Nematic Fluctuations in Iron-Oxychalcogenide Mott Insulators

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Nematic fluctuations occur in a wide range of physical systems from liquid crystals to biological molecules to solids such as exotic magnets, cuprates and iron-based high-$T_c$ superconductors. Nematic fluctuations are thought to be closely linked to the formation of Cooper-pairs in iron-based superconductors. It is unclear whether the anisotropy inherent in this nematicity arises from electronic spin or orbital degrees of freedom. We have studied the iron-based Mott insulators La$_2$O$_2$Fe$_2$OM$_2$ $M=(S, Se)$ which are structurally similar to the iron pnictide superconductors. They are also in close electronic phase diagram proximity to the iron pnictides. Nuclear magnetic resonance (NMR) revealed a critical slowing down of nematic fluctuations as observed by the spin-lattice relaxation rate ($1/T_1$). This is complemented by the observation of a change of electrical field gradient over a similar temperature range using Mössbauer spectroscopy. The neutron pair distribution function technique applied to the nuclear structure reveals the presence of local nematic $C_2$ fluctuations over a wide temperature range while neutron diffraction indicates that global $C_4$ symmetry is preserved. Theoretical modeling of a geometrically frustrated spin-$1$ Heisenberg model with biquadratic and single-
ion anisotropic terms provides the interpretation of magnetic fluctuations in terms of hidden quadrupolar spin fluctuations. Nematicity is closely linked to geometrically frustrated magnetism, which emerges from orbital selectivity. The results highlight orbital order and spin fluctuations in the emergence of nematicity in Fe-based oxychalcogenides. The detection of nematic fluctuation within these Mott insulator expands the group of iron-based materials that show short-range symmetry-breaking.

1 Introduction

Nematic phases occur in a variety of very different physical systems throughout nature. A nematic phase is formed when a discrete rotational symmetry is broken or reduced, while the translational symmetry is preserved. Nematicity has been studied mostly in the structural organization of soft matter such as liquid crystals. In these materials it is easy to visualize the nematic state’s defining characteristic: the presence of a preferred axis along which liquid crystal molecules are, on average, aligned. This spatial anisotropy is generally described by $C_2$ rotational symmetry. In the context of cuprate high-temperature superconductivity (HTSC) bond-nematicity was introduced as a competing order with HTSC itself. In recent years, nematicity has become the central focus of efforts to illuminate mechanism(s) of HTSC in iron-based superconductors (FeBS). By now, a variety of iron pnictides have been shown to exhibit electronic nematic states and in numerous theoretical pictures, the nematic phase is thought to be intimately related to the superconducting mechanism in iron-based materials.

The origin of the nematic phase in iron superconductors is heavily debated. Two scenarios
are proposed: One proposal suggests that anisotropic spin fluctuations are necessary precursors of the nematic ordering that has been experimentally observed; the other claims that ferro-orbital ordering involving $d_{xz,yz}$ orbitals is responsible for nematicity. Complicating this debate is the fact that various Fe-based materials exhibit different magnetic order. Nematicity has been mainly studied in the 122 iron pnictides such as BaFe$_2$As$_2$, but recently nematic behavior was reported in the 1111 material LaAsFeO$_{1-x}$F$_x$. An important question emerges. Is nematicity a general phase behavior that exists in other Fe-based materials across the electronic phase diagram? For example, do Fe-based parent materials that are Mott insulators also exhibit nematicity? What role does electron correlation in multi-orbital systems play in the formation of the interlinked nematic and spin density wave (SDW) phase and the competing superconducting phase.

Increasing evidence points to an electronic mechanism of nematicity which would place the nematic order in the class of correlation-driven electronic instabilities, like superconductivity and density-wave transitions.

In this work, we report a combined experimental and theoretical investigation of magnetism intrinsic to the correlation-induced Mott insulators La$_2$O$_2$Fe$_2$O(S, Se)$_2$ (see Figure 1). Neutron powder diffraction was employed to make a magneto-structural comparison of the materials. A short range nematic fluctuating behavior was observed. A critical slowing down of nematic fluctuations observed in the nuclear magnetic resonance (NMR) spin relaxation rate; this result was complemented by Mössbauer spectroscopy data. In contrast to Fe-based superconductors, orbital nematicity does not play a role in the iron oxychalcogenides, since a $d_{xz,yz}$ orbital degeneracy is not present due to an alternating orientation of the FeM$_4$O$_2$ octahedra. Therefore, a different mechanism must be responsible for the nematicity we observe in La$_2$O$_2$Fe$_2$O(S, Se)$_2$. Since these
are Mott insulators, a strong-coupling view should be relevant. Our magnetic neutron diffraction data reveal the establishment of antiferromagnetic (AFM) ordering and the similarity of magnetic behavior in these materials. Our theoretical modeling explains the nematic fluctuations as being related to quadrupolar fluctuations in a strongly frustrated spin-1 magnet. This agrees well with NMR $1/T_1$ data. The quadrupolar fluctuations are closely related to geometric frustration in the non-collinear spin structure, which itself arises as a consequence of strong orbital selectivity in the compounds. Thus, orbital-selective Mott correlations are important for understanding magnetism in the Mott-insulating states of the oxychalcogenides. Such selective-Mott correlations have recently been the focus of attention in the iron-selenides \cite{11-14} and the present study provides a new instance for the relevance of orbital-selective Mott physics in Fe-based materials.

