Evidence of Slater-type mechanism as origin of insulating state in Sr$_2$IrO$_4$

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For iridates with large spatially extended 5d orbitals, it may be anticipated that distant neighbor interactions would play a crucial role in their ground state properties. From this perspective, we investigate the magnetic structure of Sr$_2$IrO$_4$ by including interactions beyond first and second neighbors, via supercell modeling. Adopting to first-principles scalar relativistic methods, it is found that the minimum in total energy among various magnetic structures correspond to a $\uparrow\downarrow\downarrow$ type antiferromagnetic ordering of the Ir ions for which the magnitude of the electronic gap, that of the Ir local moments and, the facsimile of the two-peaked structure in the optical conductivity spectra of Sr$_2$IrO$_4$ were found to be in good agreement with the experiments. The results unequivocally evidence that the origin of the electronic gap in Sr$_2$IrO$_4$ is due to an unconventional antiferromagnetic ordering of Ir ions, thereby classifying the system as a Slater magnet, rather than the spin-orbit coupling driven $J_{\text{eff}} = \frac{3}{2}$ Mott insulator.

Sr$_2$IrO$_4$ is an insulator at all temperatures [1-9] and undergoes an antiferromagnetic transition below 240 K [6,10,12,14]. Assuming that the strength of spin-orbit coupling (SOC) is comparable with that of crystal field interactions, Coulomb correlation and Hund’s coupling, a new quantum paradigm has been proposed [1]. In this model, the crystal field split Ir 5$d$ states are further split by SOC into a four-fold degenerate $J_{\text{eff}} = \frac{3}{2}$ quartet and a two-fold $J_{\text{eff}} = \frac{1}{2}$ doublet states. With Ir in its +4 formal valence state, the low energy $J_{\text{eff}} = \frac{3}{2}$ states are fully filled with two electrons each, leaving the $J_{\text{eff}} = \frac{1}{2}$ doublet singly occupied. Furthermore, since the bandwidth of the $J_{\text{eff}} = \frac{1}{2}$ doublets are significantly narrow, Coulomb correlation splits the doublets into an upper and lower Hubbard band, thereby rendering the system an insulating ground state [1,15]. The model successfully accounts for both electron localization and insulating state on equal footing and derive consistent support from resistivity measurements, photo-emission spectroscopy, optical conductivity, absorption spectroscopy and model Hamiltonian based calculations [1,2,10,11].

However, few observations had also hinted to itinerant characteristics in Sr$_2$IrO$_4$ [7,16,19]. Scanning tunneling microscopy finds that the electronic gap emerges in the close vicinity of the magnetic transition [17], whereas optical conductivity measurement deduce a strong reduction in the optical gap with increasing temperature [11]. Also, a metal-insulator transition is observed in the ultrafast dynamics of photo-excited carriers which indicate to a underlying Slater-type mechanism in Sr$_2$IrO$_4$ [24]. Magnetic susceptibility and isothermal magnetization measurements find the effective paramagnetic moment and the saturation moment as 0.5 $\mu_B$ and 0.14 $\mu_B$, respectively which is far less than the expected spin-only value of 1$\mu_B$ for localized spin of $S = \frac{1}{2}$ [16,17,20]. The reduction in the magnitude of the Ir moment indicates to strong hybridization between Ir 5$d$ and O 2$p$ orbitals. In addition, Sr$_2$IrO$_4$ displays weak ferromagnetism which is attributed to spin canting [2,12,15,20]. It has been addressed in terms of nontrivial exchange interactions accounting for the strong coupling of orbital magnetization to the lattice [21,22]. The weak ferromagnetism although vanishes with increasing pressure, system retains the insulating ground state [26]. The effect is attributed to an increased tetragonal crystal field thereby substantiating the interplay of structural distortions and SOC, which affects the balance between the isotropic magnetic coupling and the Dzyaloshinskii- Moriya anisotropic interaction. It is also highlighted that distorted in-plane bond angle in Sr$_2$IrO$_4$ can be tuned through magnetic field [27] and epitaxial strain [28]. Besides, the in-plane anisotropic nature and inter-layer coupling are also seen to play an important role in the low field magnetic nature of Sr$_2$IrO$_4$ [24]. Therefore, in the view of these experimental findings, it is clear that there is a subtle interplay of SOC, crystal field, Coulomb correlations, magnetic exchange interactions, and the local chemistry of the underlying IrO$_6$ motifs in Sr$_2$IrO$_4$.

