. The data were fitted with the resulting relaxation function

\[
A(t) = A_4 D(\omega_d t) \exp(-\lambda_4 t) + A_5 \exp(-\lambda_5 t) + A_{bg}, \tag{3}
\]

The frequency \( \omega_d \) was found to be constant at all measured temperatures, taking the value \( \omega_d = 2\pi \times 0.211(1) \text{ MHz} \), which corresponds to a constant \( \text{F}–\mu^+ \) separation of 1.19(1) Å, typical of linear bonds \[20\]. The relaxation rates only vary appreciably within 0.2 K of the magnetic transition, increasing as \( T_C \) is approached from above, probably due to the onset of critical fluctuations. This provides further evidence for our assignment of \( T_C = 13.95 \text{ K} \).

Our determination of \( \nu_i(0) \) and observation of the linear \( \text{F}–\mu^+ \)–F signal allow us to identify candidate muon sites in \( \text{Cs}_2\text{AgF}_4 \). Although the magnetic structure of the system is not known, magnetic measurements \[7\] suggest the existence of loosely coupled FM \( \text{Ag}^{2+} \) layers arranged antiferromagnetically along the \( c \)-direction. Dipole fields were calculated for such a candidate magnetic structure with \( \text{Ag}^{2+} \) moments in the \( ab \) planes oriented parallel (antiparallel) to the \( a \) direction for \( z = 0 \) (\( z = 1/2 \)). The calculation was limited to a sphere containing \( 10^5 \) Ag ions with localized moments of 0.8 \( \mu_B \). The above considerations suggest that the muon sites will be situated midway between two F– ions. Two sets of candidate muon sites may be identified in the planes containing the fluorine ions. Magnetic fields corresponding to \( \nu_2(0) \) are found in the [CsF] planes (i.e. those with \( z = 0.145 \) and \( z = 0.355 \)) at the positions (1/4, 1/4, \( \bar{z} \)), (1/4, 3/4, \( \bar{z} \)), (3/4, 1/4, \( z \)) and (3/4, 3/4, \( z \)). Sites corresponding to the frequency \( \nu_1(0) \) are more difficult to assign, but good candidates are found in the [AgF\(_2\)] planes (at \( z = 0, 1/2 \)) at positions (1/4, 1/2, \( \bar{z} \)), (3/4, 1/2, \( z \)), (1/4, 0, \( z \)) and (3/4, 0, \( z \)). The candidate sites are shown in Fig. \[1\].

We note that there are twice as many [CsF] planes in a unit cell than there are [AgF\(_2\)] planes in agreement with our observation that components with frequency \( \nu_2 \) occur with twice the amplitude of those with \( \nu_1 \). Such an assignment then implies that the presence of the muon distorts the surrounding F– ions such that their separation is \( \sim 2.38 \text{ Å} \). This contrasts with the in-plane F–F separation in the unperturbed material of 4.55 Å ([CsF] planes) and \( \sim 3.2 \text{ Å} \) ([AgF\(_2\) planes] \[\footnote{\text{Electronic address: t.lancaster1@physics.ox.ac.uk}}\] ). Thus the two adjacent F– ions in the magnetic [AgF\(_2\)] planes each shift by \( \sim 0.4 \text{ Å} \) from their equilibrium positions towards the \( \mu^+ \), demonstrating that the muon introduces a non-negligible local distortion; however, the distortion in the \( \text{Ag}^{2+} \) ion positions is expected to be much less significant.

In conclusion, we have shown unambiguous evidence for magnetic order in \( \text{Cs}_2\text{AgF}_4 \) with an exchange anisotropy of \( |J'|/|J| \approx 10^{-2} \) and critical behavior intermediate in character between 2D and 3D. The presence of coherent \( \text{F}–\mu^+ \)–F states allows a determination of candidate muon sites and an estimate of the perturbation of the system caused by the muon probe. This study demonstrates that \( \mu^+ \)SR is an effective and useful probe of the \( \text{Cs}_2\text{AgF}_4 \) system. In order to further explore this system as an analogue to the high-\( T_C \) materials it is desirable to perform investigations of doped materials based on the \( \text{Cs}_2\text{AgF}_4 \) parent compound.

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