Frustrated Magnetism from Local Moments in FeSe

Harrison Ruiz,1,2 Yao Wang,2,3,4 Brian Moritz,2,5 and Thomas P. Devereaux2

1Department of Physics, Stanford University, Stanford, California 94305, USA
2Stanford Institute for Materials and Energy Sciences, SLAC National Accelerator Laboratory and Stanford University, Menlo Park, CA 94025, USA
3Department of Applied Physics, Stanford University, Stanford, California 94305, USA
4Department of Physics, Harvard University, Cambridge 02138, USA
5Department of Physics and Astrophysics, University of North Dakota, Grand Forks, North Dakota 58202, USA

(Dated: December 27, 2018)

We investigate properties of a spin-1 Heisenberg model with extended and biquadratic interactions, which captures crucial aspects of the low energy physics in FeSe. While we show that the model exhibits a rich phase diagram with four different magnetic ordering tendencies, we identify a parameter regime with strong competition between Néel, staggered dimer, and stripe-like magnetic fluctuations, accounting for the physical properties of FeSe. Through the comparison of numerically evaluated spin and Raman response with experiments, we find evidence for enhanced magnetic frustration between Néel and co-linear stripe ordering tendencies, which increases with increasing temperature. The explanation of these spectral behaviors with this frustrated spin model supports the idea of local spin interactions in FeSe.

Magnetic excitations are believed to play a significant role in the high-\(T_c\) copper and iron-based superconductors.1,2 Among the latter, FeSe has gained attention recently, in part because of the discovery of a superconducting phase above 100 K3 for monolayers grown on appropriate substrates. Bulk FeSe exhibits a superconducting transition temperature \(T_c\) of 9 K, which rises dramatically under pressure4,5; in contrast, a single-layer FeSe film deposited on SrTiO\(_3\) substrate increases \(T_c\) by an order of magnitude6–9.

Like other iron chalcogenides, FeSe consists of alternating iron and chalcogenide planes, with van der Waals bonds holding together quasi-2D layers in the bulk10,11. When cooled across a characteristic temperature \(\sim 90 \text{K}\), FeSe undergoes a nematic transition that breaks \(C_4\) crystal rotational symmetry in the iron-plane with a tetragonal to orthorhombic structural transition12,13. While the iron pnictides display a collinear striped spin-density-wave (SDW) phase immediately following a similar structural transition14–16, and other iron chalcogenides possess magnetic orders17,18, no long-range magnetic order has been observed for FeSe19.

Considering the critical role that spin fluctuations may play in the unconventional, iron-based superconductors2,11,20, understanding the magnetic properties of iron chalcogenides, in particular FeSe, is helpful in identifying the nature of the pairing mechanism. To that end, evidence for magnetic frustration from neutron scattering experiments19 and competing magnetic properties of FeSe models from mean-field theoretical work21 paint a picture of finely balanced interactions among various magnetically ordered phases.

Experimental and theoretical evidence suggests that despite the fact that FeSe is a metal with itinerant electrons, the low energy physics in FeSe can be described well in terms of localized electrons, owing to strong electronic correlations22–24, with a magnetic moment of \(\sim 2\mu_B\) per Fe atom25. A mean-field phase diagram for this type of localized electron model shows four dominant magnetic phases: Néel order (NO) \([(\pi,\pi)]\), a collinear striped (CS) phase \([(\pi,0)\text{ or } (0,\pi)]\), a staggered dimer (SD) phase \([(\pi,\pi/2)\text{ and equivalent}]\), and a double stripe (DS) phase \([(\pi/2,\pi/2)\text{ and equivalent}]\)21. Previous experiments and first-principles studies have measured spin correlations consisting of multiple wavevectors, demonstrating a magnetic frustration lacking long-range order19,24. This motivates the use of a spin-1 Heisenberg model with long-range spin interactions in a regime with magnetic frustration21,26. Two regions of the phase diagram were previously identified as appropriate for FeSe: a parameter regime with competition between the Néel and CS orders, and one between the SD and CS orders.

