Strongly gapped spin-wave excitation in the insulating phase of NaOsO₃

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NaOsO₃ hosts a rare manifestation of a metal-insulator transition driven by magnetic correlations, placing the magnetic exchange interactions in a central role. We use resonant inelastic x-ray scattering to directly probe these magnetic exchange interactions. A dispersive and strongly gapped (58 meV) excitation is observed, indicating appreciable spin-orbit coupling in this 5d³ system. The excitation is well described within a minimal model Hamiltonian with strong anisotropy and Heisenberg exchange (J₁ = J₂ = 13.9 meV). The observed behavior places NaOsO₃ on the boundary between localized and itinerant magnetism.

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The underlying mechanisms driving a metal-insulator transition (MIT) are an enduring focus of condensed matter physics [1]. Recent interest has extended investigations to 5d-based transition metal oxides that host new paradigms of competing interactions, creating novel MITs [2]. For example, spin-orbit coupling (SOC) in 5d³ iridates dramatically influences the electronic ground state to allow even the presence of the reduced on-site Coulomb interaction (U) to drive a relativistic Mott MIT [3]. Conversely, in 5d³ osmium-based compounds, MITs occur that cannot be reconciled with the reduced U in 5d systems, even when the large SOC is taken into account. These compounds therefore fall outside the Mott approximation. Of particular interest in this regard are the osmates NaOsO₃ and Cd₂Os₂O₇, which undergo a MIT that approximates. Of particular interest in this regard are the osmates NaOsO₃ and Cd₂Os₂O₇, which undergo a MIT that

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approximates. Outside of a Mott MIT, several other mechanism exist to describe a MIT, including an Anderson MIT driven by disorder [8] and a Peirels MIT driven by a structural distortion in a low-dimensional system [9]. Slater considered a route in which magnetism could drive a MIT, with the central observation being that within a magnetically ordered system, the potential created by an up spin is different from that created by a down spin [10]. By this definition, three-dimensional magnetic ordering with oppositely aligned spins is a route to a MIT, and implicitly includes q = 0 antiferromagnetic structures. NaOsO₃ exhibits several features consistent with Slater’s general scenario [6,7,11–15]. The MIT occurs concomitant with the onset of antiferromagnetic ordering (TN = TMIT = 410 K) that can create a periodic potential. Furthermore, in NaOsO₃, the MIT is continuous and no structural symmetry change occurs. However, several important questions have so far remained experimentally inaccessible, hindering the development of further insight into the mechanism of this unusual MIT and prohibiting a quantitative description beyond the mean-field approach invoked by Slater for a magnetic MIT.

Principally, since the MIT is driven by magnetic ordering, the magnetic exchange interactions (J) are central to the creation of the MIT in NaOsO₃. Therefore, measuring the dominant exchange pathways and interactions is required to build robust models of the MIT. Additionally, the energy scales of the interactions that are required to describe the electronic behavior, such as crystal field splitting, Hund’s coupling, and SOC, have not been accessed. In particular, the nominal 5d³ electronic occupancy suggests zero orbital angular momentum in the L-S coupling limit, and previous experimental descriptions did not require the inclusion of strong SOC. However, mounting experimental evidence in other 5d³ systems indicates SOC is required to describe the magnetism [16–18]. To answer these questions, we performed resonant inelastic x-ray scattering (RIXS) to directly probe the 5d electrons of the Os ion in NaOsO₃.

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RIXS measurements at the Os $L_3$ edge (10.87 keV) were performed on the ID20 spectrometer at the ESRF, Grenoble. A single crystal of NaOsO$_3$, space group $Pnma$, was oriented with the (H0L) plane normal to the sample surface. The scattering plane and incident photon polarization were both horizontal. The incident beam was focused to a size of $20 \times 10 \mu$m$^2$ ($H \times V$) at the sample position. Measurements were performed with low- ($\Delta E = 275$ meV) and high-resolution ($\Delta E = 46$ meV) setups by switching between a Si(311) channel-cut secondary monochromator and a (664) four-bounce, respectively. Both setups used a Si(664) diced spherical analyzer at 2 m radius from the detector. Preliminary measurements were performed at the Advanced Photon Source (APS) on the MERIX instrument using an identical setup to that described in Ref. [18].

