Electronic Structure of Hyperkagome Na$_4$Ir$_3$O$_8$

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We investigate the electronic structure of the frustrated magnet Na$_4$Ir$_3$O$_8$ using density functional theory. Due to strong spin-orbit coupling, the hyperkagome lattice is characterized by a half-filled complex of $d$ states, making it a cubic iridium analogue of the high temperature superconducting cuprates. The implications of our results for this unique material are discussed.

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I. INTRODUCTION

Recently, several materials have been identified as possible candidates for a long sought state of matter - the quantum spin liquid. One of these candidates, Na$_4$Ir$_3$O$_8$, is characterized by a three dimensional cubic space group, where the iridium sites form a hyperkagome lattice of corner sharing triangles. This remarkable material is an insulator with a large Curie-Weiss temperature (650 K) and a large effective moment (1.96 $\mu_B$), yet does not exhibit any sign of magnetic order down to the lowest measured temperature.

There have been a number of theoretical studies of this iridate which attempt to address the nature of the spin liquid ground state. These studies invariably assume that the material is described by an isotropic Heisenberg model, since anisotropy acts to stabilize magnetic order. Isotropy would be a surprise given the strong spin-orbit coupling for the iridium ions. But in an exhaustive study, Chen and Balents formulated under what conditions such an effective model might be realized. To address various issues raised in that paper, we calculated the electronic structure of this material within the local density approximation, then performed a tight binding fit in order to estimate the various exchange integrals which enter the spin Hamiltonian for this frustrated magnet. We find that the spin Hamiltonian should be strongly anisotropic, but offer two possible scenarios where isotropy might be restored.

II. CALCULATIONAL DETAILS

Although Na$_4$Ir$_3$O$_8$ has a cubic space group, the unit cell is quite complicated, comprising four formula units (60 atoms). Moreover, the lattice breaks inversion symmetry. The space group, P4$_1$32, is also found in the non-centrosymmetric superconductors Li$_2$Pd$_3$B and Li$_2$Pt$_3$B. The material is formed from distorted IrO$_6$ octahedra, each comprised of two different oxygen sites - four of type 2 (O2), two of type 1 (O1). The latter should not be thought of as ‘apical’ oxygens in the cuprate sense, since they are not related by inversion through the iridium site. Rather, each octahedron is described by a C$_2$ axis along a (110) direction. There are twelve of these axes, one associated with each of the twelve iridium ions in the unit cell. Each oxygen ion is also at the center of a distorted octahedron, with O1 octahedra of the form OIr$_3$Na$_3$, and O2 octahedra of the form OIr$_2$Na$_4$. Each oxygen ion is also surrounded by a very distorted array of twelve other oxygen ions along approximate (110) directions. Finally, each iridium ion is surrounded by four other iridium ions, also along approximate (110) directions. These form the corner sharing triangles that characterize the hyperkagome lattice. A list of the first few coordination shells around an iridium ion in the Na$_4$Ir$_3$O$_8$ structure out to a distance of 0.49a. Listed is the type of ion, their number, (approximate) direction, and distance (in units of the lattice constant, a).

| type | number | direction | distance |
|------|--------|-----------|----------|
| O2   | 2      | 100       | 0.2273   |
| O2   | 2      | 100       | 0.2280   |
| O1   | 2      | 100       | 0.2333   |
| Ir   | 4      | 110       | 0.3464   |
| Na3  | 2      | 110       | 0.3501   |
| Na3  | 2      | 110       | 0.3587   |
| Na1  | 2      | 110       | 0.3612   |
| Na3  | 1      | 110       | 0.3627   |
| Na2  | 1      | 110       | 0.3683   |
| O2   | 2      | 111       | 0.4065   |
| O2   | 2      | 111       | 0.4225   |
| O1   | 2      | 111       | 0.4375   |
| O2   | 2      | 111       | 0.4838   |

When considering an electronic structure calculation for this material, the first issue is that there are three different types of sodium ions, two of which are partially occupied with a stochiometry of 75%. Therefore, to form a simple unit cell, some approximation has to be made for these other two sodium sites. We choose to fully occupy the 12d sites (sodium type 3) and replace the 4a sites (sodium type 2) by empty spheres. The resulting lattice has 64 sites in the unit cell - 12 Ir, 8 O1, 24 O2, 4 Na1, 4 empty (i.e., Na2), and 12 Na3.

