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Pressure Dependence of the Exchange Anisotropy in an Organic Ferromagnet

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The combination of high-pressure ferromagnetic resonance (FMR) and an ab-initio scheme suitable for calculation of spin-orbit mediated anisotropic exchange interactions in molecular materials provides insights into the role of spin-orbit coupling (SOC) in a Se-based organic ferromagnet. FMR measurements reveal a continuous increase in the magnetic anisotropy with increasing pressure (up to 2.2 GPa), in excellent agreement with calculations based on the known pressure-dependence of the structure. The large value of anisotropic exchange terms in this heavy atom organic ferromagnet emphasizes the important role of SOC in a wide range of organics where this effect is usually considered to be small.

I. INTRODUCTION

The discovery of weakly correlated materials with non-trivial band topologies has recently brought into prominence the study of spin-orbit coupling (SOC) in the solid state.1,2 This interaction also plays an important role in magnetic insulators, where SOC manifests itself as anisotropic exchange interactions between local spin-orbital moments.3,4 These anisotropic terms, such as the celebrated Dzyaloshinsky-Moriya interaction, are instrumental in many magnetic phenomena including magnetic coercivity and spin-canting, as well as the more exotic multiferroicity5 and topological spin phases.6–8 Engineering such states in real materials requires understanding the relationship between spin-orbit parameters and crystal structure, emphasizing the need for both experimental and ab-initio probes of SOC.9 In search of materials with strong SOC, the majority of developments in the field have focused on inorganic solids, drawing particularly from heavy elements with principle quantum number n ≥ 5.10–13 In this report we focus instead on the bis-diselenazolyl radical (Fig. 1(b), hereafter denoted 1), a selenium-based organic ferromagnet in which significant SOC induced anisotropic exchange has been previously identified.14,15

Compound 1 crystallizes in the non-centric tetragonal space group P421m, with each of the four molecules in the unit cell forming the basis for π-stacked radical “chains” extending in the c-direction (Fig. 1(a)).16 Each π-stack is bisected by a local mirror plane and neighbouring stacks are related by 21 axes. At ambient pressure, 1 is a Mott insulator, and orders as a bulk ferromagnet below Tc = 17 K. Previous ferromagnetic resonance (FMR) studies revealed uniaxial easy c-axis anisotropy characterized by a large anisotropy field μcHc = 0.88 T at ambient pressure, which was shown to arise from anisotropic exchange between S = 1/2 radical sites.14,15 It was shown that this degree of magnetic anisotropy is several orders of magnitude larger than one would expect on the basis of classical shape/demagnetizing effects.14,17 thus necessitating consideration of SOC mediated anisotropic exchange interactions between S = 1/2 radical sites (for which single site SOC anisotropy is forbidden in the absence of a magnetic field). Indeed, the observation of an anticipated reduction of Hc upon partial substitution of selenium (n = 4) for lighter sulfur (n = 3) has provided important indications of the importance of SOC physics,15 thereby motivating the present investigation of the pressure-dependence of inter-site hopping processes and their role in mediating anisotropic exchange interactions.

Under pressure, x-ray studies on 1 have demonstrated uniform compression of the unit cell, with approximately 2% and 7% reduction in a and c, respectively, up to 3 GPa (Fig. 1(c)).18 Concomitant with this compression is a reduction of the relative π-stack slippage, as measured by the angle between the normal of the molecular plane and crystallographic c-axis, which modulates the hopping integrals between adjacent radicals in the same π-stack. This effect initially enhances the isotropic ferromagnetic exchange, resulting in an increase of Tc from 17 K to 21 K at 1.0 GPa.18,19 At still higher pressures, further reduction of slippage finally drives the antiferromagnetic exchange within the stacks antiferromagnetic, and results in a monotonic decrease of Tc. In this report, we explore the evolution of SOC exchange terms through a recently developed high-pressure FMR technique. We also intro-
II. AB-INITIO CALCULATIONS