We begin by considering the results using the low-resolution setup ($\Delta E = 275$ meV) before focusing on our main finding of a spin-wave excitation with high-resolution measurements ($\Delta E = 46$ meV). A RIXS map of the orbital excitations, that involve intra or inter $d$-$d$ transitions, in NaOsO$_3$ obtained by measuring the inelastic energy loss spectrum at several fixed incident energies through the Os $L_3$ resonant edge, is shown in Fig. 1(a) at 300 K. Three broad inelastic features are observed, labeled $E_B$, $E_C$, and $E_D$. On a qualitative level the excitations appear analogous to RIXS measurements on 5$d^3$-based Cd$_2$Os$_2$O$_7$ [18] and exhibit notable differences from measurements of 5$d^3$-based iridates [19]. The incident energy dependence of features $E_B$ and $E_C$ in the RIXS map is consistent with a nominal splitting of the 5$d$ manifold into states with $t_{2g}$ and $e_g$ symmetry, with the scattering following dipole selection rules ($\Delta S = 1$). $E_B$ involves intra-$t_{2g}$ transitions whereas $E_C$ is due to $t_{2g}$-$e_g$ excitations. We assign excitation $E_D$ to ligand-metal charge transfer (LMCT).

The inelastic excitation $E_B$ is centered at 1.27(2) eV and corresponds to intra-$t_{2g}$ transitions. As shown in the inset of Fig. 1(b), even when measured with the high-resolution RIXS setup, $E_B$ remained as a broad single-peak excitation, significantly broader than the instrumental resolution of 46 meV. This makes any splitting of the $t_{2g}$ manifold from SOC or a structural distortion unresolvable in NaOsO$_3$. This contrasts to the case of the iridium-based relativistic Mott insulators, where SOC strongly splits the $t_{2g}$ electronic ground state into $J_{\text{eff}} = \frac{1}{2}$ and $J_{\text{eff}} = \frac{3}{2}$ bands and results in a measured splitting of $E_B$ [19,20]. Since $E_B$ consists of intra-$t_{2g}$ transitions, we follow the reasoning outlined in Ref. [18] to experimentally define the Hund’s coupling energy ($J_H$) value in NaOsO$_3$ as $J_H = 1.27$ eV/$3.75$ = 0.34 eV based on the center of $E_B$. The 3.75 factor derives from the consideration of $E_B$ as consisting of eight $\frac{1}{2}$ states, five of which have relative energy $J_H$ and three having $5J_H$, yielding an average of 3.75$J_H$. We note that since any underlying splitting of $E_B$ is unresolved, this is an approximate measurement of $J_H$, and, however, is useful for comparing with similar 5$d^3$ systems such as Cd$_2$Os$_2$O$_7$.

Excitation $E_C$ is located at 3.6(1) eV and is a direct measure of the crystal field splitting. NaOsO$_3$ and Cd$_2$Os$_2$O$_7$ have a similar local OsO$_6$ octahedral environment, however, the $t_{2g}$-$e_g$ splitting is 0.9 eV lower in NaOsO$_3$ [18]. This indicates that considerations beyond the local 5$d$ octahedral environment are crucial, which is in line with expectations of the importance of the spatially extended 5$d$ orbitals.

The magnetic order and consequently the magnetic exchange interactions are central to the creation of the MIT in NaOsO$_3$. Therefore, measuring and modeling the dominant exchange pathways is required to yield a complete picture of the MIT. The crystal size of NaOsO$_3$ is currently beyond the limits of inelastic neutron scattering, however, RIXS offers a route to quantitatively probe the collective magnetic excitations in 5$d$ systems [19]. The low-energy scattering for NaOsO$_3$ using high-resolution Os RIXS is shown in Fig. 2. Measurements along high-symmetry directions shows a single resolution limited inelastic excitation ($E_A$). The excitation, along with the elastic line, were fit with a Gaussian peak shape to follow the dispersion. Figure 3(a) reveals $E_A$ is strongly dispersive, indicative of a spin-wave excitation. The bandwidth is ~80 meV with maxima at the zone boundary along the $Z$ and $X$ directions and a reduced energy at $Y$. A large spin gap of 58 meV is observed at the zone center ($\Gamma$) that signifies the presence of strong anisotropy in NaOsO$_3$.