The calculations in this paper were performed using...
the local density approximation (LDA) within a linear muffin tin orbital scheme.Overlap (combined) corrections were incorporated, but the Coulomb potential at each site was treated in a spherical approximation. The exchange-correlation potential used was that of Hedin and Lundqvist. Noting that the cubic lattice constant is 8.985 Å, a muffin tin radius of 1.238 Å was used on the iridium sites, and 1.425 Å was used on all other sites. These radii were chosen based on the various near neighbor separations. s, p basis functions were used on all sites (including the empty ones) except for the iridium sites, where d basis functions were also included. For the scalar relativistic calculation (all relativistic effects but spin-orbit), this resulted in a secular matrix of dimension 316, which was double this (632) for the full relativistic (Dirac equation) calculation. The calculations were converged using 56 \( k \) points in the irreducible wedge of the Brillouin zone. We should note that the Brillouin zone for this material is simple cubic. Though inversion symmetry is broken, one can restrict the irreducible wedge to 1/48th of the zone. The eigenvalues at a general \( k \) point are doubly (Kramers) degenerate unless spin-orbit is incorporated, where this degeneracy is broken. After convergence, 165 \( k \) points were generated in the irreducible wedge of the Brillouin zone. The eigenvalues were then fit using a Fourier spline series with 560 lattice periodic functions. A linear tetrahedron method was used to evaluate the density of states, with the zone broken down into 48 \( \cdot \) 85 tetrahedra.

III. RESULTS

We first present results from the scalar relativistic calculation, with the density of states shown in Fig. 1. The O1 states form a narrow complex of bands ranging from -8.2 to -6.7 eV, followed by the wider O2 complex ranging from -6.7 to -3 eV (there is only a narrow gap between these two complexes). There is a gap of 1.9 eV to the \( \Gamma \) complex of iridium d bands ranging from -1.1 eV to 0.4 eV. This is followed by a crystal field gap of 1.9 eV to an \( e_g \) complex ranging from 2.3 eV to 3.6 eV. For energies above this, the states are primarily from the sodium sites.

The main complex of interest is the \( t_{2g} \) one (Fig. 2). It is split into an array of 28 bands (each Kramers degenerate) separated by a gap of 0.2 eV to an upper array of 8 bands. This basic splitting of 28 and 8 arises from the \( t_{pd} \) hopping integral, as identified from tight binding fits, and is related to the four-fold degeneracy of the eigenvalues at the \( \Gamma \) point of the zone. There is a crystal field splitting of the \( t_{2g} \) states which was identified by projecting onto the three crystal field components due to the \( C_2 \) axis of the distorted IrO\(_6\) octahedra (scalar relativistic calculation).