Here, we study the physics of a spin-1 Heisenberg model on a two-dimensional, 16-site cluster using exact diagonalization. Through benchmarking with mean-field theory and two different experiments, our study sets the stage for investigating the nature of FeSe within the spin model. For parameters tuned to a frustrated region among the NO, SD, and CS phases, evaluating the temperature dependence of the dynamical spin structure factor \(S(q,\omega)\) and the Raman scattering cross-sections finds intense fluctuations of the CS at low temperatures that give way to enhanced fluctuations at the NO wavevector for higher temperatures, consistent with neutron scattering19 while Raman scattering27,28 suggests a dominant spin character to a persistent peak in the \(B_{1g}\) symmetry, which softens slightly at higher temperatures.

Due to the local magnetic moment, the spin-1 \(J_1-J_2-J_3-K\) Heisenberg model, and similar variants, have been used to study the magnetic properties of FeSe21,29. The
Hamiltonian can be written as
\[ \mathcal{H} = \sum_{\langle i, j \rangle} \left[ J_1 S_i \cdot S_j + K (S_i \cdot S_j)^2 \right] + \sum_{\langle\langle i, j \rangle\rangle} J_2 S_i \cdot S_j + \sum_{\langle\langle i, j \rangle\rangle} J_3 S_i \cdot S_j, \]

where \( S_i = (S_i^x, S_i^y, S_i^z) \) is a spin operator at site \( i \), \( J_\alpha (\alpha = 1, 2, 3) \) are the nearest, next-nearest, and next-next-nearest neighbor exchange interactions, and \( K \) is the nearest-neighbor biquadratic interaction. The nearest neighbor exchange term \( J_1 \) favors a Néel state, while the longer-range exchange terms (\( J_2 \) and \( J_3 \)) frustrate it. A large \( J_2 \) or \( J_3 \) can overwhelm \( J_1 \) and drives the SD or DS phase\textsuperscript{32}. In addition, the biquadratic term \( K \) modulates fluctuations depending on the sign: a negative \( K \) suppresses quantum fluctuations towards an Ising-like model\textsuperscript{21}, while a positive \( K \) enhances quantum fluctuations\textsuperscript{39} and leads to a semi-ordered phase, containing some correlation between neighboring sites in an otherwise disordered system.\textsuperscript{30} In this work, we adopt a small positive \( K \) to enhance quantum fluctuations.

We study the model on a 4×4 cluster with periodic boundary conditions. While determining the ground state for such a problem is not computationally challenging, a study of the temperature dependence requires an accurate evaluation of the excited states to cover an energy spectrum in excess of the thermal energy scale set by the temperature \( T \). The 16-site system used in this work provides access to all the relevant momenta, while remaining computationally tractable for the temperature range of interest. We adopt the parallel Arnoldi method\textsuperscript{31} to determine the eigenstates and energies, and use the continued fraction expansion\textsuperscript{32} to calculate the finite-temperature dynamical structure factor and Raman response functions.

A crucial task of this work is determining a physical set of model parameters, within the \( J_1-J_2-J_3-K \) Heisenberg model, that accounts for the low-energy properties of FeSe. To examine its dominant magnetic fluctuations and ordering instability as a function of these parameters, and use the continued fraction expansion\textsuperscript{31} momenta, while remaining computationally tractable used in this work provides access to all the relevant scale set by the temperature

\[ 0 \leq I \leq 1 \]

and energies, and use the continued fraction expansion\textsuperscript{31} to calculate the finite-temperature dynamical structure factor and Raman response functions.