Significantly, what appears less emphasized in Sr$_2$IrO$_4$ is the effect of distant near neighbor interactions on the magnetism and its electronic structure properties. The magnetic structure as refined from neutron diffraction associates a non-collinear Neel type ordering of the Ir spins in the crystallographic $a - b$ plane, with the spin orientation rigidly tracking the staggered rotation of the IrO$_6$ along the $c$-axis [20]. However, the Ir 5$d$ orbitals being much extended in space and that they strongly hybridize with the near neighboring O 2$p$ orbitals, it may be anticipated that the magnetic interactions in the $a - b$ plane would significantly extend over distant neighbors than those along the $c$-axis. The antiferromagnetic ordering temperature as high as 240 K, can be well thought of one such consequence of distant neighbor magnetic exchange interactions.

Here, we present a comprehensive investigation of the electronic and magnetic structure of Sr$_2$IrO$_4$, by means of first principles density functional theory. To include interactions beyond first nearest neighbors, we model few antiferromagnetic structures on an underlying super-cell of dimension $2a \times 2a \times c$, where $a$ and $c$ are the tetragonal lattice parameters of Sr$_2$IrO$_4$. Consistent with the
previous works, we find that the local approximations to the exchange correlation potential, such as local density approximation (LDA) \cite{21} and generalized gradient approximation (GGA-PBE) \cite{22} fail to capture the antiferromagnetic insulating ground state of Sr$_2$IrO$_4$. However, using the modified Becke- Johnson potential (mBJ) \cite{31}, we find that the equilibrium corresponds to an unconventional $\uparrow\uparrow\downarrow\downarrow$ type antiferromagnetic ordering of the Ir ions in the $a$-$b$ plane. The predictive powers of the calculation are substantiated by the consistency it yields with the experiments. The magnitude of the insulating gap and that of the Ir local moment and, the double peak structure in the materials optical absorption spectra are found to be in good agreement with the experiments. These findings suggest that the underlying mechanism that drives Sr$_2$IrO$_4$ as an antiferromagnetic insulator is Slater-type, which is in stark contrast with the widely discussed SOC driven $J_{eff} = \frac{1}{4}$ Mott model.

Calculations are based on the full potential linearized augmented plane-wave (FP-LAPW) method as implemented in the Wien2k code \cite{30}. The lattice parameters were adopted to the experimental values, with $a = 5.48$ Å, and $c = 25.83$ Å \cite{12}, and the position coordinates of the Sr and O ions were fully relaxed. The ground state properties were obtained using well-converged basis sets using the Wien2k parameters; $R_{MT}$-$K_{\text{max}} = 7$, $G_{\text{max}}=24$ a.u.$^{-1}$ and $l_{\text{max}} = 7$ \cite{30}. Additional local orbitals were also used to account for the semi-core Ir 5$p$ states. The exchange correlation potential to the crystal Hamiltonian was considered in mBJ formalism \cite{31}.

Few collinear magnetic structures with different initial Ir spin alignment were considered in the study. These are shown in Table I which are described in terms of the Ir spin alignment in the first, second, third and fourth near neighbors designated as $d_{NN}^{(i)}$: $i = 1$, 4. Neglecting non-collinearity, AF1 then represents the experimentally determined structure and FM represents ferromagnetic ordering. In LDA spin polarized calculations, all structures converged to a paramagnetic metallic solution. However, in GGA the AF3 spin configuration converged to an antiferromagnetic metallic solution with an Ir moment of 0.2 $\mu_B$, while all other structures converged to a nonmagnetic solution. The AF3 structure was $-1.4$ meV/t.u lower in energy in comparison to its non-magnetic counterpart. A schematic representation of the AF3 structure is shown in Fig.1. The AF3 unit cell consists of 16 formula units, with an underlying $Pnma$ symmetry of crystal lattice dimensions $a = 5.48$Å, $b = 25.83$Å and $c = 10.96$Å.