In the following section, we describe a new scheme for accurate calculation of anisotropic exchange interactions for magnetic organic materials using quantum chemistry methods. At each radical site \( i \), molecular orbitals are labeled by an index \( \alpha_i \), and have associated orbital energy \( \epsilon_\alpha \). The highest occupied of these \( (\alpha_i = 0) \) is the \( \pi \)-antibonding singly occupied molecular orbital (SOMO) depicted in Fig. 2(a). Within the SOMO band, with inclusion of SOC effects, hopping is described by:

\[
T = \sum_{i,j} c_{ij}^1 \left( t_{00}^{ij} \mathbb{I} + \frac{1}{2} \sum_\mu \left[ C_{00}^{ij} \right]_\mu \sigma_\mu \right) c_{j,0} + \text{H.c.} \tag{1}
\]

where \( \mu \in \{x, y, z\} \), \( \sigma_\mu \) are Pauli matrices, and \( \mathbb{I} \) is the 2\( \times 2 \) identity matrix. The two component operator \( c_{ij}^1 \left( c_{ij,0}^1, c_{ij,0}^\dagger \right) \) creates an electron in the SOMO at site \( i \).

Hopping integrals are denoted \( t_{ij}^{\alpha\alpha} = \langle \alpha_i| F |\alpha_j \rangle \), where \( F \) is the Fock operator. The components of the purely imaginary spin-orbit hopping parameter \( C_{00}^{ij} \) are given by a summation over all (valence) orbitals:

\[
\left[ C_{00}^{ij} \right]_\mu = \sum_{\alpha \neq 0} \frac{\langle 0 | \mathcal{L}_i^{\mu} | \alpha_i \rangle \langle \alpha_j | \mathcal{L}_j^{\mu} | 0 \rangle}{\epsilon_\alpha - \epsilon_0} \tag{2}
\]

where \( \mathcal{L}_i^{\mu} \) are effective orbital angular momentum operators for site \( i \) described in Ref. 20. Assuming a large and orbital independent Coulomb repulsion \( U \gg \{t, C\} \), perturbative treatment of the hopping gives rise to the spin Hamiltonian:

\[
\mathcal{H} = \sum_{i,j} -J_{ij} S_i \cdot S_j + D_{ij} \cdot (S_i \times S_j) + S_i \cdot \Gamma_{ij} \cdot S_j \tag{3}
\]

where the cartesian components of the Dzyaloshinsky-Moriya (DM) vector \( D_{ij} \) and pseudo-dipolar (PD) tensor \( \Gamma_{ij} \) are given by:

\[
[D_{ij}]_\mu = \frac{2t_{ij}^{\mu}}{U} \left( [C_{00}^{ij}]_\mu \left[ t_{00}^{ij} - t_{00}^{ij} \right] \right) \tag{4}
\]

\[
[\Gamma_{ij}]_{\mu\nu} = \frac{1}{U} \left( [C_{00}^{ij}]_\mu \left[ C_{00}^{ij} \right]_\nu + [C_{00}^{ij}]_\mu \left[ C_{00}^{ij} \right]_\nu \right) \tag{5}
\]

In principle, \( D_{ij} \) and \( \Gamma_{ij} \) may be estimated from zero-field splitting calculations in the triplet state of the radical pair \( (i, j) \) via wave function-based perturbative density functional-based approaches. However, given (i) the small magnitude of these terms \((\sim 0.1 - 1.0 \text{ K})\), (ii) the importance of correlation effects, and especially (iii) the large number of potentially relevant valence orbitals \( \{\alpha_i\} \) to consider in the SOC treatment, obtaining accurate estimates of \( D_{ij} \) and \( \Gamma_{ij} \) for organic systems by existing methods represents a significant challenge. Our new approach instead uses density functional theory first to compute the hopping integrals (in the absence of SOC), orbital energies, and spin-orbit matrix elements, and then to compute \( C_{00}^{ij} \) directly by eqn (2). The anisotropic exchange parameters \( D_{ij} \) and \( \Gamma_{ij} \) can then estimated on the basis of Moriya’s perturbative model (eqns (3) to (5)). Necessary terms for this calculation were computed using the ORCA package on the basis of site-localized B3LYP/6-311G** orbitals, constructed to have maximum overlap with the corresponding orbitals in the isolated molecule. Orbital energies, \( \epsilon_\alpha \), were approximated by the Kohn-Sham eigenvalues of the isolated molecules. Hopping integrals were estimated for each unique radical pair by rotation of the converged Fock matrix for the pair into the site local basis. Matrix elements of \( \mathcal{L}_i^{\mu} \) were computed using the Spin Orbit Mean Field (SOMF) method implemented in the ORCA_soc module. Geometries for each radical pair were obtained from previously reported room temperature structures in the range 0.0 - 3.0 GPa. The Coulomb repulsion, \( U \sim 0.8 \text{ eV} \), was experimentally estimated from solution electrochemical measurements on 1 and related S/Se variants.

