Singlet-Triplet Excitations and Long-Range Entanglement in the Spin-Orbital Liquid Candidate FeSc₂S₄

N. J. Laurita,[1] J. Deisenhofer,[2] LiDong Pan,[1] C. M. Morris,[1] M. Schmidt,[3] M. Johnsson,[4] V. Tsurkan,[3,5]
A. Loidl,[3] and N. P. Armitage[1]

[1]*The Institute for Quantum Matter, Department of Physics and Astronomy, The Johns Hopkins University,*
Baltimore, Maryland 21218, USA
[2]*Institute of Physics, University of Augsburg, 86135 Augsburg, Germany*
[3]*Experimental Physics V, Center for Electronic Correlations and Magnetism, University of Augsburg,*
D-86135 Augsburg, Germany
[4]*Department of Materials and Environmental Chemistry, Stockholm University, 10691 Stockholm, Sweden*
[5]*Institute of Applied Physics, Academy of Sciences of Moldova, MD-2028 Chisinau, Republic of Moldova*
(Received 24 October 2014; revised manuscript received 2 April 2015; published 22 May 2015; corrected 15 June 2015)

Theoretical models of the spin-orbital liquid (SOL) FeSc₂S₄ have predicted it to be in close proximity to a quantum critical point separating a spin-orbital liquid phase from a long-range ordered magnetic phase. Here, we examine the magnetic excitations of FeSc₂S₄ through time-domain terahertz spectroscopy under an applied magnetic field. At low temperatures an excitation emerges that we attribute to a singlet-triplet excitation from the SOL ground state. A threefold splitting of this excitation is observed as a function of applied magnetic field. As singlet-triplet excitations are typically not allowed in pure spin systems, our results demonstrate the entangled spin and orbital character of singlet ground and triplet excited states. Using experimentally obtained parameters we compare to existing theoretical models to determine FeSc₂S₄'s proximity to the quantum critical point. In the context of these models, we estimate the characteristic length of the singlet correlations to be $\xi/(\mathbf{a}/2) \approx 8.2$ (where $\mathbf{a}/2$ is the nearest neighbor lattice constant), which establishes FeSc₂S₄ as a SOL with long-range entanglement.

The search for ground states without classical analogs, e.g., quantum ground states, is a central focus of modern condensed matter physics. A zero temperature spin liquid would be a prime realization of such a state [1]. Such systems possess local moments, but, due to quantum fluctuations, typically enhanced due to geometric frustration, do not order even at zero temperature. They are proposed to have quantum mechanically entangled wave functions, with exotic fractionalized excitations. Orbital degrees of freedom can also be disordered by quantum fluctuations [2]. Systems with both spin and orbital fluctuations as well as spin-orbit coupling (SOC) have been proposed to form a "spin-orbital liquid" (SOL) ground state, characterized by entangled spin and orbital degrees of freedom but no long-range order [3–7].

Recent experiments have shown a SOL phase may exist in the geometrically frustrated A site cubic spinel compound FeSc₂S₄. A tetrahedral S₄ crystal field splits a $3d$ shell into an upper t_2 orbital triplet and a lower e orbital doublet. With Hund's coupling, an Fe²⁺ ion in a tetrahedral environment assumes a high spin $S = 2$ configuration with a lower ⁵E orbital doublet ground state and an upper ⁵T_2 orbital triplet excited state (Fig. 1). The ground state's twofold orbital degeneracy is associated with the freedom to place a hole in either e orbital. Although orbital degeneracy is often relieved by Jahn-Teller distortions,

heat capacity experiments show no sign of orbital ordering down to 50 mK and the magnetic susceptibility displays essentially perfect Curie-Weiss behavior with $\theta_{CW} = -45.1$ K in the range from 15–400 K [3]. The possible removal of the ground state orbital degeneracy by random
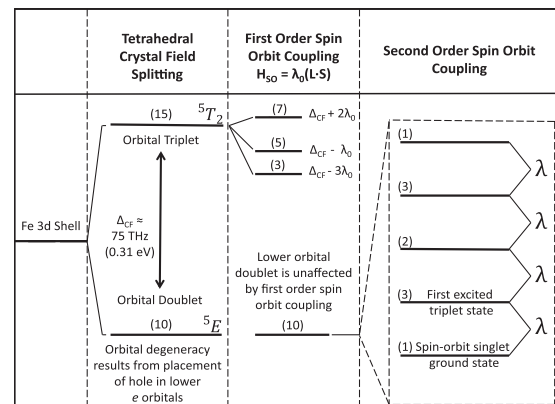