![Figure 1: The schematic representation of the AF3 structure showing the antiferromagnetic ordering of Ir moments in the $a-b$ plane of Sr$_2$IrO$_4$.](image)

It is well known that the electron density representation of the Coulomb potential in both LDA and GGA leads to an unphysical self interaction. As a result, these approximations tend to reduce the self-repulsion of electrons thereby stabilizing artificially delocalized electronic states \cite{33,34}. Among various correction schemes that have been proposed \cite{35,37}, we adopt to the mBJ formalism. With $t$ and $\rho$ representing the kinetic energy density and electron density, respectively, a screening term of the form $\sqrt{\frac{\rho}{\rho}}$ is introduced in the mBJ exchange potential, the contribution of which is calculated by $\frac{\nabla \rho}{\rho}$ \cite{31}.

As a result, regions with low density are associated with higher positive potential thereby increasing the energy of these states \cite{31,38}. The mBJ formalism is applicable for Sr$_2$IrO$_4$ and also for other iridates \cite{39,40} since the states in the vicinity of Fermi energy are predominantly anti-bonding in character. It should be noted that the anti-bonding orbitals have less electron density, thus the choice of mBJ exchange potential for iridates is well justified.

In Fig.2 we show the mBJ generated total, atom resolved and Ir 5$d$ resolved density of states (DOS) of Sr$_2$IrO$_4$ with AF3 spin configuration in the Ir sub-lattice. The spectra reveal Sr$_2$IrO$_4$ to be an insulator with an electronic gap of 0.47 eV, consistent with the experimental value of 0.54 eV \cite{41}. Here, we note that the magnitude of the insulating gap in Sr$_2$IrO$_4$ have been reported

| Space group | $d_{NN}^{(1)}$ (Å) | $d_{NN}^{(2)}$ (Å) | $d_{NN}^{(3)}$ (Å) | $d_{NN}^{(4)}$ (Å) |
|-------------|------------------|------------------|------------------|------------------|
| AF1         | I-4_2d           | 4(↓)             | 4(↑)             | 4(↑)             | 4(↑)             |
| AF2         | P4_1_2_1_2       | 2(↑)             | 4(↓)             | 4(↑)             | 4(↑)             |
| AF3         | Pnnn             | 2(↑)             | 2(↑)             | 4(↑)             | 4(↑)             |
| FM          | I4_1/acd         | 4(↑)             | 8(↑)             | 8(↑)             | 4(↑)             |
On the other hand, for apical O1 ions the hybridize with the Ir $d_x$ and $d_y$ states. Thus, the crystal chemistry suggests a mixing of the Ir $t_{2g}$ and $e_g$ states in Sr$_2$IrO$_4$ primarily due to the rotation of the IrO$_6$ octahedra. The rotation of the octahedra mixes the otherwise orthogonal Ir $d_{xy}$ and $d_{xy-y^2}$ orbitals and consequently push the $x_y$ states below the Fermi energy. The $d_{xy}$ and $d_{xy-y^2}$ hybridization also results in a pseudo-gap like feature which is manifested $\simeq -0.6$ eV below $E_F$. Further, the valence band energy integration of the orbitals states showed that the $d_{xy} + d_{xy-y^2}$ orbitals are occupied with $\simeq 2$ electrons per Ir ion, while the electron occupation in the $d_{xz} + d_{yz} + d_{z^2}$ sums to 3 electrons per Ir ion, with $d_{xz}$ and $d_{yz}$ occupancy being 1.15 and 1.29 electrons, respectively. Also, the integrated DOS of the $d_{xy} / d_{yz}$ orbitals above $E_F$ was determined to be $\simeq 1$ e$^{-}$ per Ir ion. Thus, we find that the scalar relativistic calculations with exchange potential as described in the mBJ formalism predicts Sr$_2$IrO$_4$ to be an antiferromagnetic insulator.