Given the various instabilities of the \( J_1-J_2-J_3-K \) model, can one find a parameter regime appropriate for FeSe? Previously, F. Wang et al. adopted a \( J_1-J_2 \) model near the quantum paramagnetic phase around \( J_2 \sim 0.5 J_1 \)\textsuperscript{26} and Q. Wang et al. suggested a point in the SD region near the boundary with CS order (for negative \( K )\textsuperscript{19}. Both involve competition between CS order and some other state. This would be consistent with recent neutron scattering data, showing both CS and, slightly weaker, NO fluctuations at low temperatures, with spectral weight transfer between them upon changing the temperature. Such an experimental observation suggests that the low-energy magnetic properties of FeSe can be described by a parameter set inside the CS region close to its boundary.

In addition to neutron scattering, the Raman response provides another clue about a proper parameter regime for FeSe as it captures the two-magnon excitations. As a collective mode, the two-magnon

\[ S(q) = \frac{1}{N} \sum_{l} \sum_{i} e^{iq \cdot r_i} \langle S_{r_i} \cdot S_{r_j} \rangle, \]

where \( r_i \) represents the coordinate of site \( l \) on the cluster and the expectation value taken with respect to the ground state at zero temperature. To fairly parameterize the relative strength of fluctuations with different characteristic wavevectors, we normalize the relative intensity of the dominant and largest subdominant correlation functions. Thus, the relative strength of fluctuations is projected onto the range \([0,1]\) by

\[ I = 1 - \frac{d_{q_{\text{sub}}} S(q_{\text{sub}})}{d_{q_{\text{dom}}} S(q_{\text{dom}})} \]

where \( d_q \) is geometric degeneracy for each equivalent momentum point on the 4×4 cluster and \( q_{\text{dom/sub}} \) denote
excitations depend sensitively on the form and strength of magnetic interactions\textsuperscript{33}. At low energy, the experimental Raman response in $B_{1g}$ symmetry consists of a quasi-elastic peak comprising a temperature-dependent charge nematic contribution and an additional broad peak, which softens slightly and loses weight with increasing temperature\textsuperscript{27,28}. In the Fleury-Loudon formalism, the Raman scattering operator is written as $\hat{O} = \sum_{i,j} J_{ij}(\hat{e}_{in} \cdot \hat{d}_{ij})(\hat{e}_{out} \cdot \hat{d}_{ij}) S_i \cdot S_j \frac{1}{Z}$, where $J_{ij}$ are exchange coupling strengths in the spin Hamiltonian, $\hat{d}_{ij}$ represent unit vectors connecting sites $i$ and $j$, and $\hat{e}_{in/out}$ are the polarization vectors for the incoming/outgoing photons, respectively. The light polarizations that encode the Raman symmetry channels are

$$\begin{cases} \hat{e}_{in} = \frac{1}{\sqrt{2}} (\hat{x} + \hat{y}), \hat{e}_{out} = \frac{1}{\sqrt{2}} (\hat{x} + \hat{y}) & \text{for } A'_{1g}, \\ \hat{e}_{in} = \hat{x}, \hat{e}_{out} = \hat{y} & \text{for } B_{2g}, \\ \hat{e}_{in} = \frac{1}{\sqrt{2}} (\hat{x} + \hat{y}), \hat{e}_{out} = \frac{1}{\sqrt{2}} (\hat{x} - \hat{y}) & \text{for } B_{1g}, \end{cases}$$

where $A'_{1g} = A_{1g} \oplus B_{2g}$. In this work, we mainly focus on the $B_{1g}$ channel as it directly reveals the two-magnon excitation, while the $A_{1g}$ and $B_{2g}$ spectra serve as additional experimental comparison.

![Figure 2](image_url)  
**FIG. 2:** Raman susceptibility $\chi''(\omega)$ at zero temperature as a function of $J_2$, with $J_1 = 0$ and $K = 0.1J_1$ for $A_{1g}$ (top), $B_{1g}$ (middle), and $B_{2g}$ (bottom) symmetries. The two vertical black boundary lines and the top color bar sketch regions with distinct dominant correlations [NO (left), SD (middle), and CS (right), as in Fig. 1].

