Electronic and magnetic structure of neutral radical FBBO

Stephen M. Winter, Aaron Mailman, and Richard T. Oakley*  
Department of Chemistry, University of Waterloo, Waterloo, Ontario N2L 3G1 Canada

Komalavalli Thirunavukkuarasu, Stephen Hill,† David E. Graf, and Stanley W. Tozer
National High Magnetic Field Laboratory and Department of Physics, Florida State University, Tallahassee, Florida 32310, USA

John S. Tse
Department of Physics and Engineering Physics, University of Saskatchewan, Saskatoon, Saskatchewan S7N 5E2 Canada

Masaki Mito and Hiroshi Yamaguchi  
Faculty of Engineering, Kyushu Institute of Technology, Kitakyushu 804-8550, Japan

(Received 7 February 2014; revised manuscript received 11 May 2014; published 5 June 2014)

The fluorinated oxobenzo-bridged bisdithiazolyl radical FBBO was recently observed to undergo a pressure-induced Mott insulator-to-metal transition, suggesting a novel organic system for studying Mott physics. This report describes the electronic structure of this material in relation to the observed magnetic response at low pressures. Through analysis of antiferromagnetic resonance measurements, we identify a layered antiferromagnetic ordered phase below \( T_X = 13 \) K at ambient pressure, which requires strong ferromagnetic coupling between nearest neighbours. The origin of such coupling is elucidated from both molecular and solid-state electronic-structure calculations, which suggest a minimal two-orbital model with strong Hund’s-rule coupling. This layered phase is partially frustrated by a second-nearest-neighbor antiferromagnetic coupling, which drives a magnetic phase transition at elevated pressure. On the basis of the two-orbital model, we suggest the pressure-induced Mott transition to proceed via rehybridization of the frontier molecular orbitals, resulting in a half-filled insulator to quarter-filled metal crossover.

DOI: 10.1103/PhysRevB.89.214403 PACS number(s): 76.50.+g, 75.30.Et, 71.30.+h

I. INTRODUCTION

The exploration and understanding of strongly correlated electron systems represents a challenging but fruitful subject, driven by the synthesis of new materials, and the development of new experimental and theoretical avenues of investigation. In this vein, multicomponent organic materials such as radical ion salts [1,2] \((\text{ET})_{2}X\) and \((\text{TMNTTF})_{2}X\) and alkali-metal-doped fullerences [3,4] \(X_{n}\text{C}_{60}\) have played a prominent role, offering unique opportunities for the study of superconductivity [5], Mott criticality [6–8], and frustrated magnetism [9,10]. In all of these systems, unpaired electrons are generated by charge transfer between separate electron donor and acceptor components. A potential alternative approach is to use neutral radicals, which require neither doping nor charge transfer to generate unpaired electrons [11,12]. In such systems, the individual organic molecules possess an odd electron count, guaranteeing that the highest-occupied orbital is half filled. To date, all radicals have displayed Mott insulating behavior at ambient pressure, and work has largely focused on their magnetic properties [13–18], with various ordered states observed from ferromagnetism [19,20] to canted antiferromagnetism [21,22]. The insulating behavior is not surprising, because the small size typical of radical molecules ensures higher values of effective on-site Coulomb repulsion \( U \) than is seen in \( \text{C}_{60} \) molecules or ET dimers, impeding attempts to break away from the Mott insulating state. As a result of this technical challenge, radical materials capable of accessing strongly correlated regimes are only beginning to appear, and much of the possible physics of these materials remains relatively unexplored [23].

This report focuses on the fluorinated oxobenzo-bridged bisdithiazolyl radical (FBBO, Fig. 1), which was recently shown to undergo a crossover, at room temperature, from Mott insulator to a metallic state \((d\sigma/dT < 0)\) under pressures of \( \sim 3 \) GPa [24]. This material belongs to a new class of radicals (denoted XBBO) built around a similar molecular framework, but with varying exocyclic groups \((X = F, H, Me, Ph, Cl)\). These materials display a variety of structural, magnetic, and electronic properties [24–28]. While all are Mott insulators at ambient pressure, they have generically displayed lower charge gaps and orders of magnitude higher conductivity than previous generations of thiazyl radicals [12,29]. A metallic state has also recently been achieved in HBBO, at

FIG. 1. (Color online) Molecular structure of XBBO family of radicals. This report focuses on the fluorine-substituted derivative, FBBO, shown with x-ray geometry.
FIG. 2. (Color online) (a) Unit cell of FBBO viewed parallel to \( a \). Molecules at \( x = \frac{1}{2} \) are shaded to indicate depth. (b) Unit cell of FBBO viewed parallel to \( c \). In both cases, \( n \)-th-nearest-neighbor contacts are labeled (1)–(4), with corresponding magnetic interactions shown in Fig. 3. In the \( Cmc\bar{2}1 \) space group, radicals related by \( C \)-centering, i.e., through contact (1), form the basis for extended two-dimensional layers in the \( ab \) plane.

\(~6\) GPa \([30]\), while further investigation of the remaining radicals is ongoing. This work motivates the need for further understanding of the electronic structure of these materials, which we derive in this report through study of the magnetic phases of FBBO.

In order to discuss the interactions between molecular pairs, we consider up to fourth-nearest-neighbor contacts, with \( n \)-th nearest neighbours labeled by \( (n) = (1) – (4) \). As shown in Fig. 2, FBBO crystallizes in the high-symmetry orthorhombic space group \( Cmc\bar{2}1 \), with first (1) and second (2) nearest-neighbor pairs providing the basis for \( \pi \)-stacked layers in the \( ab \) plane. In both cases molecules are related by translation, either by \( C \)-centering or by translation along \( b \). These layers are bound together by electrostatic interactions through close S–N, S–O, and S–F contacts with third (3) and fourth (4) nearest neighbours in adjacent layers, which are related by \( 2_1 \) axes. Associated with each contact is a magnetic interaction \( J_1 – J_4 \) (Fig. 3). Within each two-dimensional \( ab \)-layer of radicals, the two unique intra-plane magnetic interactions \( J_1 \) and \( J_2 \) form an anisotropic triangular network. The inter-plane interactions \( J_3 \) and \( J_4 \), together with \( J_2 \), also form a triangular network when viewed parallel to the \( a \)-axis.