In the solid state, compound 1 has three unique nearest neighbour pairs \( (i, j) \), as shown in Fig. 3. The first of these, for which \( i \) and \( j \) are in the same \( \pi \)-stack and related by translation along the \( c \)-axis, is labelled \( (\pi) \). The
remaining two, in which \(i\) and \(j\) are in different \(\pi\)-stacks and related by \(2\gamma\) axes at \(c = \frac{1}{2}\) and 0, are labelled (1) and (2), respectively. Results of calculations are summarized in Fig. 4, with numerical values given in the supplemental information. The small scatter in the computed values may be related to uncertainty in the high pressure structural parameters, which were obtained by rigid body refinement of powder diffraction data rather than single crystal methods. At ambient pressure, we find that the largest SOMO-SOMO hopping integral \(t_{00}^{ij}\) occurs for \((\pi^-)\)-type interactions, between adjacent radicals within the same \(\pi\)-stack. In contrast, the spin-orbit mediated hopping parameter \(|C_{00}^{ij}|\) are greatest between \(\pi\)-stacks. For all three interactions, the largest component of \(C_{00}^{ij}\) lies within the crystallographic ab-plane. In order to facilitate qualitative discussion of these results, it is useful to interpret the orbital summation of eq’n (2) as defining a set of orbital-like functions \(|\eta_\mu^i\rangle\) shown in Fig. 2(b):

\[
|\eta_\mu^i\rangle = \sum_{\alpha \neq 0} |\alpha_i\rangle \frac{\langle \alpha_i | \mathcal{L}_{\mu}^i | 0_i \rangle}{\epsilon_{\alpha} - \epsilon_0}
\]

(6)

The purely imaginary \(|\eta_\mu^i\rangle\) functions are neither normalized nor eigenstates of the Fock operator, and so have no well-defined \(\epsilon\), but consider their spatial density and symmetry properties is nonetheless useful. In terms of these functions the components of the spin-orbit mediated hopping parameter \(C_{00}^{ij}\) are simply hopping integrals between the SOMO and \(|\eta_\mu^i\rangle\) functions on adjacent radicals:

\[
[C_{00}^{ij}]_\mu = t_{\nu\mu 0}^{ij} + t_{\gamma\nu 0}^{ij}
\]

(7)

The magnitude and character of the anisotropic exchange between any two radicals may therefore be anticipated from the shapes of the \(|\eta_\mu^i\rangle\) functions. For the purpose of discussion, we define local coordinates for each molecular site \(i\), shown in Fig. 2: the \(\hat{z}_i\)-axis is normal to the crystallographic mirror plane bisecting the molecule, while the \(\hat{\xi}_i\)-axis is chosen along the normal of the molecular plane. For this choice of coordinates, the \(\pi\)-SOMO is approximately a linear combination of \(p_z\) orbitals, so that \(|\eta_\mu^i\rangle \sim 0\) since \(\mathcal{L}_{\mu}^i | 0_i \rangle \sim 0\). This result, which is easily confirmed by ab-initio calculation, holds for any planar organic \(\pi\)-system and suggests that \(C_{00}^{ij}\) will tend to be oriented perpendicular to \(\hat{z}_i\) and \(\hat{\xi}_j\), since \(t_{\nu\mu 0}^{ij}\) vanishes. For radical 1 this preference ensures that all \(C_{00}^{ij}\) lie within, or close to the crystallographic ab-plane. The remaining functions \(|\eta_\mu^i\rangle\) and \(|\eta_\nu^i\rangle\) are linear combinations of orbitals in the \(\sigma\)-framework, and have density largely confined within the molecular plane, but with significant extension around the periphery of the molecule. This shape enhances interstack \(t_{\nu\mu 0}^{ij}\) integrals which explains the finding that \(|C_{00}^{ij(1)}|, |C_{00}^{ij(2)}| > |C_{00}^{ij(\pi)}|\).