Using the Raman scattering operator $\hat{O}_\alpha$, we evaluate the temperature-dependent Raman response in different symmetry channels as

$$R_\alpha(\omega) = -\sum_n \frac{e^{-\beta E_n}}{Z} \text{Im} \langle \psi_n | \hat{O}_\alpha | W^{-1} \hat{O}_\alpha | \psi_n \rangle,$$

where $\alpha$ denotes a particular symmetry channel, $Z$ is the partition function, $W = \omega + E_n + i\epsilon - \mathcal{H}$, $|\psi_n\rangle$ and $E_n$ are the $n$-th eigenstate and energy, with the sum taken over all eigenstates of the Hamiltonian in Fock space\textsuperscript{32}. To remove the elastic peak, it is convenient to calculate the Raman susceptibility $\chi''(\omega) = R_\alpha(\omega) - R_\alpha(-\omega)$. Due to the computational challenges, we truncate the summation at an energy $E_0 + 2J_1$, while providing sufficient states for evaluating the temperature-dependence of spectra up to $T = 0.25J_1$ (all states contributing a weight $e^{-\beta E_n} > e^{-5}$).

As shown in Fig. 2, the Raman susceptibility changes dramatically with $J_2$ at zero temperature. In $B_{1g}$ symmetry (middle panel) the two-magnon excitation starts around an energy of $7.5J_1$ for $J_2 = 0$, then softens uniformly approaching the boundary between the SD and CS phases. Taking a value of $J_1 = 123.1$ meV from first principles calculations\textsuperscript{21}, it becomes clear that to obtain a two-magnon energy consistent with the position of the peak at roughly 500 cm$^{-1}$ observed in experiments on FeSe\textsuperscript{28}, requires $J_2/J_1 \sim 0.5$, near the boundary between the SD and CS phases. This parameter region is also consistent with the general notion of highly frustrated magnetism in FeSe. We identify the best agreement in this region with $J_2 = 0.528J_1$, $J_3 = 0$, and $K = 0.1J_1$ (the black dot shown in Fig. 1). As we show next, the finite temperature Raman and neutron scattering experiments compare favorably with simulations for these parameters.

**FIG. 3:** The imaginary part of the Raman susceptibility for $B_{1g}$ symmetry as a function of temperature. The insets are the EDC cuts at $T = 0$ (blue) and 0.12$J_1$ (orange), indicated by the arrows.

Figure 3 displays the temperature dependence of the $B_{1g}$ Raman susceptibility for the chosen parameters. We observe a single dominant peak. With increasing temperature, this peak softens slightly, before hardening again at higher temperature. The peak gradually loses intensity up to the highest simulated temperatures. In fact, thermal broadening occurs in all symmetries, while $B_{1g}$ remains dominant. This dominant peak that softens with increasing temperature before hardening again agrees well with experiment\textsuperscript{27,28}, suggesting that a local spin model provides an adequate description of the dominant degrees of freedom in Raman scattering from FeSe in this energy range. We will see that the
temperature dependence of this softening coincides with the temperature dependence of spectral weight transfer observed in \( S(q, \omega) = (\pi, \pi, \omega) \), further reinforcing the connection between the peak in the Raman response and two magnon excitations.

In \( A_{1g} \) symmetry [Fig. 4(a)], there is a single peak at slightly higher energy than the one found in the \( B_{1g} \) channel. This peak decreases in intensity and hardens slightly with increasing temperature. In \( B_{2g} \) symmetry, shown in [Fig. 4(b)], we see several peaks spread out over the energy range of \( 2J_1 \) to \( 8J_1 \). The general trends for each of these symmetries, and in particular the dominant peak in \( B_{1g} \) symmetry, correspond well with recent Raman scattering data.\(^{28}\)