Because the strength of each of these magnetic interactions is closely related to the underlying electronic structure of FBBO, careful investigation of the magnetically ordered phases of FBBO provides insight into the Mott transition in these materials. In this report, we suggest that the minimal model for the XBBO family derives from a two-band Hubbard Hamiltonian, in which Hund’s-rule coupling plays a prominent role. In the first section, through combined analysis of susceptibility and antiferromagnetic resonance (AFMR) data, we identify the ambient-pressure ordered magnetic structure of FBBO. The second part of the paper concerns the effects of pressure, which induces a magnetic phase transition in the insulating region near 0.2 GPa. Finally, in the third part, we describe the electronic structure of FBBO through solid-state density functional theory (DFT) calculations and evaluation of the low-energy magnetic Hamiltonian of the insulating state. The insights gained through this analysis allow for understanding the Mott transition in terms of a two-band description.

II. EXPERIMENT

A. Ambient-pressure electron magnetic resonance

At ambient pressure, FBBO orders as a spin-canted antiferromagnet, displaying a bifurcation in the field-cooled (FC) and zero-field-cooled (ZFC) magnetic susceptibility at \( T_N = 13 \text{ K} \) (Fig. 4)\([24]\). Below this temperature, a spontaneous moment of \((1.8 \times 10^{-3}) \mu_B \) per molecule is observed. Fits of the Curie–Weiss law to the high-temperature data (50–300 K) give an antiferromagnetic Weiss constant of \( \Theta = -18.3 \text{ K} \). In

FIG. 4. (Color online) (a) Field-cooled (FC) and zero-field-cooled (ZFC) susceptibility showing a bifurcation at \( T_N = 13 \text{ K} \) as a result of spin canting. (b) The spontaneous magnetization due to the small canted moment. Data taken from Ref. [24].
order to investigate the nature of this ordered state, we have performed a series of powder EPR measurements aimed at observing the antiferromagnetic resonance (AFMR) modes; that is, the spin-wave excitations. This technique has been used extensively for the investigation of organic materials, including radical ion salts [31], doped fullerenes [32], and neutral radicals [33]. Typically, in order to observe such AFMR modes in organics one requires relatively large sample sizes (∼10 mg); because large high-quality single crystals were unavailable, EPR measurements were performed on powder samples of FBBO [34]. Measurements were carried out at the NHMFL, in the frequency range from 27 to 112 GHz using a homodyne quasi-optical spectrometer [35]. The temperature dependence of the resonances were recorded at 112 GHz in the range from 250 to 3 K.

Above $T_N$, a sharp paramagnetic resonance signal is observed at the resonance field $H_{res} \sim \hbar/\omega (g \mu_B)$, which is slightly split at high fields due to a small anisotropy in the local molecular $g$ tensor ($g_{xx} = 1.999$, $g_{yy} = g_{zz} = 2.078$) [Fig. 5(a)] [36]. Below $T_N$, the paramagnetic signal gives way to coherent AFMR excitations, which results in substantial broadening, and the development of a prominent shoulder on the low-field side of the resonance. Characteristic of antiferromagnetic resonance, the total linewidth of the powder resonance was observed to decrease with increasing field. In single-crystal measurements, the magnitude of the resonant field $H_{res}$ strongly depends on the orientation of the external magnetic field due to the effects of magnetocrystalline anisotropy [37]. In powder measurements, orientation averaging therefore results in a broad signal, the width of which is determined by the magnitude of the anisotropy, parameterized by the anisotropy field $H_A$. In the present case, the powder lineshape is consistent with predominantly easy-plane anisotropy [38] for which, above the spin-flop field, excitation of AFMR modes occurs between the limits:

$$H_{res} = \left\{ \frac{\hbar \omega}{g \mu_B} \left( 1 + \frac{H_A}{2H_e} \right)^{-1/2}, \quad H_{ext} \perp \hat{n}, \right. 
\left. \sqrt{(\frac{\hbar \omega}{g \mu_B})^2 - 2H_e H_A}, \quad H_{ext} \parallel \hat{n}, \right.$$  \hfill (1)

where $\hat{n}$ is the normal of the easy plane, and the exchange field $H_e$ can be estimated as half of the field required for magnetic saturation, $H_e \sim 25$ T. In the present case $H_e \gg H_A$ so that the high-field edge of the powder AFMR signal, corresponding to orientation of the field within the easy plane, appears at $H_{res} \sim \hbar \omega / (g \mu_B)$, the same position as the paramagnetic resonance. This condition is characteristic of easy-plane anisotropy and is related to the presence of gapless modes at zero-field guaranteed by continuous rotational symmetry about $\hat{n}$. The shoulder appearing on the low-field side of the resonance is due to orientation of the external field away from the easy plane; inspection of Eq. (1) reveals this shoulder should narrow at high frequency, as observed. In order to emphasize this discussion, we show in Figs. 5(b) and 5(c) the theoretical powder lineshapes obtained by numerical simulation for 56 and 112 GHz assuming a two-sublattice antiferromagnet. Individual powder grains were assumed independent, and with no preferred orientation, so the combined response was simply the summation over all field orientations. For single-crystal easy-plane antiferromagnets, one often finds very broad, weak signals when $H_{ext}$ is oriented along the hard axis [39]; for this reason, we assumed the AFMR intensity of the grains varied as $\sin^2 \theta$, where $\theta$ is the angle between $H_{ext}$ and $\hat{n}$, but an otherwise uniform linewidth of 300 Oe and Lorentzian lineshape. The close resemblance of theoretical and experimental curves confirms predominantly easy-plane anisotropy for FBBO, although small anisotropy within the easy plane cannot be ruled out. The best-fitting theoretical curves were obtained by using a spin-flop field of $H_{s} = \sqrt{2}H_e H_A = 1.0$ T. This provides an estimate of the anisotropy field to be $H_A \sim 200$ Oe, on the order of the observed coercive field $H_c = 290$ Oe [24].