2 Experimental and Theoretical Results

Neutron Diffraction Neutron powder diffraction experiments were performed on powder samples of $\text{La}_2\text{O}_2\text{Fe}_2\text{O(S, Se)}_2$ using the C2 high-resolution diffractometer at the Canadian Nuclear Laboratories in Chalk River, Ontario. The C2 diffractometer is equipped with an 800 wire position sensitive detector covering a range of 80 degrees. Data were collected in the $2\theta$ angular range from 5° to 117° using a Si (5 3 1) monochromator at a wavelength $\lambda$ of 1.337 Å. The lattice parameters of $\text{La}_2\text{O}_2\text{Fe}_2\text{O(S, Se)}_2$ were determined by Rietveld analysis of the diffraction data: for $\text{La}_2\text{O}_2\text{Fe}_2\text{OS}_2$ [$a = 4.0453(5)$ Å, $c = 17.9036(3)$ Å] and $\text{La}_2\text{O}_2\text{Fe}_2\text{OSe}_2$ [$a = 4.4087(5)$ Å, $c = 18.6005(3)$ Å]. We did not observe nuclear Bragg peak splittings, that would be indicative of a structural phase transition, in the $\text{La}_2\text{O}_2\text{Fe}_2\text{O(S, Se)}_2$ diffraction data collected over the temperature range from 4 to 300
K. Thus we did not detect a change of lattice symmetry over this temperature range.

We verified the consistency of the data with the non-collinear 2-k magnetic structure previously obtained for \( \text{La}_2\text{O}_2\text{Fe}_2\text{OSe}_2 \).\(^{15}\) The high-temperature paramagnetic (PM) phase is compared to the 2-k antiferromagnetic phase in Fig. 7. The Sarah suite of programs\(^ {16}\) was used to analyze the representations and provide the magnetic basis vectors for refinement with Fullprof.\(^ {17,18}\) The magnetic cell is commensurate and is doubled, in both \( a \) and \( c \), with respect to the structural cell. The ordering is associated with \( k_1 = (1/2, 0, 1/2) \) and \( k_2 = (0, 1/2, 1/2) \), and the single Fe site on (1/2, 0, 0) in the nuclear \( \text{I4/mmM} \) cell is described by two distinct orbits governing the two (1/2, 0, 0) and (0, 1/2, 0) Fe sites that are independent in the magnetically ordered state. However, we note that for powder samples the diffraction pattern is indistinguishable from the pattern assigned as the collinear AFM3 model in the literature.\(^ {15,19}\) Neutron diffraction shows that the magnetic structures of \( \text{La}_2\text{O}_2\text{Fe}_2\text{O(S, Se)}_2 \) are similar with a distinction in the AFM onset temperatures \( T_N \).

The magnetic peak intensity over a temperature range from 4 to 300 K, shown in Figure 1, is proportional to the square of the magnetic order parameter. The magnetic peak intensity data reveals the onset of AFM ordering at 90.1(9) ± 0.16 K and 107.2(6) ± 0.06 K for \( \text{La}_2\text{O}_2\text{Fe}_2\text{OSe}_2 \) and \( \text{La}_2\text{O}_2\text{Fe}_2\text{OS}_2 \), respectively. The \( T_N \) value for \( \text{La}_2\text{O}_2\text{Fe}_2\text{OSe}_2 \) is in excellent agreement with values in the literature.\(^ {10,15,19}\)