While we have seen that Raman scattering provides some information about magnetic excitations in the model, much more detailed information comes from the dynamical spin structure factor

\[
S(q, \omega) = -\sum_n e^{-\beta E_n} \frac{\omega}{\pi Z} \text{Im} \langle \psi_n | S_{-q}^z W^{-1} S_q^z | \psi_n \rangle , \tag{6}
\]

where \( S_q^z = \frac{1}{\sqrt{N}} \sum_i e^{iq \cdot r_i} S_i^z \). Figure 5 shows \( S(q, \omega) \) as a function of temperature for \( q = (\pi, 0), (\pi, \pi), \) and \( (\pi, \frac{\pi}{2}) \). At \( T = 0 \), the lowest-energy spin excitation occurs at \( (\pi, 0) \), with significant fluctuations at slightly higher energy in \( (\pi, \frac{\pi}{2}) \) and \( (\pi, \pi) \), indicative of a frustrated magnetic system. With increasing temperature, the spin excitation at \( (\pi, 0) \) hardens slightly and loses intensity, while it softens substantially at \( (\pi, \pi) \) and \( (\pi, \frac{\pi}{2}) \). This temperature dependence is reminiscent of the neutron scattering data\(^{10} \), and this enhanced competition is consistent with the evolution of the \( B_{1g} \) Raman response in Fig. 3, further highlighting the role of magnetic frustration in FeSe.

Interestingly, only a small region of parameter space with \( K \sim 0.1J_1 \) displays a temperature-dependent behavior consistent with the \( B_{1g} \) Raman and spin response, at least in this 16-site cluster calculation (response functions for other parameters not shown). The origin of this softening and its sensitivity to \( K \) is difficult to assess in a simple spin-wave picture due to the many-body nature of this biquadratic term. Fortunately, with the full wavefunctions obtained by exact diagonalization, we can study the magnetic fluctuations and competition directly through eigenstates of the Hamiltonian. Figure 6 shows detailed information about the five lowest eigenstates as a function of \( J_2 \) for two different values of \( K \). The color of each point represents the dominant magnetic character of the eigenstate, following the same convention as Fig. 1. Crossing the boundary to the CS phase, there is a small region (highlighted in the black boxes) where the low-lying excited states possess a SD or mixed character. In this region, while both values of \( K \) result in similar ground states and zero-temperature Raman and neutron scattering spectra, only \( K = 0.1J_1 \) provides the ingredients for a temperature dependence consistent with experiments, because of its much smaller excitation gap and larger density of excited states. These states are responsible for the softening of the \( B_{1g} \) peak, as well as the energy shift and weight transfer of the dynamical spin structure factor.

In summary, we present a systematic exact-diagonalization study of the magnetic fluctuations and spectra in a local spin \( J_1-J_2-J_3-K \) model. This model displays a rich phase diagram influenced by magnetic frustration. A comparison of the dynamical spin and Raman response to experimental results underscores that this model provides a consistent description of the magnetic properties of FeSe, lying at the boundary between the CS, NO, and SD phases. Through a detailed analysis of the eigenstates, we attribute the temperature evolution of the spectra to the competition between various finely balanced magnetic ground and excited states, and hence explain the crucial role of the biquadratic coupling. Our results suggest that magnetic frustration plays a dominant role in the low-energy physics of FeSe, which may
FIG. 6: Energy and magnetic fluctuations associated with the five lowest energy excited states for $K = 0$ (top) and $0.1J_1$ (bottom), as a function of $J_2$ for $J_3 = 0$. The black boxes enclose a range of $J_2$ where the ground state and possibly a nearly degenerate state of CS order are followed by states characterized by a dominant SD phase. The color coding of each circle follows the same convention as Fig. 1.

Additionally support the intrinsic connection between spin fluctuations and unconventional superconductivity. We find that local spins give an adequate description of these magnetic properties.

ACKNOWLEDGEMENTS

Supported by the U.S. Department of Energy (DOE), Office of Basic Energy Sciences, Division of Materials Sciences and Engineering, under contract DE-AC02-76SF00515. Computational work was performed using the resources of the National Energy Research Scientific Computing Center, under contract DE-AC02-05CH11231.