The magnitude of the local magnetic moment at the Ir sites in the AF3 structure was calculated as $\simeq 0.57 \mu_B$. The value is significantly higher than those determined from experiment, the latter which deduce the value as 0.2 $\mu_B$ [20]. The overestimation of the Ir local moment might be due to the PBE-GGA functional in the calculation. However, the Ir magnetic moment is found to be much smaller than spin only value of 1 $\mu_B$ anticipated for a $S = \frac{3}{2}$ system. This may be partly attributed to the strong hybridization of the Ir $5d - O$ 2p orbitals. The effects of hybridization are also manifested on the induced moments at the O sites. We note that the AF3 structure has a $\uparrow \uparrow \downarrow \downarrow$ type antiferromagnetic ordering of Ir ions in the $a-b$ plane of the tetragonal unit cell. For those in-plane O ions which bridge the Ir ions in the $a-b$ plane with same polarization, i.e., $\uparrow \uparrow$ or $\downarrow \downarrow$, the induced magnetic moment is calculated as $\simeq 0.12 \mu_B$ while for oppositely polarized Ir ions the moment is $\simeq 0.06 \mu_B$. The induced moments on the apical O ions were found to be 0.03 $\mu_B$.

One of the well accepted methods to validate the electronic structure is by its optical response. In experiments, a double-peak structure with maxima around 0.5 eV and 1 eV have been observed, with the former peak being relatively sharper than the latter [13 42 47]. These peaks are associated with two Ir $d-d$ transitions, which in terms of the $J_{eff}$ model are due to the transitions from occupied $J_{eff} = \frac{3}{2}$ and $\frac{1}{2}$ states to the unoccupied $J_{eff} = \frac{1}{2}$ states. The spectra has been well reproduced by the LDA+U+SOC calculations, thereby suggesting the importance and interplay of SOC and Coulomb correlations in Sr$_2$IrO$_4$ [1].

In Fig. 8, we show the optical conductivity calculated for Sr$_2$IrO$_4$ with the underlying AF3 structure. Consistent with the experimental spectra, we obtain two characteristic peaks, centered on the energy scale at $\simeq 0.82$ eV and 1.32 eV, respectively. We note that the position of the peaks are shifted to higher energies in comparison with experiments [42 46] which is primarily due to the larger band gap estimated (0.57 eV) in our calcu-
The energy difference between the two peaks, which is found to be 0.5 eV, but also decreases the magnitude of the Ir local moment to 0.47 \( \mu_B \).

So to check whether the insulating gap is originally due to the unconventional antiferromagnetic ordering of Ir spins and not pertained to the choice of the exchange potential described in mBJ formalism, we also performed GGA+\( U_{\text{eff}} \) calculations, with \( U_{\text{eff}} = 2 \) eV. Quite interestingly, the overall features in the density of states (Fig. 4) were found very much similar to that obtained with the mBJ-GGA. However, the calculated band gap and Ir local moment was 0.11 eV and 0.41 \( \mu_B \), respectively. In general, our results following a comprehensive set of calculations concisely and convincingly show that SOC is lesser significant interaction in rendering \( \text{Sr}_2\text{IrO}_4 \) an antiferromagnetic insulating ground state.

In summary, using the first-principles density functional theory based scalar relativistic calculations with exchange potential described in mBJ formalism, we find that \( \text{Sr}_2\text{IrO}_4 \) is an unconventional Slater-type antiferromagnetic system. The calculated magnitude of the electronic gap, that of the Ir local moment and, the two peak structure in the materials optical conductivity are found to be very consistent with the experimental results. Contrary to the present understanding that \( \text{Sr}_2\text{IrO}_4 \) is a SOC driven \( J_{\text{eff}} \) Mott insulator, our calculations show that the role of of SOC in \( \text{Sr}_2\text{IrO}_4 \) is of lesser significance in rendering the system its insulating ground state. Our
results, which are based on density functional theory, are expected to stimulate further experimental works with an objective to unravel the magnetic structure of the system and the nature of Ir magnetism, thereby providing robust understanding of iridates, in general.

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