FIG. 1. Energy levels of the Fe²⁺ ion in an $S = 2$ configuration after tetrahedral crystal field splitting and first and second order SOC, without including lattice effects. Numbers in parenthesis represent the degeneracy of each level. Second order SOC splits the lower ⁵E doublet into 5 equally spaced levels separated by $\lambda = 6(\lambda_0^2/\Delta_{CF})$.

strains was proposed previously [8], but the expected T^2 contribution to the specific heat [9] was not observed experimentally [3]. The orbital degeneracy's contribution to the specific heat and magnetic entropy have been verified experimentally [3].

In the single ion case, SOC splits the upper orbital triplet into three levels with energies $\Delta_{CF} - 3\lambda_0$, $\Delta_{CF} - \lambda_0$, and $\Delta_{CF} + 2\lambda_0$, where Δ_{CF} is the ^5E–$^5T_2$ splitting and λ_0 is the SOC constant [10,11]. The potentially huge tenfold ground state degeneracy coming from $S = 2$ and the orbital doublet is split at second order in the spin-orbit interaction into 5 levels equally separated by $\lambda = 6\lambda_0^2/\Delta_{CF}$ (Fig. 1). The ground state is a spin and orbitally entangled singlet [12] with the form

$$\psi_g = \frac{1}{\sqrt{2}}|3z^2 - r^2\rangle|S_z = 0\rangle + \frac{1}{2\sqrt{2}}|x^2 - y^2\rangle$$
$$\times [|S_z = +2\rangle + |S_z = -2\rangle].$$

The first excited state is a spin-orbital triplet, predicted to split Zeeman-like with g factors of $\pm[1-2(\lambda_0/\Delta_{CF})]$ [10].

It was suggested by Chen, Balents, and Schnyder [4,5] that the spin and orbitally entangled singlet character of the wave function is preserved when the Fe^{2+} ion is incorporated into the $FeSc_2S_4$ lattice. They proposed that the SOL state results from competition between magnetic spin-orbital exchange, which favors a magnetically ordered classical ground state, and on-site SOC, which favors a SOL quantum disordered state. In the framework of a mean-field next-nearest neighbor (NNN) Kugel-Khomskii-type "J_2/λ" model, in which J_2 is the NNN exchange constant and λ is the excitation energy of single ion Fe^{2+} discussed above, Chen, Balents, and Schnyder predict a quantum phase transition (QPT) at $x_c = 1/16$ (with $x = J_2/\lambda$), which separates SOL and ordered phases [4,5]. The dominance of NNN exchange is demonstrated by the fact that the lowest energy magnetic excitations are found in neutron scattering at the wave vector for a simple Néel state $\mathbf{q} = (2\pi/a)(1,0,0)$ [13] and density functional theory, which predicts the ratio of NNN to nearest neighbor exchange to be ≈ 37 [14]. The SOL presumably differs from the ionic limit in that spin and orbital degrees of freedom may be entangled over longer length scales in that a spin on one site becomes entangled with the orbital of another site. Presumably this length scale diverges as the system approaches the QPT. The estimated value for x was such as to put $FeSc_2S_4$ slightly into the ordered regime [15]. However, the actual proximity to the QPT and the nature of the ground state has yet to be verified.

Intuitively, one might expect the spectrum of $FeSc_2S_4$ in the SOL phase to be similar to that of the single ion Fe^{2+} described above since the SOL results from degeneracies on individual Fe^{2+}, and $FeSc_2S_4$ breaks no other symmetries aside from those inherent to the crystal. Chen, Balents, and Schnyder [4,5] predicted that while the first

excited state would be a triplet, its energy would be substantially renormalized by exchange. In the simplest case with only NNN exchange (e.g., the J_2/λ model) through an expansion in the exchange (valid at $x \ll x_c$), it was shown that the lowest singlet-triplet excitation energy of $FeSc_2S_4$ is

$$E(q) = \lambda + 2J_2\sum_A \cos(\mathbf{q} \cdot \mathbf{a}), \tag{1}$$

where $\mathbf{a}$ represents the lattice vectors of the 12 NNN. Such excitations can be probed with optical measurements such as time domain terahertz spectroscopy (TDTS) through the magnetic dipole operator. Because of the negligible momentum of light compared to the lattice scale, we probe the $\mathbf{q} \to \mathbf{0}$ limit, reducing Eq. (1) to $E = \lambda(1 + 24x)$. For $FeSc_2S_4$, with x of order x_c, one expects the excitation energy to be substantially renormalized from the ionic value.