To provide a quantitative description of the magnetic excitations, we invoke a minimal model Hamiltonian with
using Eq. (1), a minimal model Hamiltonian with the exchange interactions:

$$\mathcal{H} = J_1 \sum_{nn} \mathbf{S}_i \cdot \mathbf{S}_j + J_2 \sum_{nnn} \mathbf{S}_i \cdot \mathbf{S}_j + \Delta.$$  

A SOC induced anisotropic term is included to account for the gap. For the case of symmetric exchange anisotropy, \(\Delta = \Gamma \sum_{nn,nnn} \mathbf{S}_i^z \mathbf{S}_j^z\), and for single-ion anisotropy, \(\Delta = D \sum (\mathbf{S}_i^2)\).

The RIXS data for NaOsO₃ were modeled within a linear spin-wave (LSW) approximation [21] and the results checked against numerical calculations using SpinW [22]. The nominal spin-only value of \(S = \frac{3}{2}\) was used throughout. Fitting the experimental dispersion to Eq. (1) produces close agreement to both the dispersion and corresponding intensity (Fig. 3), indicating the minimal model Hamiltonian captures the essential features and consequently provides an experimental assignment of the dominant magnetic exchange interactions and their energy. The fitting yields \(J_1 = J_2 = 13.9(5)\) meV and \(\Gamma = 1.4(1)\) meV. Allowing \(J_1\) and \(J_2\) to vary independently did not improve the fit, reflecting the pseudocubic nature of the structure. Adding a third-nearest-neighbor term \(J_3\), or \(J_1 = J_3\), to recover the cubic limit, alters the energy at \(Z\) with respect to \(X\), however, within resolution the measured energy at \(X = Z\). Therefore, we conclude that exchange interactions \(J_1\) and \(J_2\) have a magnitude appreciably less than \(J_1\) or \(J_2\) and limit the Hamiltonian to Eq. (1). Consequently, NaOsO₃ is well described by dominant nearest-neighbor magnetic interactions in three dimensions forming a robust \(G\)-type antiferromagnetic order in this pervoskite. Replacing exchange anisotropy with a spin-only term yields the same \(J_1\) and \(J_2\) values and \(D = 4\) meV.

The mechanism for the spin gap is effectively disconnected from the magnetic exchange interactions in Eq. (1). However, the presence of such a large spin gap is significant in terms of the underlying physics in NaOsO₃. In particular, all possible mechanisms to open a spin gap, single-ion anisotropy (SIA), the Dzyaloshinskii-Moriya (DM) interaction, and exchange anisotropy, require SOC. We briefly consider how the anisotropies influence NaOsO₃. SIA arises due to a noncubic environment and in NaOsO₃ the OsO₆ octahedra are weakly trigonally and tetragonally compressed. However, such a large gap due to SIA does not appear consistent with the reduced spin gaps of 15–20 meV observed in other 5d³ osmates with similar distortions [17]. In NaOsO₃ a nonzero local DM vector exists since the oxygen mediating the superexchange interaction between the two Os sites does not sit at an inversion center. Experimentally, there is evidence of weak ferromagnetism [6], however, the spin canting producing this was undetectable with neutron diffraction [7]. This would suggest that the DM interaction, while present, is weak to first order. Exchange anisotropy, a pseudodipolar effect, results as a consequence of second-order SOC effects between neighboring Os ions, and hence is generally weaker than the DM interaction and SIA. However, in 5d³ systems the extended orbitals result in enhanced collective behavior within the lattice compared to, for example, that which occurs in 3d transition metal oxides. Indeed, this was shown in NaOsO₃ with the observation of a record large spin-phonon shift at the MIT due to the extended Os orbitals [15].
The measurement of a large spin gap indicates that SOC is required in a complete description of NaOsO$_3$. The magnitude of SOC scales with the atomic number, therefore, in 5$d^3$ osmates it is comparable to 5$d^5$ iridates. However, when describing the properties of NaOsO$_3$, the role of SOC has only been required to be included as a perturbation [6,7,11–15]. Conversely, for 5$d^5$ iridates, SOC is necessary to describe both magnetism and the insulating state. This has created an apparent dichotomy between the effect of SOC, particularly when considering the divergent electronic ground states indicated from the RIXS spectra between 5$d^3$ and 5$d^5$. A first approximation is that the altered electronic occupancy causes an increased Hund’s coupling in 5$d^3$ systems, favoring a quenching of orbital momentum. However, the broad scattering observed for $E_B$ in Fig. 1 indicates an underlying splitting of the $t_{2g}$ orbitals, either through structural distortions or SOC or a combination of both. One consequence of an increased role of SOC in NaOsO$_3$ was considered theoretically to reduce the effective $U$ and place the system closer to the itinerant limit description of magnetism [23]. However, the agreement of the minimal model Hamiltonian, based on localized spins, to the RIXS spectra would suggest that the behavior of NaOsO$_3$ appreciably departs from being fully itinerant. Indeed, this would be expected even within the mean-field Hartree-Fock description used by Slater to describe a magnetic MIT since, at the transition, local moments are necessarily formed [24]. While in a pure Slater description this would be treated by self-consistent single electron theory, at least to a good approximation the behavior can be described by a Heisenberg model and places NaOsO$_3$ on the boundary between local-moment and itinerant magnetism.