Under pressure, we find that \(t_{00}^{ij(1)}\) remains relatively constant while \(|t_{00}^{ij(\pi)}|\) and \(|t_{00}^{ij(2)}|\) are initially suppressed as both hopping integrals are driven more positive (from initially negative ambient pressure values). This effect, which was previously anticipated in Ref. 18, results in a reduction of antiferromagnetic exchange \(J_{AFM} \sim 4(t_{00}^{ij})^2/U\), and thus explains the enhancement of the ferromagnetic ordering \(T_C\) up to 1.0 GPa. In contrast, \(|C_{00}^{ij(1)}|\) and \(|C_{00}^{ij(2)}|\) are predicted to increase monotonically (Fig. 4) with pressure, while \(|C_{00}^{ij(\pi)}|\) remains small. This observation implies important consequences for the pressure dependence of the anisotropic exchange parameters \(D_{ij}\) and \(\Gamma_{ij}\), which we have estimated from the computed \(C_{00}^{ij}\) and \(t_{00}^{ij}\) values (see supplemental). From eq’n (4), it is easy to see that \(D_{ij} |C_{00}^{ij}|\) so that the DM-interaction is minimized when the spins at sites \((i, j)\) are canted, and lie in the plane \(S_i, S_j \perp C_{00}^{ij}\). For ferromagnetically oriented spins, the pseudo-dipolar interaction is also minimized for this orientation, which may be seen by rotating \(\Gamma_{ij}\) so that one of the principle axes is parallel to \(C_{00}^{ij}\). In this case, for example:

\[
\Gamma_{ij} = \frac{2}{U} \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & |C_{00}^{ij}|^2 \end{pmatrix}
\]

(8)

which is minimized, for parallel spins, when \((S_i, \Gamma_{ij}, S_j) = 0\), for \(S_i, S_j \perp C_{00}^{ij}\). As a result \(D_{ij}\) and \(\Gamma_{ij}\) provide complementary contributions to the magnetocrystalline anisotropy. However, the small values of \(t_{00}^{ij}\) required for net ferromagnetic interactions also result in small \(D_{ij}\) in 1, so that \(\Gamma_{ij}\) represents the most important contribution to the anisotropy. To a first approximation, we therefore ignore contributions from the DM-interaction,
and assume a collinear magnetic structure. The finding that $C_{00}$ tends to be oriented close to the $ab$-plane for all pairs of radicals is thus consistent with the observed easy $c$-axis anisotropy, which is associated with a zero-field gap $\Delta_g$ in the collective ferromagnon spectrum at $k = 0$ (see Refs. 14 and 15 for a detailed explanation):

$$\Delta_{gt} \equiv g\mu_B H_A = \frac{1}{2} \sum_j \left[ |\Gamma_{ij}|_{aa} + |\Gamma_{ij}|_{bb} - 2 |\Gamma_{ij}|_{cc} \right]$$

(9)

where the summation is over nearest neighbours, $\{a,b,c\}$ refer to the crystallographic axes, and $H_A$ is the so-called anisotropy field. Calculated values of $H_A$ as a function of pressure are shown in Fig. 5(d).