Dense polycrystalline $FeSc_2S_4$ samples were prepared by spark plasma sintering at $1000\,°C$ from precursor synthesized binary sulfides Sc_2S_3 and FeS. Structural, magnetic, and optical properties were identical to previous samples prepared by conventional solid state synthesis [3]. TDTS transmission experiments were performed using a home built spectrometer with applied magnetic fields up to 7 T in the Voigt geometry (light $\mathbf{k}\perp\mathbf{H}_{dc}$). TDTS is a high resolution method for accurately measuring the electromagnetic response of a sample in the experimentally challenging THz range. Coupling of the THz fields to magnetic dipole transitions allows access to the frequency dependent *complex* magnetic susceptibility between 100 GHz and 2 THz. Through the use of a rotating polarizer technique [16,17], we measure the sample's response to two polarization directions with respect to H_{dc}, simultaneously. Reflectivity measurements were performed in the midinfrared frequency range from 1000 to 8000 cm^{-1} using a BRUKER IFS 113v Fourier-transform spectrometer equipped with a He flow cryostat.

Figures 2(a) and 2(b) show the magnitude of the $T = 5$ K transmission coefficient as a function of applied field for the longitudinal (THz magnetic field $h_{ac}\|H_{dc}$) and transverse (THz magnetic field $h_{ac}\perp H_{dc}$) configurations. In zero field, a sharp absorption develops at 1.08 THz (4.46 meV) below 10 K [18]. As shown below, its energy is in reasonable agreement with the predicted singlet-triplet excitation energy of Eq. (1). Further evidence for this assignment is found in the field dependence of the transmission. While no splitting is observed in the longitudinal configuration, the transverse configuration shows a clear splitting into two separate resonances with increasing field, suggesting the presence of distinct selection rules in the system.

Pure spin singlet-triplet excitations are typically forbidden in electron spin resonance measurements due to the parity change between spin singlet and triplet states [19,20] and are usually only seen in the presence of a Dzyaloshinskii-Moriya (DM) interaction or staggered magnetization
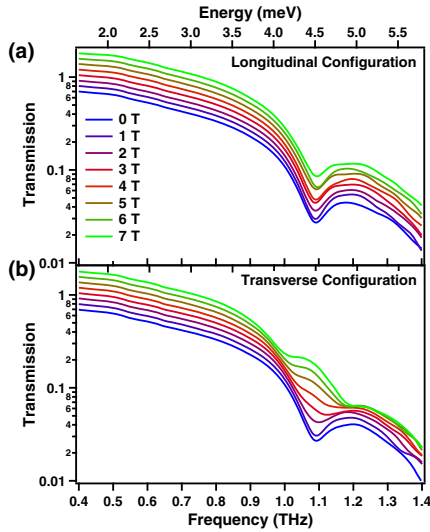
FIG. 2 (color online). (a)–(b) Field dependence of the transmission magnitude of $FeSc_2S_4$ taken at $T = 5$ K for the longitudinal (a) configuration (THz magnetic field $h_{ac}\|H_{dc}$) and transverse (b) configuration ($h_{ac}\perp H_{dc}$). Offsets of 0.05 are included between the curves for clarity.

arrangements along crystallographic axes. Chen, Balents, and Schnyder estimate the static DM interactions to be ≈ 100 times weaker than both exchange and spin orbit couplings [5]. In principle, dynamic DM interactions can also weakly allow pure spin singlet-triplet excitations, [20] but such interactions involve a phonon and are assumed to be even weaker than static contributions. However, neither of these effects are thought to be relevant in $FeSc_2S_4$ since the spin-orbital singlet and triplet states belong to the same

$S = 2$ ^5E multiplet and are different from the pure spin states [21]. In the single ion case of Fe^{2+} in tetrahedral crystal fields, it has been shown that a similar singlet-triplet excitation is magnetic dipole active with selection rules that agree with the results presented in this work [12,22]. Therefore, we believe the observation of this singlet-triplet excitation is further evidence for the entangled spin-orbital singlet character of the ground state and establishes $FeSc_2S_4$ as a SOL.