**B. Ambient-pressure magnetic structure**

The observed anisotropy and spin canting arise from a combination of long-range magnetic dipolar and spin-orbit anisotropic exchange interactions, both of which are expected to be much weaker than the isotropic interactions $J_1-\Delta_4$. In order to identify the magnetic structure of FBBO, it is therefore appropriate to first consider which ordered states may emerge from purely isotropic exchange and, second, how such states are modified by perturbatively weak anisotropic terms. For the FBBO lattice, away from perfect frustration (e.g., $J_2 = J_3 = J_4$), the isotropic exchange is expected to provide a simple two-sublattice antiferromagnetic ground state [40]. In this sense, a substantial clue in regard to the magnetic structure is that FBBO exhibits a net canted moment, which for two-sublattice antiferromagnets may only be induced by weak anisotropic interactions provided the ordered structure retains all the translational symmetry of the underlying lattice [41]. If translational symmetry is broken at the level of isotropic interactions, the magnetic state will be perturbatively unstable only to “hidden” canting, where spins may not be collinear, but all moments cancel, producing no net magnetization. The observation of spontaneous magnetization in FBBO therefore...

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**FIG. 5.** (Color online) Variable-temperature and -frequency powder EPR response. (a) Temperature dependence of the EPR lineshape; a significant broadening is observed below $T_N$ signaling the appearance of AFMR modes. (b), (c) Comparison of experimental and theoretical lineshapes for $\omega = 56$ and 112 GHz, respectively. Theoretical curves were obtained assuming easy-plane anisotropy (see text).
requires all spins within the \(ab\) planes, which are related by translation (\(C\)-centering), to belong to the same sublattice, i.e., to be ferromagnetically (FM) aligned. The only structure consistent with canting therefore has ordering vector \((0,0,2\pi)\), with adjacent \(ab\) plane layers antiferromagnetically (AFM) coupled as shown in Fig. 3. However, the observation of such ferromagnetism in close proximity to a metallic state is unexpected, as single-band Hubbard models are characterized by strong antiferromagnetic interactions in such a case. The mechanism for ferromagnetic coupling for FBBO is described in Sec. IV within the context of a multi-orbital model incorporating Hund’s-rule coupling.

Full analysis of the magnetic anisotropy for FBBO requires modification of the conventional microscopic theory of spin-orbit exchange to include such multiple orbitals and Hund’s-rule terms \[42\]. A full description of the terms arising in this case is beyond the scope of the current report and will be presented elsewhere; here we briefly summarize the relevant results for FBBO. The anisotropic exchange may be described by the Hamiltonian

\[
\mathcal{H}_{\text{ans}} = \sum_{i,j} \mathbf{D}_{ij} \cdot \mathbf{S}_i \times \mathbf{S}_j + \mathbf{S}_i \cdot \mathbf{\Gamma}_{ij} \cdot \mathbf{S}_j, \tag{2}
\]

where \(\mathbf{D}_{ij}\) is the Dzyaloshinskii–Moriya vector, and \(\mathbf{\Gamma}_{ij} \propto \mathbf{D}_{ij} \otimes \mathbf{D}_{ij}\) describes the pseudodipolar component of the anisotropic exchange. The former term is related to the orientation of unquenched orbital angular momentum in the magnetic moments at sites \(i\) and \(j\). For FBBO, as a consequence of the \(p_x\) character of the magnetic \(\pi\) orbitals (see Sec. III), the \(x\) component of \(\mathbf{D}_{ij}\) nearly vanishes for all nearest-neighbor interactions \((1)-(4)\). The presence of a common crystallographic mirror plane additionally restricts the \(y\) and \(z\) components for interactions \((2)-(4)\), so that both \(\mathbf{D}_{ij}\) and \(\mathbf{\Gamma}_{ij}\) vanish almost exactly for such interactions \[43\]. The only anisotropic interactions are therefore between first nearest-neighbor spins, labeled \((1)\). Provided ferromagnetic alignment of these spins, as in the predicted magnetic structure, the orientation of \(\mathbf{\Gamma}_{ij}(1)\) provides the two magnetic sublattices with different easy axes, both of which lie in the \(bc\) plane. The combined effect of these noncollinear easy axes leads to an easy \(bc\) plane overall, with a canted moment within the same plane, as emphasized in Fig. 3. In this sense, we find the anticipated effects of spin-orbit anisotropic exchange are in agreement with the observed magnetic response of FBBO. However, we cannot discount the possibility of an incommensurate modulation of such spins within the \(ab\) plane to form conical order with average moments in the directions indicated in Fig. 3. Finally, we remark that the effects of long-range magnetic-dipole interactions may modify this picture; for the simple example of a two-sublattice antiferromagnet, the orientation of a particular local moment is preferred along directions of maximum spin density associated with the same sublattice. For the suggested magnetic structure, this observation suggests a preference for alignment of spins within the \(ab\) plane, although the magnitude and specific angular dependence of this effect is unknown.