spin-orbit coupling has a profound impact on these re-
results, as can be seen in the remaining figures. The $t_{2g}$ states now split (Figs. 4 and 5) into a lower complex of 48 bands and an upper complex of 24 bands (the number of bands are now doubled because of the coupling of inversion breaking with spin-orbit), with the $e_g$ complex composed of another 48 bands. The upper $t_{2g}$ complex is half-filled, with the Ir $d$ states mostly of $j = 5/2$ character, with weak admixture of $j = 3/2$ character (Fig. 4). As explained by Chen and Balents,\textsuperscript{5} and found as well for the electronic structure of Sr$_2$IrO$_4$,\textsuperscript{11} this behavior is due to crystal field admixture of the $j = 5/2$ and $j = 3/2$ states, which acts to form a mixed lower ($t_{2g}$) quartet of states (i.e., four per iridium site), a mixed ($e_g$) upper quartet, with an unmixed ($t_{2g}$, $j = 5/2$) doublet in between that is half-filled. This doublet is predicted to have 83% $j = 5/2, m_j = \pm 3/2$ and 17% $j = 5/2, m_j = \pm 5/2$ character, which is in good agreement with the results we find for the lowest 8 bands of this complex (Fig. 6). The upper 16 bands have a slightly reduced $m_j = \pm 3/2$ weight due to weak admixture with $m_j = \pm 1/2$ states as well as $j = 3/2$ states, which is a consequence of the low iridium site symmetry. Again, the density of states at the Fermi energy is not large - per Ir per spin it is 1.51 states/eV. The Fermi surface is composed of three electron like sheets around $\Gamma$, and two hole-like sheets around the $R$ point (Fig. 7). The bands are doubly degenerate on the zone face due to the non-symmorphic nature of the space group.

We now wish to connect these results to the insulating behavior of the actual material. In the case of Sr$_2$IrO$_4$, inclusion of the Coulomb repulsion is not sufficient to open an energy gap unless spin-orbit is included. In essence, spin-orbit produces a half-filled doublet which can then ‘Mott-Hubbardize’ and form an insulator, similar to what occurs in the cuprates.\textsuperscript{12} Only a small $U$ is needed to cause this.\textsuperscript{11} Similar considerations should apply to Na$_4$Ir$_3$O$_8$. From the centroids of the two quartets and the doublet, we have inferred the parameters $\Delta_{CF}$ (splitting of $t_{2g}$ and $e_g$) and $\lambda$ (coefficient of $l \cdot s$ for the spin-orbit coupling) of 3.43 eV and 0.58 eV, respectively.
IV. TIGHT BINDING ANALYSIS

To investigate these issues further, we performed tight binding fits to the electronic structure, restricting to Ir 5d and O 2p orbitals. This involved generating Slater-Koster parameters, and then performing a least squares fit to the band eigenvalues using Powell’s method. Because of the distorted nature of the lattice, there are a large number of tight binding parameters, even if one restricts to near neighbors. This is because there is not a unique distance for several of the atom combinations (Ir-O2, O1-O1, O1-O2, and O2-O2). To compensate for this, we assumed that the tight binding parameters for each atom combination vary as the fourth power of the distance. This assumption works well for the O-O hopping in IrO$_2$ (note from Table I that the two Ir-O2 distances are almost identical). This reduced us to four $t_{pd}$ parameters ($\sigma$ and $\pi$ for Ir-O1 and Ir-O2), three $t_{dd}$ parameters ($\sigma$, $\pi$, and $\delta$ for Ir-Ir), six $t_{pp}$ parameters ($\sigma$ and $\pi$ for O1-O1, O1-O2, and O2-O2), four on-site energies ($2p$ energies for O1 and O2, and $t_{2g}$ and $e_g$ energies), and the spin-orbit coupling of the Ir $d$ ($\lambda$), for a total of 18 parameters. We have explored putting in the residual crystal field splittings due to the low Ir site symmetry (Fig. 3), but this did not lead to improved fits.

We first converged the fit for the scalar relativistic calculation, using 42 eigenvalues (top and bottom of the O1 complex, O2 complex, $e_g$ complex, and all 36 $t_{2g}$ bands) at the four symmetry points ($\Gamma$, $X$, $M$, and $R$). As input, we used IrO$_2$ hopping parameters scaled to the sodium iridate distances, as well as on-site energies estimated from averages extracted from the $l$ decomposed density of states. The fit (not shown) yielded a band structure in good agreement with Fig. 2. We then used these fit parameters as input to fitting the full relativistic calculation, with the same set of eigenvalues (now numbering 78) at each of the 4 $k$ points. The fit gives a good description of the bands and Fermi surface, as can be seen in Figs. 8 and 9. These fit values are listed in Table II. One can see that the $t_{pd}$ and $t_{dd}$ parameters have comparable magnitude, and that the O1 and O2 integrals are quite different. Note that the difference of the $t_{2g}$-$e_g$ energies is only 2.60 eV. The difference from the centroid splitting of 3.43 eV quoted earlier is due to the contribution of the hoppings to the splitting.