**Nuclear Pair Distribution Function** Nuclear pair distribution function (PDF) measurements on \( \text{La}_2\text{O}_2\text{Fe}_2\text{O(S, Se)}_2 \) were performed using the Nanoscale Ordered Materials Diffractometer (NOMAD)\(^ {20}\) beamline at the Spallation Neutron Source (SNS) at Oak Ridge National Laboratory.
PDF measurements are well-suited to provide details of the structural arrangement of atoms. Pair distribution function analysis involves obtaining the Fourier transform of the measured total scattering intensity $S(Q)$ in order to obtain a real space representation of inter-atomic correlations. The pair distribution function is given as

$$G(r) = 2\pi \int_0^{Q_{\text{max}}} Q[S(Q) - 1] \sin(Qr) dQ$$

where $Q$ is the scattering vector and $r$ is the interatomic distance. PDF is a total scattering method i.e., meaning that both Bragg and diffuse scattering intensity data is simultaneously collected. Therefore, the technique is sensitive to deviations from the average structure. Our PDF data were generated from the total scattering experiments using neutrons of a wavelength band from 0.1 to 2.9 Å. The maximum momentum transfer used for the Fourier transform was 31.4 Å$^{-1}$. The instrument parameters $Q_{\text{damp}} = 0.017$ Å$^{-1}$ and $Q_{\text{broad}} = 0.019$ Å$^{-1}$ were fixed for all of our fits and structural refinements of the data were performed using the PDFGUI program and DIFFPY-CMI suite.

We performed data refinements using an orthorhombic model of La$_2$O$_2$Fe$_2$O(S, Se)$_2$ with a sliding fit range from (1.5-21.5) Å to (29.5-49.5) Å in 1 Å steps to investigate the temperature dependent structure on these various length scales. This resulted in 29 fits for each temperature at which PDF data were collected. We have extracted the orthorhombicity parameter $\delta = (a-b)/(a+b)$ for both length scale and temperature series sequential refinements where $a, b$ are lattice parameters. Figure 2 shows the refined orthorhombicity $\delta$ extracted from fits of neutron PDF data. Structural models obtained from refining PDF data are strictly valid within the refined length scale; this specificity condition enables the probing of local structure on different length scales by varying the refinement range. By conducting such fittings, we observed higher orthorhombicity for short-range fitting (1.5 - 21.5) Å compared to long-range fitting (30.0-50.0)
Å. This suggests that by tracking the orthorhombicity parameter we observe local scale distortions from tetragonal to orthorhombic structure. These spatially limited distortions represent fluctuating nematic order \(^{25,26}\) over a broad range of temperatures. It should be emphasized that neutron powder diffraction, from the same samples, provides clear evidence that the average, long-range structures of La\(_2\)O\(_2\)Fe\(_2\)O(S, Se)\(_2\) remain tetragonal throughout the high and low temperature regimes. \(^{27}\) However, the PDF results provide evidence of local symmetry breaking that results in nematic \(C_2\) regions of fluctuating order. \(^{25,26,28,29}\)

**Mössbauer spectroscopy** In order to investigate the magnitude and the orientation of the ordered static Fe magnetic moment with respect to the electric field gradient (EFG) principal axis within the distorted FeO\(_2\)S\(_4\) octahedra, and to study the modification of the electronic surroundings via the electric quadrupole interaction, \(^{57}\)Fe Mössbauer spectroscopy was performed on La\(_2\)O\(_2\)Fe\(_2\)OS\(_2\) and is discussed in comparison to similar work on La\(_2\)O\(_2\)Fe\(_2\)OSe\(_2\). \(^{30}\) The \(^{57}\)Fe nucleus probes the onsite magnetism of the Fe ion, therefore any significant changes in orbital and spin degrees of freedom should be reflected in the \(^{57}\)Fe Mössbauer spectra.

Figure 3a shows the low temperature zero field \(^{57}\)Fe Mössbauer spectra for La\(_2\)O\(_2\)Fe\(_2\)OSe\(_2\) and La\(_2\)O\(_2\)Fe\(_2\)OS\(_2\). At high temperatures, in the paramagnetic (PM) state, we observe a single asymmetric doublet (spectra not shown here) with a quadrupole splitting of \(\Delta = 1.95\) mm/s corresponding to a principal EFG component of \(V_{zz} = 117\) V/Å\(^2\). The basic features of the spectra in the PM phase look similar to previously reported La\(_2\)O\(_2\)Fe\(_2\)OSe\(_2\) results. \(^{30-32}\) As the temperatures goes below 110 K a sextet develops thereby indicating the long range magnetic ordering of
La$_2$O$_2$Fe$_2$OS$_2$.

Mössbauer spectra were analyzed by using the full static Hamiltonian

$$H_s = \frac{eQ_{zz}V_{zz}}{4I(2I-1)} \left[ (3I_2^2 - I^2) + \frac{\eta}{2}(I_+^2 + I_-^2) \right] - g_I \mu_N B \left( \frac{I_+ e^{-i\phi} + I_- e^{+i\phi}}{2} \sin \theta + I_z \cos \theta \right),$$

with nuclear spin operators $I_z$, $I_+ = I_x + iI_y$, and $I_- = I_x - iI_y$. Here $B$ is the hyperfine field at the $^{57}$Fe site while $Q$, $g_I$, and $\mu_N$ indicate the nuclear quadrupole moment, g factor and magneton, respectively. The polar angle $\theta$ and the azimuthal angle $\phi$ describe the orientation of the Fe hyperfine field $B$ with respect to the EFG $z$ axis. The azimuthal angle $\phi$ was set to zero to avoid cross correlation. This is justified, because the asymmetry parameter $\eta$ is small and the polar angle $\theta$ is close to zero for both systems. For both samples, the whole temperature series was fitted simultaneously to determine $\eta$, then $\eta$ was fixed, and then the spectra were fitted individually. Within error bars, both samples La$_2$O$_2$Fe$_2$O(S, Se)$_2$ have $\eta \approx 0.1$.