### C. Magnetic response under pressure

In order to investigate the stability of the layered antiferromagnetic state under pressure, field-cooled susceptibility at 100 Oe was measured using a piston cylinder cell installed into a commercial superconducting quantum interference device (SQUID) magnetometer, in the range 0.0 to 1.2 GPa [Fig. 6(a) \[44\]]. At low pressures \(<0.2\) GPa, a surge in \(\chi T\) is observed in the field-cooled susceptibility at \(T_N = 13\) K, signaling the transition to the spin-canted ordered state described in the previous section. However, above 0.2 GPa, this surge is reversibly suppressed, indicating either the absence of magnetic order or a new magnetic order with no net canted moment. Upon further compression, \(>0.6\) GPa, \(\chi T\) is further reduced and shows only weak temperature dependence below 20 K. This high-pressure response is roughly consistent with a Curie-like paramagnetic state, but with significantly reduced moment of \(\sim 0.2 \mu_B\) compared to the expected \(1.0 \mu_B\) for an \(S = \frac{1}{2}\) material.

Given the previous observation of room-temperature metallic conductivity in FBBO for pressures exceeding 3.0 GPa, it is tempting to associate the changes in low-temperature magnetic response with the onset of a conducting state. However, evidence against such an electronic phase transition can be seen in the temperature dependence of the resistivity, which was measured in the pressure range 0.0 to 2.0 GPa [Fig. 6(b) \[45\]]. Throughout the entire pressure range, FBBO displays activated (insulating) behavior down to the lowest measured temperatures of \(\sim 10\) K. This observation suggests the pressure-induced changes in magnetic response between 0.2 and 0.6 GPa are related to a genuine magnetic phase transition, rather than the onset of a metallic state. In the following sections, through analysis of the electronic structure and magnetic interactions of FBBO, we suggest a possible origin of this magnetic phase transition.

### III. ELECTRONIC STRUCTURE

#### A. Molecular electronic structure

At each FBBO molecular site in the crystal, the highest-occupied orbital in the ground state, labeled \(\alpha = 0\), is

![FIG. 6. (Color online) (a) Field-cooled (FC) susceptibility under pressure. The increase in \(\chi T\) at low temperatures is suppressed by pressure, indicating a magnetic phase transition. (b) High pressure resistivity. Insulating behavior under pressure indicates the absence of an electronic phase transition below 2.0 GPa.](image-url)
respectively: energy, Coulomb repulsion, and on-site Hund’s-rule coupling, properties. Accordingly, at the single-site level, we consider of the magnetic interactions, but also for charge-transport and LUMO are shown, as computed at the B3LYP/6-31G(d,p) level.

FIG. 7. (Color online) Cartoon representation of the states of the anion of FBBO. Comparison of calculated state energies allows estimation of various molecular parameters. The molecular SOMO and LUMO are shown, as computed at the B3LYP/6-31G(d,p) level.

nondegenerate and singly occupied; it is denoted SOMO or “singly occupied molecular orbital”. A particular feature common to oxobenzo bridged bisdihiazolyl radicals is that the π-accepting character of the carbonyl group ensures that the lowest unoccupied molecular orbital (LUMO, α = +1) is low lying and of π-character, as shown in Fig. 7. As described below, explicit consideration of this empty orbital is of key importance not only in the character of the magnetic interactions, but also for charge-transport properties. Accordingly, at the single-site level, we consider an effective two-orbital Hamiltonian that is the sum of orbital energy, Coulomb repulsion, and on-site Hund’s-rule coupling, respectively:

where

where \( c_i^{\dagger} \) creates an electron in \( \psi_a \) and site \( i \), and with spin \( \sigma \). The orbital summation is restricted to \( \alpha, \beta \in \{0, 1\} \). The density operators are given by

We have neglected the pair hopping term proportional to \( c_{i,\alpha}^\dagger c_{i,\alpha} c_{i,\beta} c_{i,\beta}^\dagger \), because it leads only to a slight redefinition of the orbital energies. Parameters of the Hamiltonian can be estimated by state-energy calculations on the molecular anion obtained by adding an electron to FBBO. When mapped into the two-orbital model, the low-energy anionic states consist of one triplet in which the SOMO and LUMO are both singly occupied \( |\alpha, \beta; \alpha, \beta\rangle \), and three singlets with varying occupancies \( \{ |\alpha, \beta; \alpha, \beta\rangle + |\alpha, \beta; \alpha, \beta\rangle \}. \) The energies of these states are

From these reference states, the true low-energy states may be obtained by explicit inclusion of correlation effects, which mix these configurations not only with one another, but also with those outside the two-orbital active space. It is in this sense that Eq. (3) must be considered an effective Hamiltonian, for which \( \{ K^{01}, U, V, \Delta \epsilon \} \) are chosen to reproduce the exact low-energy spectrum when acting on the unphysical reference space. Accordingly, the state energies were estimated using the difference dedicated configuration interaction method [46,47] with three degrees of freedom (DDCI-3), on the basis of the above CAS(2,2) reference states, as implemented in the ORCA program [48]. Starting orbitals were obtained from a single point B3LYP/6-31G(d,p) calculation on the closed shell anion using molecular geometry from the ambient-pressure crystal structure [24].

Relative to the lowest singlet \( |\alpha, \beta; \alpha, \beta\rangle \), the energies were found to be \( E(|\alpha, \beta; \alpha, \beta\rangle) = +0.174 \text{ eV}, E(|\alpha, \beta; \alpha, \alpha\rangle) = +0.581 \text{ eV}, \) and \( E(|\alpha, \beta; \beta, \beta\rangle) = +1.234 \text{ eV}. \) Using the relationships

we obtain \( K^{01} = 0.20 \text{ eV}, \Delta U = U - V = 0.24 \text{ eV}, \) and \( \Delta \epsilon = 0.62 \text{ eV} \). Because these values may be significantly influenced by the solid-state environment, they should be considered only an appropriate starting point for further analysis. It is worth mentioning that the results also depend greatly on the level of theory; broken symmetry DFT calculations, for example, suggest triplet ground states for such anions [30]. Finally, we note that, while explicit calculation of the solid-state Coulomb potential \( U \) is not possible by this method, an experimental estimate can be obtained from electrochemical measurements. In this approach, the potential difference between oxidation and reduction of the radical in the screening environment of an electrolyte solution (the cell potential \( E_{\text{cell}} \)) serves as a measure of the \( U \). Given the known \( E_{\text{cell}} = 0.69 \text{ V} \) for FBBO [24], we therefore estimate \( U \approx 0.69 \text{ eV} \) and \( V \approx 0.45 \text{ eV} \).