The strongly dispersing excitation in NaOsO$_3$ contrasts with the dispersionless excitation of Cd$_2$Os$_2$O$_7$ observed previously with RIXS [18]. The use of an Ising-like description to describe Cd$_2$Os$_2$O$_7$ and a Heisenberg model to capture the behavior for NaOsO$_3$ indicates an underlying splitting of the ground state. This has created an apparent dichotomy between the essential features. Nearest- and next-nearest-neighbor Heisenberg exchange interactions of $J_1 = J_2 = 13.9$ meV were found to describe the dispersion, indicating strong three-dimensional magnetic interactions. The presence of significant anisotropy in the system was observed with the measurement of a large spin gap of 58 meV. This is a direct consequence of intrinsically strong SOC in this 5$d$ compound, however, the role of SOC on the ground state departs from 5$d^5$ iridates. In terms of the mechanism of the MIT, the results support a three-dimensional magnetically driven route, consistent with the general scenario proposed by Slater. The Hamiltonian presented here provides the magnetic interaction energy scales and their pathways required to describe the MIT. Moreover, the presence of SOC and the influence this has within a system with extended orbitals and strong hybridization has to be considered as playing an important role when considering the collective interactions and the MIT.

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The 5$d$ orbital and collective magnetic excitations in NaOsO$_3$ have been probed with RIXS. Well-defined spin waves were observed and described within linear spin-wave theory using a minimal model Hamiltonian that captured the essential features. Nearest- and next-nearest-neighbor Heisenberg exchange interactions of $J_1 = J_2 = 13.9$ meV were found to describe the dispersion, indicating strong three-dimensional magnetic interactions. The presence of significant anisotropy in the system was observed with the measurement of a large spin gap of 58 meV. This is a direct consequence of intrinsically strong SOC in this 5$d$ compound, however, the role of SOC on the ground state departs from 5$d^5$ iridates. In terms of the mechanism of the MIT, the results support a three-dimensional magnetically driven route, consistent with the general scenario proposed by Slater. The Hamiltonian presented here provides the magnetic interaction energy scales and their pathways required to describe the MIT. Moreover, the presence of SOC and the influence this has within a system with extended orbitals and strong hybridization has to be considered as playing an important role when considering the collective interactions and the MIT.

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Diagonalizing the Hamiltonian in Eq. (1) within a LSW approximation gives the spin-wave energy
\[
\omega = S \sqrt{D - X - Y},
\]
where
\[
D = 36 \Delta_e^2 + 48 \Delta_D + 24 \Delta J_2 + 12 J_1^2 + 2 J_2^2 + 16 J_1 J_2,
\]
\[
X = 4 J_1^2 \cos 2\pi h + 2 J_2^2 \cos 2\pi h + 4 J_2^2 \cos 2\pi l,
\]
and
\[
Y = 2 J_1^2 \cos [2\pi (h - l)] + 2 J_2^2 \cos [2\pi (h + l)] + 16 J_1 J_2 \cos \pi h \cos \pi l.
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In a similar fashion, the intensity can be expressed by
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