In the magnetically ordered state a clear magnetic sextet is observed in La$_2$O$_2$Fe$_2$O(S, Se)$_2$ data, indicating the presence of a long range ordered (LRO) state. The nature of this LRO state is the same for both systems in terms of the magnitude of the ordered moment (magnetic hyperfine field $B_{\text{hyp}}(T)$) and its temperature dependence. The lines in Figure 3b) indicate fits of the sublattice magnetization $M(t)$ by using the equation $M(t) \propto B_{\text{hyp}}(T) \propto (1 - T/T_N)^{\beta_{\text{crit}}}$ applied to the magnetic hyperfine field data. The magnetic critical exponents $\beta_{\text{crit}}$ can be estimated as a fit
parameter (see Table 1).

The $^{57}$Fe Mössbauer spectroscopy provides clear evidence that in both systems the angle between the strongest EFG component (local $z$ main axis) and the magnetic hyperfine field $B$, $\theta$, is equal to 0 in the magnetically ordered regime, i.e., the magnetic hyperfine field $B$ is oriented parallel to the local $z$ axis of the EFG principal axis system. The strongest EFG component is aligned along the O-Fe-O chains in agreement with local spin density approximation + $U$ (LSDA+$U$) calculations.  

This indicates that the Fe moments are oriented parallel to O-Fe-O chains. Therefore, both La$_2$O$_2$Fe$_2$OS$_2$ and La$_2$O$_2$Fe$_2$OSe$_2$ exhibit non-collinear magnetic order with a 90 degree angle between different magnetic sublattices. This is consistent with three different spin structures discussed for La$_2$O$_2$Fe$_2$OSe$_2$. However, the $^{139}$La NMR experiments presented below decisively identify the 2-$k$ structure as the actual magnetic structure in both systems.

The temperature dependence of the EFG is comparable in La$_2$O$_2$Fe$_2$O(S, Se)$_2$. At $\approx 1.4 T_N$ the principal component $V_{zz}$ decreases significantly in a near-linear fashion (Figure 3c). Previously reported thermal expansion data of La$_2$O$_2$Fe$_2$OSe$_2$ also showed an unusual change in this temperature range. It is known that thermal behavior can influence the values of the EFG tensors; however, another relevant possibility is that any degree of orbital electronic anisotropy can significantly modify the orbital occupancy. This would lead to a change in the valence contribution reflected in the EFG tensors. This particular scenario is well supported by the NMR spin-lattice relaxation rate data presented below.
Nuclear Magnetic Resonance (NMR)  Figure 4 shows the representative $^{139}$La field sweep NMR spectra on La$_2$O$_2$Fe$_2$OS$_2$. Each spectrum consists of three pairs of satellites, and one split central transition. For lower symmetries, such as tetragonal systems, in the presence of finite EFG at the probed nucleus with nuclear spin $I = 7/2$, one would expect such NMR spectra. Upon lowering $T$, the spectral shape remains unchanged down to 109 K (the line in the temperature range 109-105 K could not be resolved). This indicates the AFM ordering within the system. In the ordered state the spectral shape changes considerably because of the development of the static internal magnetic field associated with Fe ordered moment. The field swept NMR spectra can be well described by diagonalizing the full nuclear Hamiltonian

$$H = h\gamma \left[ (B + B_\parallel + B_\perp)I + h\frac{\nu}{6}(3I_x^2 - I_y^2 + \eta (I_x^2 + I_y^2)) \right], \tag{2}$$