B. Solid-state electronic structure

In the solid state, the single-site Hamiltonian of Eq. (3) must be supplemented by an intermolecular hopping
FIG. 8. (Color online) (a) Computed DFT band structure of FBBBO (open circles). Tight-binding bands obtained by Wannier interpolation are shown with solid lines, the color of which indicates the contribution of MLWOs. (b) Tight-binding Fermi surfaces shown in the first Brillouin zone. The two bands associated with each of the $ab$-layers in the unit cell are colored gray and red. (c) Density of states obtained from MLWO interpolation. The Fermi level is indicated by $\epsilon_f$, while the energies of the SOMO and LUMO in the rotated basis are indicated by $\epsilon_0$ and $\epsilon_1$, respectively.

$$\mathcal{H} = T + \sum_i \mathcal{H}_i,$$

where

$$T = \sum_{a,\beta,\sigma} \sum_{i,j} t_{ij}^{ab} \left( c_{i,a,\sigma}^\dagger c_{j,\beta,\sigma} + \text{H.c.} \right).$$

In order to determine appropriate hopping integrals $t_{ij}^{ab}$ for FBBBO, band structures were first computed at the DFT level with the QUANTUM ESPRESSO package [49] using ultrasoft PBE pseudopotentials and a plane-wave cutoff of 25 Ry and a 250 Ry integration mesh. Self-consistent-field calculations employed a $4 \times 4 \times 4$ Monkhorst–Pack $k$-point mesh and the molecular geometry was taken from the ambient-pressure crystal structure [24]. It is worth noting that such calculations implicitly assume a metallic state, so the results best represent a zeroth-order description of the high-pressure metallic phase, rather than the low-pressure insulator. At first glance, the resulting band structure [Fig. 8(a), open circles] is quite simple. In the first Brillouin zone, there are a pair of bands associated with each of the SOMO and LUMO, arising from the two $ab$-layers of radicals in the unit cell (a total of four bands). Each pair of bands is only very weakly split, due to little interaction between layers and consequently only weak dispersion along the $c$-direction. The Fermi level resides in the lower band, and the resulting Fermi surfaces are open [Fig. 8(b)], resembling roughly that of an isotropic square lattice near half filling. However, this relatively simple electronic structure hides a more complicated orbital picture.

![Image](image_url)

FIG. 9. (Color online) Comparison of the maximally localized Wannier orbital (MLWO) basis, and rotated SOMO-LUMO basis orbitals from solid-state calculations. The latter may be compared with the orbitals obtained from single molecule calculations in Fig. 7.

We have employed the WANNIER90 code [50,51] to generate maximally localized Wannier orbitals (MLWOs) $\{\phi_-,\phi_+\}$ for each $ab$-layer (pictured in Fig. 9) [52]. The Wannier interpolated band structure is shown in Fig. 8(a) by a solid line, the color of which indicates the parentage of the crystal orbitals at each $k$ point. Excellent agreement is observed between the interpolated and DFT bands, validating the fitting procedure. Derived tight-binding hopping integrals for this MLWO basis are shown in Table I.

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<th>Hopping parameter</th>
<th>Location of site</th>
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TABLE I. Tight-binding parameters for maximally localized orbitals shown in Fig. 9; in this basis, $\phi_-$ and $\phi_+$ orbitals are nearly degenerate and $T$ is not diagonal at a given site, indicated by $t_{ij}^{+} \neq 0$. The number in parentheses beside each label $t_{ij}^{+}$ indicates the associated contact defined in Fig. 2.
Visual inspection of the MLWOs $\phi_+$ and $\phi_-$ suggests they are in- and out-of-phase combinations of the molecular SOMO and LUMO; they are nearly degenerate with orbital energy $\sim(\epsilon_0 + \epsilon_1)/2$. At each site, occupation of a hybrid MLWO by a single electron therefore costs energy $\Delta\epsilon/2$ with respect to single occupation of the pure SOMO due to the admixture of LUMO character. However, this local hybridization energy cost is offset by minimization of the intermolecular kinetic energy (hopping) so that, over a large region of $k$ space, the computed crystal orbitals are well described as arising from purely $\phi_+$ or $\phi_-$. Inspection of the hopping integrals in Table I suggest that, within the $ab$ plane, the bands arising from $\phi_-$ and $\phi_+$ are described in terms of nearly isotropic square and triangular lattices, respectively. The signs of the hopping integrals are opposite, so that the two bands are well separated over a large region of $k$ space. Where they meet, interband hopping leads to avoided crossings, ultimately producing discrete lower (half filled) and upper (empty) bands. Integration of the partial density of filled states [Fig. 8(c)] for each orbital reveals the occupancy to be 0.6 and 0.4 electrons per site on average, in either of two degenerate hybrid orbitals.

In contrast, in the Mott insulating state, intermolecular kinetic energy is suppressed by the large Coulomb repulsion barrier, thus eliminating the impetus for local hybridization. For this reason, the hybrid MLWO basis is inappropriate for describing the electronic structure of the low-pressure insulator.