To better resolve the splitting, the complex ac susceptibility of the sample was calculated from the transmission coefficient [23]. Figure 3 shows the field dependence of the calculated susceptibility for the transverse [3(a)–3(b)] and longitudinal [3(c)–3(d)] configurations, respectively. The splitting of the resonance with increasing field is apparent in the transverse configuration. To extract the peak positions for both configurations the spectra was fit using Lorentzian oscillators and a linear background, which related work proposed derives from a continuum of zone boundary pairs of triplet excitations [18].

Figure 4(a) shows the field dependent splitting of the excited state triplet. Quantitative values for the splittings could not be resolved below 3 T. Linear fits were performed on each branch to determine the g factors. Only data between 5 T $\leq H_{dc} \leq$ 7 T was used in the upper branch fit since low transmission in the high frequency range causes error below 5 T. We find g factors of 0.93 and -0.92 for the upper and lower branches, respectively.

Midinfrared reflectivity at higher energy was performed in order to determine the crystal field splitting and SOC constant of the sample. Figure 4(b) shows the 5 K MIR reflectivity (black, left axis) spectrum, which displays a
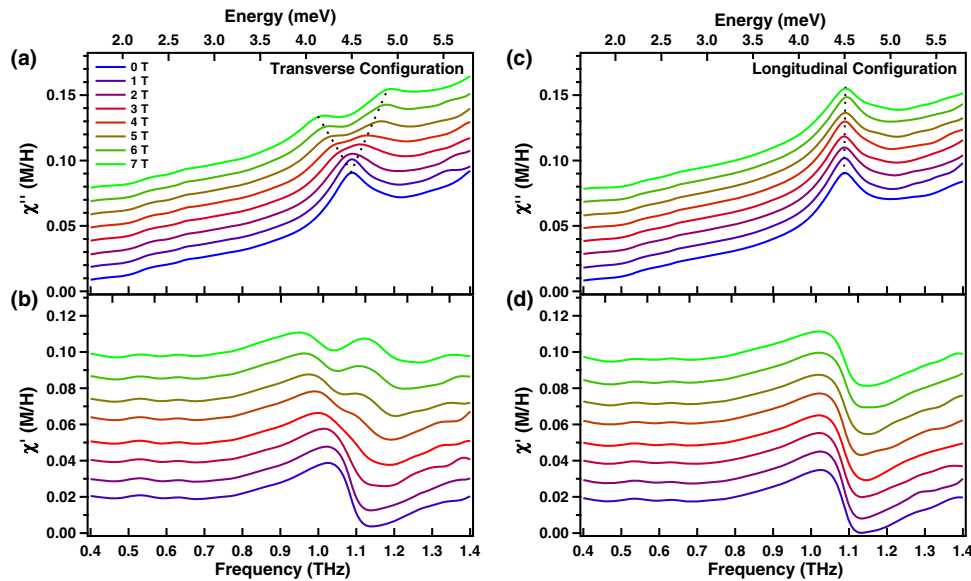

FIG. 3 (color online). Field dependence of the imaginary χ'' and real χ' parts of the complex ac susceptibility in the transverse (a)–(b) and longitudinal (c)–(d) configurations. All spectra were taken at $T = 5$ K. The susceptibility is shown in SI units, given by the ratio of the magnetization to the applied field. Dashed lines are guides to the eye. Offsets of 0.1 are included for clarity.
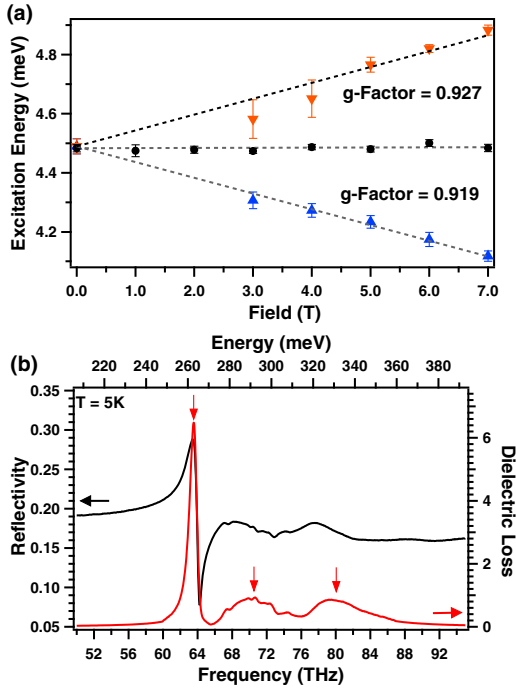
FIG. 4 (color online). Excitation energies for both configurations. Error bars are based on the quality of the fits. (b) Midinfrared reflectivity data taken at $T = 5$ K (black, left axis) along with the dielectric loss (red, right axis). Three features are seen with energies of 63.52 (0.262), 70.32 (0.290), and 80.16 THz (0.331 eV), corresponding to crystal field excitations to the $^5T_2$ energy levels plus coupling to Jahn-Teller modes of Fe^{2+} in a tetrahedral environment.