where $B$ is the external magnetic field, $z$ axis being the principle axis of EFG and $\frac{\gamma}{2\pi} = 6.0146 \frac{MHz}{T}$. $B_\perp$ ($B_\parallel$) are the hyperfine fields (internal fields) at the La site due to the Fe ordered moment. At temperatures $T > T_{N\text{M}}$ NMR field sweep spectra can be adequately described without any additional internal fields ($B_\perp = 0$ mT, $B_\parallel = 0$ mT); however two different local fields $B_1$ and $B_2$ at magnetically nonequivalent $^{139}$La sites must be introduced in Eq. (2) to describe the observed spectra in the ordered state. The shape of the presented NMR spectra look very similar to the Se variant La$_2$O$_2$Fe$_2$OSe$_2$, and we ascertain a non-collinear magnetic structure for La$_2$O$_2$Fe$_2$OS$_2$ in agreement with the $^{57}$Fe Mössbauer results. The presence of two different sub-spectra of equal intensity with local hyperfine fields parallel and perpendicular to the $c$-axis unambiguously confirm the 2-$k$ magnetic structure to be realized in both systems. The applied fields do not change the magnetic structure of the sublattices due to anisotropy fields much larger than 7 T. This was
checked by $^{57}$Fe Mössbauer spectroscopy, where a model based on pure superposition of internal and external field reproduces the measured spectra, similar to the NMR results.

There are no $^{139}$La NMR spectral anomalies near or below 150 K in La$_2$O$_2$Fe$_2$OS$_2$ nor near or below 125 K in La$_2$O$_2$Fe$_2$OSe$_2$. 30 In contrast, there are almost linear decreases in the principal component $V_{zz}$ of EFG near 125 K and 150 K in La$_2$O$_2$Fe$_2$OSe$_2$ and La$_2$O$_2$Fe$_2$OS$_2$, respectively. The changes in the $^{57}$Fe Mössbauer EFG suggest that the behavior is orbitally-dependent on Fe 3$d$-states, because the anisotropy caused by different occupation of the $d$ orbitals should affect the $V_{zz}$. That such an effect is not discerned in the NMR static parameter is not surprising because the La nucleus is coupled by hyperfine interaction, which is not necessarily sensitive to the on-site Fe magnetism.

Figure 5 shows the temperature dependence of La$_2$O$_2$Fe$_2$OS$_2$ $^{139}(1/T_1)$ data collected at 5.0 T. The data is qualitatively similar to La$_2$O$_2$Fe$_2$OSe$_2$ both in the paramagnetic and antiferromagnetic states. 30 Upon lowering $T$ below approximately 150 K ($T_S^x$) the La$_2$O$_2$Fe$_2$OS$_2$ $^{139}(1/T_1)$ data starts to increase reaching a divergence around 108 K. Similarly, the $^{139}(1/T_1)$ signal is enhanced below approximately 125 K ($T_{Se}^x$) and approaches a divergence near 90 K. The divergences are associated with the critical slowing down of the Fe spin fluctuations. The enhancements of $^{139}/(TT_1)$ below ($T_S^x$) and ($T_{Se}^x$) occur in the same temperature ranges where Mössbauer spectra exhibit a decrease of the principal component $V_{zz}$ of the EFG for La$_2$O$_2$Fe$_2$O(S, Se)$_2$. The enhancements are related to short range correlations above $T_N$ which influence the spin-lattice relaxation rate. We emphasize that the thermal behavior of the $c$-lattice constant of La$_2$O$_2$Fe$_2$O(S, Se)$_2$ have
been reported to exhibit anomalous contractions near $(T^*_S)$ and $(T^*_Se)$. The $c$-lattice reductions manifest as a deviation from the Einstein temperature model. The lattice change is concomitant with the decrease in $V_{zz}$ which suggests that EFG is influenced by the change in the crystal field associated with octahedral height.

Generally, the NMR spin-lattice relaxation rate is proportional to the imaginary part of the dynamic susceptibility at the Larmor frequency $(1/T_1 T \sim \chi''(q,\omega_0))$, where $q$ is the wave vector and $\omega_0$ is the Larmor frequency. Therefore NMR $^{139}(1/T_1)$ is very sensitive to fluctuations related to the orbital and spin degrees of freedom at the Fe site. The NMR $^{139}(1/T_1)$ data in Figure 5 provide a clear indication of a continuous slowing down of the Fe spin or orbital degrees of freedom far from the AFM ordered phase. Similar observations were also reported for LaFeAsO where, just below the structural transition, $^{139}(T_1)$ starts to increase before it diverges at the antiferromagnetic ordering temperature. Both La$_2$O$_2$Fe$_2$O(S, Se)$_2$ fit well into this framework albeit they have not been observed to undergo structural phase transitions.

For $T < T_N$, the spin-lattice relaxation rate $^{139}(1/T_1)$ is strongly reduced over a very short temperature interval. Below 87 K, for La$_2$O$_2$Fe$_2$O$_2$S$_2$ $^{139}(1/T_1)$ can be fitted by activation gap-like behavior $\sim T^2 \exp(-\Delta/T)$, with a gap $\Delta = 70$ K, where as for the Se variant it is $\Delta = 55$ K. This observation is consistent with opening up of a spin gap as reported in a neutron scattering study. For $T < 30$ K, we find a smooth crossover from gap-like behavior to a gapless regime, where $1/T_1 \simeq T^3$. Therefore, two distinct regimes are observed where $1/T_1 \simeq T^3$ for $T \ll \Delta$, while $1/T_1 \simeq T^2 \exp(-\Delta/T)$ for $T > \Delta$. 