In the MLWO basis, hybridization of the SOMO and LUMO results in a kinetic energy $T$ that is not site diagonal (i.e., $t_{ij}^\pm \neq 0$). Diagonalizing the on-site kinetic energy by orbital rotation undoes the hybridization, resulting in a more appropriate basis for describing the Mott insulator. Inspection of these rotated orbitals (Fig. 9) reveals that they correspond well with the molecular SOMO and LUMO, apart from slight asymmetry due to the local crystal field. Interestingly, $\Delta\epsilon$ is predicted to be only $\sim0.18$ eV by this method, which is much reduced from the 0.62 eV predicted by molecular calculations. In the rotated (SOMO-LUMO) basis, hopping between $ab$ planes is enhanced due to the more even distribution of electron densities across the molecule. Thus, the two-dimensional (2D) electronic structure of the metallic state arises directly from SOMO-LUMO mixing; in the insulating-state interactions are significantly more three-dimensional (3D). For molecules in the same $ab$ plane, the largest hopping integrals are found to occur between the SOMO and LUMO on different sites ($t_{ij}^{01}$, $t_{ij}^{10}$). This fact not only drives orbital hybridization in the metallic state but also has important consequences on the magnetic interactions in the insulator. In the next section, we consider such interactions arising from the multiple orbitals together with strong Hund’s-rule coupling.

IV. MAGNETIC MODEL

As a consequence of a low-lying $\alpha = +1$ LUMO, and strong Hund’s-rule coupling, molecular calculations suggested a low-lying triplet state $^3[I\bar{1}]$ in the molecular anion. In the Mott insulator, the importance of this observation can be seen from the fact that magnetic interactions arise from virtual hopping of electrons between sites, which mixes such higher-energy “charged” states into the low-energy manifold (composed of “neutral” states with equal electron distribution among sites). In the usual treatment of the single-band Hubbard model, the only charged states considered are singlets, so that virtual hopping always stabilizes antiferromagnetic alignment of spins [53]. In the present two-band case, hopping between bands allows access to excited high-spin states, which are themselves stabilized by on-site Hund’s-rule coupling. The resulting ferromagnetic interaction from this second contribution is colloquially known as “exchange through empty orbitals” and has been discussed extensively in the context of metal-centered magnetism [54,55]. For the two-band model, at second order in hopping, one obtains the familiar Heisenberg Hamiltonian

$$H_{\text{spin}} = -\sum_{\langle i,j \rangle} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j,$$

with the exchange constant given by contributions from the usual antiferromagnetic kinetic exchange and ferromagnetic empty-orbital exchange, respectively:

$$J_{ij} = -\frac{4(t_{ij}^{00})^2}{U} + 2K_{ij}^0 \left[ (t_{ij}^{01})^2 + (t_{ij}^{10})^2 \right],$$

In cases where $K_{ij}^0$ and/or $t_{ij}^{01}$, $t_{ij}^{10}$ are large, one expects the ferromagnetic term to dominate, providing a signature of multiband character in the magnetic structure. Using Eq. (19), together with the hopping integrals for the site-diagonal basis from Table II, and the molecular parameters described in Sec. III, we have estimated the exchange parameters for the Mott insulating state of FBBO. Results are shown in Table III. We have also computed corrections up to fourth order in hopping (not shown) and confirm little qualitative difference, justifying use of the SOMO-LUMO basis to describe the Mott insulating state.

The computed exchange interactions are in complete agreement with the experimental ambient-pressure magnetic structure for FBBO (Fig. 3). Within the $ab$ planes, there are two competing terms $J_1$ and $J_2$. As a result of the dominant interband hopping integral $t_{ij}^{10}(1) = +143.3$ meV between molecules related by $C$-centering, $J_1$ is found to be the strongest magnetic interaction and is ferromagnetic, a fact that agrees with the experimental alignment of spins in the $ab$ planes. This ferromagnetic interaction is partially frustrated by the antiferromagnetic $J_2$ term, so that every triangular plaquette contains two ferromagnetic and one antiferromagnetic interaction. While the frustration may reduce both the ordering temperature and the observed Weiss constant, even for the fully frustrated case where $J_1 = J_2$, a quantum disordered (spin-liquid) state is not expected. This is because quantum fluctuations are likely suppressed by interlayer couplings $J_3$ and $J_4$. These antiferromagnetic interactions between planes stabilize the experimentally observed layered antiferromagnetic structure.

In the ambient-pressure magnetic structure, the $J_2$ interaction is the only term not minimized energetically. As $J_2$ is increased, we suggest stabilization of a new striped ordered phase with wave vector $(\pi, \pi, 2\pi)$ or $(\pi, -\pi, 2\pi)$ as shown.
TABLE II. Tight-binding parameters obtained from a rotation of maximally localized orbitals to ensure a site-diagonal ($t_{ij}^{0} = 0$) hopping Hamiltonian, as described in the text. The number in parentheses beside each label $t_{ij}^{0}$ indicates the associated contact defined in Fig. 2.

<table>
<thead>
<tr>
<th>Hopping parameter</th>
<th>Location of site</th>
<th>Value (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$t_{ij}^{0}$</td>
<td>$(x,y,z)$</td>
<td>0.0</td>
</tr>
<tr>
<td>$t_{ij}^{0}(1)$</td>
<td>$(x,y,z)$</td>
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<tr>
<td>$t_{ij}^{0}(1)$</td>
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<td>$(x,y,z)$</td>
<td>+143.3</td>
</tr>
<tr>
<td>$t_{ij}^{0}(1)$</td>
<td>$(x,y,z)$</td>
<td>-91.3</td>
</tr>
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<td>$(x,y,z)$</td>
<td>+37.0</td>
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<td>+17.8</td>
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</tr>
<tr>
<td>$t_{ij}^{0}(4)$</td>
<td>$(x,y,z)$</td>
<td>-2.0</td>
</tr>
</tbody>
</table>

in Fig. 10. This phase arises as a compromise in which all of the $\mathcal{J}_2$ interactions, but only half of the $\mathcal{J}_1$ interactions, are satisfied and should occur around $|\mathcal{J}_2/\mathcal{J}_1| \gtrsim 1$. Based on the above estimates, the ambient-pressure structure has $|\mathcal{J}_2/\mathcal{J}_1| = 0.85$, already on the verge of this transition. This observation may therefore explain the magnetic transition observed around 0.2 GPa; as this striped structure breaks translational symmetry, no canted moment can be observed, in agreement with experiment.