V. EXCHANGE INTEGRALS

As we are in the strong spin-orbit coupling limit in the sense of Chen and Balents, we can use the expressions in their paper to estimate the various exchange integrals (Table III). We caution that these values are very sensitive to the tight binding parameters, as well as the values of the Coulomb $U$. The exchange Hamiltonian is of the form:

$$H_{ex} = (J_d + J_s)\mathbf{S}_n \cdot \mathbf{S}_m + D^{nm} \cdot (\mathbf{S}_n \times \mathbf{S}_m) + \mathbf{S}_n \cdot \Gamma^{nm} \cdot \mathbf{S}_m$$

(1)

where $J_d$ is the direct exchange between iridium ions, $J_s$ the isotropic component of the superexchange mediated by the oxygen ions, $D$ the Dzyaloshinski-Moriya interaction.

|     | $\sigma$ | $\pi$ | $\delta$ |
|-----|---------|-------|----------|
| Ir-O1 | -2.5579 | 0.3186 |
| Ir-O2 | -2.1070 | 1.1817 |
| Ir-Ir | -0.6372 | 0.0719 | 0.1545 |
| O1-O1 | 0.6156  | 0.0354 |
| O2-O2 | 0.5463  | -0.2121 |
| O1-O2 | -1.1327 | 0.0663 |
The assumed value of $U$ in the $(0,1,-1)$ direction relative to Ir site $n$ is given in Eq. 1. Quoted are values where Ir site is along an $(0,1,-1)$ direction relative to Ir site $n$. $D$ are the Dzyaloshinski-Moriya, and $\Gamma$ the anisotropic superexchange terms (in the second row for $\Gamma$, the $jk$ refer to the parenthesis, $xy$, etc.). In addition, the direct exchange is $J_d = 20.1$, and the isotropic superexchange term is $J_s = 12.9$. The last row, $J_{ii}$, is the total exchange for the diagonal components ($J_d + J_s + \Gamma_{ii}$).

The assumed value of $U$ is 0.5 eV (with $U_p$ set to zero).

| $i (jk)$ | $x (xy)$ | $y (xz)$ | $z (yz)$ |
|----------|----------|----------|----------|
| $D_{ii}$ | 47.3     | 1.3      | -4.7     |
| $\Gamma_{ii}$ | 36.1     | -36.8    | -36.2    |
| $\Gamma_{jk}$ | 2.1      | -8.3     | -0.2     |
| $J_{ii}$ | 69.2     | -3.7     | -3.1     |

due to the the difference between O1 and O2, with the magnitude little affected by the distortion.

There are only two ways we know to reduce these large values of the superexchange. First, in the limit of large $U_p$ (Coulomb repulsion on the oxygen sites), they would vanish. Second, because the sodium sites about the oxygens are only partially occupied in the real material, it is possible that the resulting randomness would dephase

FIG. 10: (Color online) Superexchange pathway between two Ir ions as marked by the arrows. The Ir ions are the large (red) spheres and the oxygen ions the small ones. The lower left (green) pathway is via an O2 (blue) ion, the upper right (purple) pathway via an O1 (brown) ion.

the various superexchange pathways. Unless one of these mechanisms is effective, the total exchange is predicted to be anisotropic. This would cast doubts on theories for Na$_4$Ir$_4$O$_8$ based on an isotropic Heisenberg model. Regardless, we believe that the tight binding parameters we provide here will be useful for future modeling of this fascinating material. In particular, given the resemblance of its electronic structure to that of cuprates, one might wonder whether a doped version of this material would be a high temperature superconductor.

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