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The NMR $1/T_1$ behavior for $30 \text{K} < T$ follow an unusual $T^3$ power-law form which suggests the activation of an additional spin fluctuation channel. We now address the origin of this behavior within the framework of an $S = 1$ Heisenberg model with appreciable geometric frustration, an additional bi-quadratic term, and single-ion anisotropy as is appropriate for Fe-based systems.

**Theory** Motivated by earlier local density approximation + dynamical mean-field theory (LDA+DMFT) calculations in which we estimated an $S = 1$ on each Fe site, we begin with the spin $S = 1$ bilinear-bi-quadratic model of the square lattice. This model has been widely employed in context of magnetism and nematicity in Fe-based SCs.\textsuperscript{39–41} The Hamiltonian is

$$H = \sum_{i,j} \left[ J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j + K (\mathbf{S}_i \cdot \mathbf{S}_j)^2 - D (S_i^z)^2 \right],$$  

where $\mathbf{S}_i$ is a spin-1 operator on site $i$. $J_{ij} = J_{1a}$, $J_{ij} = J_{1b}$ such that $J_{1a}$ is ferromagnetic (FM) and $J_{1b}$ is AFM. $J_{ij} = J_2$ for $[ij]$ along the square-diagonal, and $K$ is the coefficient of the bi-quadratic interaction for $S = 1$ along with $D$ being the single-ion anisotropy term that fixes the orientation of the spin. It is known that this model admits various ordered phases, depending upon the relative values of the $J_{ij}$ and $K$ for a given $D$:\textsuperscript{42} a $\mathbf{q} = (\pi, 0)$ collinear antiferromagnetic (CAF) phase, a $\mathbf{q} = (\pi/2, \pi)$ AFM* phase, a $\mathbf{q} = (\pi, \pi)$ Néel AFM phase, and a $\mathbf{q} = (\pi, 0)$ anti-ferro-quadrupolar (AFQ) phase. Additionally, the strong geometrical frustration (supported by small value of the ordered moment relative to density functional theory estimates) inherent in the model, along with sizable biquadratic and single-ion terms can yield a non-collinear AF phase as observed in our systems. The FM and AFM couplings, along with sizable $D$, also favor $D = 2$ Ising-like spin fluctuations (as extracted from the critical exponent for $M(T)$). With this in mind, we have estimated the temperature dependence of the NMR relaxation rate, $1/T_1 \simeq \lim_{\omega \to 0} \sum_{\mathbf{q}} \text{Im} \frac{\chi_{\mathbf{q} \omega}}{\omega}$ by comput-
ing the local spin correlation function, $\chi_{ii}(\omega) = \int_0^\infty dt e^{i\omega t} \langle T [S^+_i(t)S^-_i(0)] \rangle$ using quantum-Monte Carlo (QMC) methods applied to the $H$ [Eq. (3)] above. \textsuperscript{43} The $1/T_1$ QMC results (green squares) are shown in Figure 6.

Within the temperature range $30 < T < T_N(\sim 100$ K), the experimental data for NMR $1/T_1$ fits $AT^2\exp(-\Delta/T)$ to a very good approximation, with $\Delta$ estimated to be approximately 100 K. Moreover, at low temperatures $T < 30$ K, we also find that the $1/T_1 \simeq T^3$, indicating gapless spin excitations in the spin fluctuation spectrum. This is consistent with earlier findings on the Se compound. \textsuperscript{30} Our theoretical findings are consistent with strong suppression of magnetic fluctuations below $T_N$, a crossover to a gapped regime of spin fluctuations with a crossover scale $O(50$ K), consistent with available inelastic neutron scattering data, and at low $T < 30$ K, another spin relaxation channel opens up, indicating low-energy spin excitations below the gap.