V. CONSEQUENCES FOR THE MOTT TRANSITION

In this section, we consider the nature of the insulator-to-metal transition observed in FBBO around 3.0 GPa, in reference to the described electronic structure. In the insulator, the half-filled SOMO is split into lower and upper Hubbard bands (LHB and UHB, respectively), with a relatively wide LUMO band and small $V$ implying overlap of the LUMO band and UHB. Under applied pressure, a Mott transition in the SOMO band alone is unlikely, due to small $t_{ij}^{0}$ and large $U$. For this reason, we have suggested that this transition proceeds mainly through orbital rehybridization of the molecular SOMO and LUMO to produce a degenerate set of orbitals resembling the MLWOs. Concomitant with this transition is the reduction in the chemical potential due to LUMO states being drawn down to lower energy. The resulting MLWO bands are wide and nearly equally occupied in the metallic state, so that the transition is expected to occur directly between the half-filled insulator and quarter-filled metal, as represented in Fig. 11.

This scenario is in agreement with previous studies, which suggest a direct transition in the case where the splitting of the MLWOs $\Delta \epsilon' \sim 0$, but such studies considered only weak orbital hybridization ($t_{ij}^{0} - t_{ij}^{0} = t_{ij}^{0}$) [56]. Proximity to this metallic state is also related with the observation of ferromagnetic interactions in the insulator; in the same limit of negligible hybridization, the quarter-filled two-orbital model

TABLE III. Ambient pressure magnetic exchange parameters $\mathcal{J}_i^{\perp}$ up to second order in hopping c.f Eq. (19) using hopping integrals from Table II. $K^{01} = 0.20$ eV, $\Delta \epsilon = 0.62$ eV, $V = 0.45$ eV, $U = 0.69$ eV obtained in Sec. III.

<table>
<thead>
<tr>
<th>Location of site</th>
<th>Value (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mathcal{J}_1$</td>
<td>+86.9 (FM)</td>
</tr>
<tr>
<td>$\mathcal{J}_2$</td>
<td>-74.3 (AFM)</td>
</tr>
<tr>
<td>$\mathcal{J}_3$</td>
<td>-38.6 (AFM)</td>
</tr>
<tr>
<td>$\mathcal{J}_4$</td>
<td>-21.1 (AFM)</td>
</tr>
</tbody>
</table>

FIG. 10. (Color online) Possible magnetic structure for pressures above 0.2 GPa viewed down the (a) $a$-axis and (b) $c$-axis. The stripe pattern emerges as a compromise between ferromagnetic $\mathcal{J}_1$ and antiferromagnetic $\mathcal{J}_2$ interactions.

FIG. 11. (Color online) Cartoon of the electronic structure in the insulating and metallic states. Occupied one-electron states are indicated by diagonal hatching. In the insulator, the SOMO is split into a filled lower Hubbard band (LHB) and empty upper Hubbard band (UHB), which overlaps with the empty LUMO band. In the metal, the SOMO and LUMO hybridize to overlapping $\phi_-$ and $\phi_+$ bands, with roughly equal occupation.
is known to display ferromagnetically ordered insulating states [57]. In Sec. III, approximate Coulomb parameters were computed in the SOMO-LUMO basis; these can be transformed into the MLWO basis:

\[
U' = \frac{U + V}{2} + K^{01} \sim 0.77 \text{ eV},
\]

(20)

\[
V' = \frac{U + V}{2} - K^{01} \sim 0.37 \text{ eV},
\]

(21)

\[
K^+ = \frac{U - V}{2} \sim 0.12 \text{ eV},
\]

(22)

\[
\Delta\epsilon' \sim 0 \text{ eV}.
\]

(23)

As expected, localizing the MOs has the effect of increasing the Coulomb repulsion between electrons in the same orbital, while decreasing the repulsion between electrons in different orbitals. On the basis of these values, the potential-energy cost for formation of a metallic state can be estimated in a mean-field sense from the expectation value of the Coulomb operator:

\[
\langle \mathcal{U} \rangle = \frac{U'}{4} \langle (n_{i,\downarrow})^2 + (n_{i,\uparrow})^2 \rangle + V' \langle n_{i,\downarrow} \rangle \langle n_{i,\uparrow} \rangle,
\]

(24)

which reduces to \( \langle \mathcal{U} \rangle \sim 0.13 \) and \( U' + 0.24 \) for all values of the antiferromagnetic order appearing at the insulating state (including the cost of orbital hybridization) can be estimated by

\[
\Delta E_k = \frac{\int_{-\infty}^{\epsilon_{0}} (\epsilon_{0} - \omega) D(\omega) d\omega}{\int_{-\infty}^{\epsilon_{0}} D(\omega) d\omega}.
\]

(25)

where \( D(\omega) \) is the total density of states for the two bands, as shown in Fig. 8(c), and \( \epsilon_{0} \) is the orbital energy of the unhybridized SOMO. We find \( \Delta E_k \sim -0.25 \text{ eV} \) per electron at ambient pressure, which is the same order as the potential cost of 0.19 eV above, consistent with proximity to the Mott transition. However, as \( |\Delta E_k| > \langle \mathcal{U} \rangle \), a metallic state is anticipated even at ambient pressure, in contrast with experimental findings. This discrepancy is most likely due to an underestimation of the SOMO-LUMO splitting \( \Delta \epsilon \sim 0.18 \text{ eV} \) in the solid-state calculations, resulting in a slight overestimation of \( \Delta E_k \). It is worth noting that extended Hückel calculations on isolated molecules incorrectly predict a reversal in the ordering of the SOMO and LUMO, giving negative \( \Delta \epsilon \) values. In this sense, \( \Delta \epsilon \) is sensitive to theoretical method and may not be properly estimated by the solid-state DFT technique.