number of prominent features. The excitation energies can be found from the maxima of the dielectric loss (indicated by arrows), which was obtained by using a Kramers-Kronig consistent variable dielectric function fitting routine [24]. Although one only expects two optically active excitations from ^5E to $^5T_2$ states, additional and shifted absorptions are expected due to strong coupling of the $^5T_2$ levels to vibrational modes [22]. Following the approach of Wittekoek, van Stapele, and Wijma [11], the crystal field splitting, SOC constant, Jahn-Teller coupling mode energies (E_{JT}), and coupling constants ($\hbar\omega_{JT}$) can be extracted from the mode energies and intensities. We determine values of $\Delta_{CF} = 71.6 \pm 5$ THz (296.1 ± 20.7 meV), $\lambda_0 = 2.14 \pm 0.30$ THz (8.85 ± 1.24 meV), and $E_{JT}/\lambda \approx 1.6$, and $\hbar\omega_{JT}/\lambda \approx 4$. From these values we can calculate $\lambda = 6\lambda_0^2/\Delta_{CF} = 0.38 \pm 0.06$ THz (1.57 ± 0.25 meV). These values correspond closely to values found in other Fe^{2+} tetrahedral compounds [25].

From our experimental value of λ and the value of J_2 [15] extracted from the Curie-Weiss constant, we find from Eq. (1) an expected singlet-triplet excitation energy of 1.31 THz (5.42 meV), which is in reasonable agreement with the observed energy of 1.08 THz (4.46 meV). Additionally, substituting our measured values into the predicted g factor expression $g = \pm[1 - 2(\lambda_0/\Delta_{CF})]$ [10]

gives expected values of ± 0.94, which are in excellent agreement with our observed g factors of 0.93 and -0.92.

With the energy scales characterized, we can work backwards to determine $FeSc_2S_4$'s proximity to the QPT in the context of the theory of Chen, Balents, and Schnyder [4,5]. With an observed excitation energy of 1.08 THz (4.46 meV) and our experimental value for λ we can solve Eq. (1) for x. Here the implicit assumption is that Eq. (1), which was considered valid far from the critical point as an expansion in the exchange, is still valid near the QPT for momenta far from the ordering wave vector. We find a value of $x = 0.08$, which puts $FeSc_2S_4$ slightly above the predicted $x_c = 1/16$ from mean field theory. The fact that $FeSc_2S_4$ does not order down to the lowest measured temperatures indicates that quantum fluctuations are presumably important in setting x_c. We may use this value of x to make an estimate for J_2 of 0.029 THz (0.120 meV), which is about 25% less than the value inferred from the Curie-Weiss constant [4,5,15].

In this work, we have demonstrated the spin-orbital singlet character of the ground state of $FeSc_2S_4$ through the observation of a singlet-triplet excitation. Its energy is significantly renormalized by the exchange interaction in agreement with the model of Refs. [4,5]. This system, in close proximity to the QPT, differs from a simple ensemble of spin-orbit singlet ions through the presence of longer range correlations. As discussed in Refs. [4,5], it is believed that the critical regime of this QPT can be described by a Euclidean multicomponent Φ^4 scalar field theory in 4 space-time dimensions. In such field theories a correlation length can be extracted through the relation $\xi = (hv/E)$, where E is a characteristic energy that vanishes at the QPT and v is a velocity, whose square is a proportionality between space and time derivatives in the effective Lagrangian. This length can be understood as the scale over which spin and orbital degrees of freedom are entangled. In the present case, $E \approx 0.17$ meV can be identified with the zone boundary soft gap in neutron scattering [13]. By inspection of the terms in the action written down in Ref. [5], we can identify $v = (a/8h)\sqrt{\lambda^3/J_2}$ and find $\xi = (\lambda a/8E)\sqrt{1/x}$. Using our experimentally determined spin-orbit and exchange parameters we estimate a correlation length of $\xi/(\mathbf{a}/2) \approx 8.2$. This demonstrates the long-range entangled character of the SOL nonclassical ground state in $FeSc_2S_4$.

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