These findings can be understood in by considering that a field-theoretic analysis for a collinear AF yields $1/T_1 \simeq T^3$ for $T >> \Delta$, but $1/T_1 \simeq T^2\Delta\exp(-\Delta/T)$ for $T << \Delta$. For an AFQ ordered state the same analysis yields $T^{-1}_1 \simeq T^3 e^{-\Delta/T}$ for $T << \Delta$, but $T^{-1}_1 \simeq T^7$ for $T >> \Delta$. Both of these are inconsistent with our experimental findings and, at first glance, would rule out both collinear AFM and AFQ phases at low $T$ in the oxychalcogenides. However, our results are not in conflict with the previously proposed non-collinear AFM phase in the iron oxychalcogenides. \textsuperscript{15,30} Three-magnon processes can be ruled out, since no $T^5$ - dependence is observed in our experimental data (nor in the calculations) at any studied temperature. \textsuperscript{44} In considering all of the presented data and our theoretical results, the clear scenario emerges in which
the La$_2$O$_2$Fe$_2$O(S, Se)$_2$ Mott insulators exhibit a non-collinear magnetic structure that might support the presence of AFQ phases. Furthermore, these materials each contain gapless excitations in the spin fluctuation spectrum. An important caveat for the low-temperature region $T << \Delta$ is the uncertainty regarding the deviation of NMR $1/T_1$ experimental data. We mention that we are not able to rule out the possibility of impurities or defects causing $1/T_1$ signal deviation from gap-like behavior at low temperatures. The presence of slight impurities was suggested to be the source of the low-temperature upturn in magnetic susceptibility data of La$_2$O$_2$Fe$_2$O(S, Se)$_2$. 27

Were it possible to electron-dope the iron oxychalcogenides by chemical substitution or strain in order to modify their Mott insulating electronic structure, one would expect the small density of metallic carriers near the Mott transition to strongly scatter off these low-lying spin correlations. This would involve carriers propagating by emitting and absorbing two magnons in the usual view of a doped Mott antiferromagnet. The doped carriers would propagate by scattering off dynamical spin fluctuations that are encoded in the one-spin-flip fluctuation spectrum. We note that these processes might give rise to anomalous metallic features but they remain un-investigated. In addition, the orbital selectivity that arises from the multi-orbital character of the iron oxychalcogenides will also generally lead to incoherent metallicity. How the interplay between these distinct electronic mechanisms might conspire to generate unconventional ordered state(s) in Mott systems remains a fascinating open issue. The current work should encourage efforts along these lines.

In summary, we have performed a combined theoretical and experimental study of the iron oxychalcogenides La$_2$O$_2$Fe$_2$O(S, Se)$_2$. A 2-k non-collinear magnetic structure was confirmed in
both systems. Striking signatures of local nematic fluctuations in the magnetic responses of these materials as the AFM phase is approached from high temperatures. Nematic fluctuations are observed to occur by virtue of short lengthscale rotational symmetry breaking. The nematic fluctuation data is consistent across a range of different experimental techniques. Quadrupolar behavior is responsible for the critical slowing down of spin fluctuations was observed in the $^{139}(T_1)$ NMR data. These emergent quadrupolar fluctuations arise from sizable geometric frustration, which is itself a consequence of strong orbital selectivity of the compounds. $^{45}$ Our theoretical modeling shows that such orbital selectivity underpins numerous behaviors in the correlation-induced Mott-insulating states of the oxychalcogenides. Along with earlier DMFT work, the present results also establish the relevance of a strong correlation-based approach for iron oxychalcogenides. Finally, we note that nematicity has been invoked $^{46}$ in both experimental and theoretical contexts to describe order competing with high-$T_c$ superconductivity in the cuprates and the iron pnictides. Therefore, the current work expands a current topic in iron-based high-temperature superconductivity while demonstrating the underlying relevance of structural nematicity to larger set of quantum materials.
Figure 1
Figure 2
Figure 3
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Figure 5
$\Delta = 98$ K

Figure 6
Figure 7
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Contributions BF, ML, LC, RS and HHK wrote the paper. BF, ZY and RF performed the neutron experiments. BF, ZY, RF, YH and IS analyzed neutron data. RS, SK, FB, VG and HHK conducted NMR and Mössbauer experiments. BFrans advised BK, AA and RB on performing and interpreting PDF refinement. ML and SA conceived and performed the theory work. MF grew the samples. BF conceived of the overall project. All authors edited and assessed the manuscript.

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Figure 1  The intensity of an antiferromagnetic peak (103) in La$_2$O$_2$Fe$_2$O(S, Se)$_2$ as a function of temperature. At room temperature La$_2$O$_2$Fe$_2$O(S, Se)$_2$ are in the paramagnetic phase. The development of magnetic ordering is observed for both materials as the temperature decreases. The Néel temperatures $T_N$, indicated by the arrows, for $M = S$ and Se are 107.2(6) ± 0.06 K and 90.1(9) ± 0.16 K, respectively. The inset shows the crystal structure of La$_2$O$_2$Fe$_2$OSe$_2$.

Figure 2  Temperature dependence of orthorhombicity for short-fitting range (1.5-21.5) Å and long-fitting range (30.0-50.0) Å for a) $M = S$ and b) $M = $ Se. In both of these figure orthorhombicity is along y-axis and temperature is in x-axis. A solid circle symbol indicates the short-fitting range (1.5-21.5) Å and a solid triangle symbol indicates the long-fitting range.