The role of Hund’s-rule coupling in stabilizing the metallic state of XBBO materials has been previously discussed but is revisited here in the context of the above picture of orbital rehybridization. In multi-orbital models with no orbital mixing, the effects of Hund coupling \( K \) has been demonstrated to have a strong filling dependence. In particular, for multiple electrons or holes per site, a large \( K \) reduces both the charge gap in the insulating state and the quasiparticle coherence in the metal, ultimately promoting bad-metallic states over a wide range of \( t/U \) [58,59]. In contrast, for the case with only one electron per site on average, the latter effect is diminished, so that a normal metallic state is always stabilized for large \( K \).

For the present picture of orbital mixing in XBBO materials, this discussion is complicated by the state dependency of the Hund-coupling magnitude (i.e., \( K^{01} \neq K^{+} \)). We therefore restrict the discussion to the influence of \( K^{01} \). On the insulating side, increasing \( K^{01} \) reduces the charge gap, thus promoting a metallic state. On the metallic side, the only effect of increasing \( K^{01} \) is to increase repulsion between electrons in the same MLWO (\( U' \)), while reducing the repulsion between electrons in different orbitals (\( V' \)). This combination should stabilize the metal, as the large value of \( U' \) is expected to have little impact on the quarter-filled metallic state [57,60]. That being said, further theoretical investigations into the interplay of orbital hybridization and Hund’s-rule coupling are of great interest.

### VI. CONCLUSION

In the first section, through analysis of susceptibility and AFMR measurements, the magnetic structure of FBBO was established to have ferromagnetic interactions within the \( ab \) plane layers. This observation was explained on the basis of both molecular and solid-state calculations, which implicate a combination of Hund’s-rule coupling, and a low-lying \( \pi \)-LUMO, both of which necessitate a two-orbital model for the electronic structure. As both of these properties are molecular in origin, they are expected to be common to the entire family of XBBO materials, and one expects to find ferromagnetism also in other members of the family. It is therefore satisfying that substitution of the exocyclic fluorine by a phenyl group to produce PhBBO led to one-dimensional chains with large ferromagnetic intrachain coupling \( J_1 = +84.9 \text{ K} \), and positive Weiss constant of \( \Theta = +32.8 \text{ K} \) [26]. Evidence for ferromagnetism has also been observed in HBBO (\( \Theta = +15.6 \text{ K} \)), although in this latter case, the complexity of the crystal structure has hindered analysis of the antiferromagnetic order appearing at \( T_N = 4.5 \text{ K} \) [25]. As with FBBO, the HBBO material displays an insulator-to-metal transition at high pressure (>6 GPa), but in this case it is accompanied by a series of structural phase transitions [30]. Given these similarities, the details of the electronic structure discussed for FBBO are expected to be common to the entire family.

The two-orbital model for the new class of XBBO materials highlights the importance of the low-lying \( \pi \)-LUMO in promoting charge delocalization, providing an explanation for enhanced conductivity in comparison with previous generations of neutral radicals [29] in which this \( \pi \)-LUMO is absent in the orbital manifold. As evidenced by the metallic state appearing under pressure, the XBBO family opens the possibility for the study of strong-correlation physics in neutral radical conductors.

### ACKNOWLEDGMENTS

We would like to acknowledge A. Ozarowski and J. van Tol, EMR division, NHMFL, for assistance with measurements, and V. Dobrosavljević for helpful discussions. We thank the Natural Sciences and Engineering Research Council of Canada (NSERC) for financial support and a Graduate Scholarship to S.M.W. and thank the Government of Canada.
for a Tier 1 Canada Research Chair to J.S.T. We also thank the Waterloo IRPG program for financial support. K.T. acknowledges financial support via Feodor-Lynen fellowship from Alexander von Humboldt foundation, Germany. D.G. and S.W.T. acknowledge support from the Department of Energy (DOE) from Grant No. DOE NNSA DE-NA0001979.

[27] High-purity microcrystalline FBBO samples suitable for the EPR and transport measurements described were prepared by reduction of the nonaflate salt of the corresponding cation with decamethylferrocene, according to the procedure of Ref. [24].
[29] The anisotropy in the g tensor arises mainly due to the local spin-orbit coupling (orbital Zeeman) effects. In this case, the extreme values are well within the expected range of dithiazolyl radicals; see S. M. Mattar, J. Sanford, and A. D. Goodfellow, Chem. Phys. Lett. 418, 30 (2006).
[34] This observation follows alternately from the requirement that any magnetic structure with a net moment be described by a trivial magnetic Bravais lattice; see S. M. Mattar, J. Sanford, and A. D. Goodfellow, Chem. Phys. Lett. 418, 30 (2006).
to the present measurement, we investigated the relationship between the contraction length and the pressure value by using elemental lead as manometer. In the actual measurement, the pressure value was estimated from the contraction length.

[45] Gold wires were attached to a thin polycrystalline pressed pellet of FBBO using Dupont 4929N conductive silver paste. The sample was mounted to the wire feedthrough of a piston cylinder pressure cell which was constructed from MP35N alloy. Daphne 7474 oil was used as the pressure-transmitting medium [61] surrounding the sample. The resistance was measured by using a Keithley 6517 electrometer while the temperature was controlled in a Quantum Design physical properties measurement system (PPMS). Resistance data at each pressure was normalized to the room temperature resistivity values previously measured using a cubic anvil press [24].