Figure 3  a) Low temperature $^{57}$Fe Mössbauer spectra of La$_2$O$_2$Fe$_2$OSe$_2$ and La$_2$O$_2$Fe$_2$OS$_2$ fitted with the full static Hamiltonian as described in the text. A single sextet indicates full long-range magnetic order rapidly arising below $T_N$. b) Magnetic hyperfine field $B_{hyp}$ or the magnetic order parameter determined from $^{57}$Fe Mössbauer measurements. The lines denote the fit of sub-lattice magnetization by using the equation $M(t) \propto B_{hyp}(T) \propto (1 - T/T_N)^{\beta_{crit}}$. c) The temperature dependence of the principal axis component $V_{zz}$ of the EFG decreases above $T_N$ for La$_2$O$_2$Fe$_2$OSe$_2$ and La$_2$O$_2$Fe$_2$OS$_2$. Dotted lines are the guides to the eye.
Figure 4 The $^{139}$La field sweep NMR spectra on La$_2$O$_2$Fe$_2$OS$_2$ taken at 30 MHz. In general, for a nuclear spin ($I = 7/2$), in a lower symmetry system such as orthorhombic and tetragonal, for the presence of finite EFG at the La site, there are seven peaks due to the selective transitions between the levels (m m-1, where m = 7/2, 5/2,... and -5/2). For $T > T_N$ typical non-magnetic $I = 7/2$ powder spectra are observed. Arrows indicate the corresponding satellite transitions. Black solid lines are simulated spectra. Green and red solid lines at 100 K, 50 K and 20 K represent calculated sub spectra due to magnetically nonequivalent sites. The vertical line indicates the field at which $^{139}(1/T_1)$ were measured.

Figure 5 Temperature dependence of the $^{139}$La spin-lattice relaxation rate of La$_2$O$_2$Fe$_2$OS$_2$ (filled circle) and La$_2$O$_2$Fe$_2$OSe$_2$ (filled square) $^{30}$. Lines indicate the activation gap model $\sim T^2 \exp(-\Delta/T)$. Dotted vertical lines denote the AFM ordering temperature. Inset shows the $1/T_1 T$ versus temperature, while arrow marks the temperature regime where principal component $V_{zz}$ of the EFG start to decrease.

Figure 6 The nuclear magnetic resonance (NMR) spin relaxation rate ($1/T_1$) as a function of temperature $T$ for La$_2$O$_2$Fe$_2$OSe$_2$ studied in this work. A large-lattice size Quantum Monte Carlo technique was used by employing the Algorithms and Libraries for Physics Simulations (ALPS) to estimate ($1/T_1$). By doing so, we computed the local transverse spin-spin correlation function for a $S = 1$ Heisenberg model with geometrical frustration, biquadratic exchange, and single-ion anisotropy as relevant for the Fe-based systems.
The QMC results (green squares) were fitted with $T^2 \exp(-\Delta/T)$ (magenta dashed line) and $T^3$ (blue line) in the high-T and low-T regions, respectively. The main panel indicates that a $1/T_1 \simeq T^2 \exp(-\Delta/T)$ form for $T > 40$ K, with an estimated spin gap of 98 K, smoothly evolves into $1/T_1 \simeq T^3$ for $T < 30$ K. The low-$T$ power law behavior emerges due to an additional two-magnon relaxation channel opening up at low $T$. Good accord between theory and experimental NMR data can be seen (see inset).

**Figure 7** Schematic illustrations of magnetic ordering. For spins (red arrows) located at Fe atom positions (blue circles), the arrangements are given for (a) the paramagnetic (PM) high-temperature phase. The low-temperature antiferromagnetic phase (b) is the non-collinear 2 - k arrangement.
| property | La$_2$O$_2$Fe$_2$OSe$_2$ | La$_2$O$_2$Fe$_2$OS$_2$ |
|----------|------------------------|------------------------|
| $T_N$ (K) | 90.3(2)                | 106.7(3)               |
| $B_{hyp}(0)$ (T) | 20.32(2)           | 21.43(1)               |
| $\beta_{crit}$ | 0.143(1)               | 0.140(1)               |
| $\Delta_0$ (mm/s) | 1.069(1)             | 1.044(1)               |
| $\Theta_D$ (K) | 300(7)                | 298(4)                |

Table 1: Properties of the measured oxychalcogenide compounds obtained by Mössbauer spectroscopy. The AFM transition temperature $T_N$, low-temperature $^{57}$Fe saturation hyperfine field $B_{sat}$, and the critical exponent $\beta_{crit}$ are found to vary only in small ranges. $\Theta_D$ is the Debye temperature.