### III. FMR MEASUREMENTS

In order to probe correlations between $H_A$ and the crystal structure and, hence, obtain experimental insights into the SOC in 1, we employed recently developed instrumentation capable of performing multi-high-frequency EPR (in this case, FMR) measurements under quasi-hydrostatic pressure. Below $T_C$, resonant absorption of microwave radiation occurs whenever the excitation energy of the $k = 0$ ferromagnon can be tuned by an external field to match the microwave frequency.\(^{25,26}\) For this reason, FMR is uniquely sensitive to the anisotropic components of the Hamiltonian. Combining FMR with high pressure techniques is challenging and unexplored. In this work, high pressures were obtained using a plastic diamond anvil cell (DAC).\(^{27}\) Multi-frequency, high pressure FMR measurements were then performed using a cavity perturbation technique (described in Refs. 28 and 29) by placing the pressure cell inside a cylindrical resonator (a cavity) with dimensions matched to those of the DAC.\(^{30,31}\) Introduction of the plastic cell significantly increases the microwave losses within the resonator, thus suppressing its quality factor, making the measurements considerably more challenging than those at ambient pressure. Nevertheless, the losses can be minimized by working at low temperatures ($< 10$ K), enabling FMR measurements up to 2.2 GPa in the $f = 40 - 160$ GHz frequency range on small single-crystals of 1 (dimensions $0.1 \times 0.1 \times 0.2$ mm\(^3\)). At each pressure, alignment of the sample with respect to the applied field was achieved by performing two-axis crystal rotation studies using a vector magnet (see Fig. 5(a) for a schematic showing the crystal and experimental coordinates). The pressure in the DAC was mediated using a 1:1 mixture of Fluorinert 70:77, and calibrated in situ at the measurement temperature by recording the luminescence from a ruby chip via the diamond window and an optical fiber.\(^{32}\) FMR spectra recorded at different polar angles, $\theta$ ($\phi$ undetermined), are shown in Fig. 5(b). The FMR signal is seen as a dip in the transmission through the cavity; its obvious angle-dependence distinguishes it from a strong angle-independent $g = 2$ impurity signal from the diamonds in the DAC. At high fields, the FMR position, $H_{res}$, for 1 was found to vary as:

$$H_{res} \approx \frac{h f_{res}}{g\mu_B H_B} - \frac{H_A}{2} \left( 3 \cos^2 \theta - 1 \right)$$

(10)

in accordance with the expected resonance condition for the easy $c$-axis anisotropy.\(^{14,15}\) The minimum of the resonance field yields the orientation of the easy $c$-axis ($\theta = 0^\circ$). For this orientation, the resonance frequency follows the relation:

$$h f_{res} = g\mu_B (H_{res} + H_A)$$

(11)
allowing $H_A$ to be extracted from multifrequency measure-
mements (Fig. 5(c)).

IV. DISCUSSION

The sensitivity of the anisotropic exchange in 1 to
structural details is highlighted by the near doubling of
$H_A$ over the range 0.0 – 2.2 GPa, despite relatively small
contraction of the unit cell (i.e. 2% for the a, b axes and
7% for the c-axis). Close agreement is found between ex-
perimental $H_A$ values and those calculated from eq’n (9)
in terms of both sign and magnitude. At ambient pres-
sure, for example, the calculated value of 0.97 T compares
favorably with the experimental value of $H_A = 0.88$ T
(Fig. 5(d)). The monotonic increase of $H_A$ found experi-
mentally under pressure is also correctly reproduced. As
explained above, this enhancement of $H_A$ under pressure
can be attributed to an average increase of $t_{0p0'}$ integrals
for interstack interactions, which by eq’n (7) leads to a
uniform enhancement of $C_{00}^{ij}$ and thus $\Gamma_{ij}$. This enhance-
ment can be visually anticipated from the shapes of the
$|\eta_i^+|^2$ functions, which have simple lobal structures around
the molecular periphery, allowing the weighted hopping
integrals $t_{0p'}^{ij}$ to increase uniformly with compression for
interactions (1) and (2). In contrast, the lobal mismatch
between the SOMO $|0_i^+\rangle$ and $|\eta_i^+|^2$ on adjacent molecules
in the same π-stack results in a small and pressure inde-
dependent $C_{00}^{ij}$ associated with nearly isotropic intra-
stack interactions at all pressures. Interestingly, the calculations
also suggest that $H_A$ arises almost entirely from
interstack interactions (1) and (2), with (π) interactions
contributing less than 2% of the observed $H_A$, in con-
trast with our previous assumptions.15 The finding that
the pressure dependence of $t_{00}^{ij}$ and $C_{00}^{ij}$ (and thus the
isotropic and anisotropic interactions) is largely unre-
related also has implications for studies of other spin-orbit
coupled materials under pressure.33,34

Taken together, the close agreement between the ex-
perimental and theoretical $H_A$ values over the studied
pressure range validates the magnitude of the calculated
spin-orbit hopping parameters $|C_{00}^{ij}| \sim 10$ meV, which,
in the present material, are of similar magnitude to the
hopping parameters $t_{00}^{ij} \sim 10$ meV. However, for organic
materials in general, typically $t \lesssim 100$ meV,35 suggesting
for Se-based organics that $|C|/t \sim 10\%$ represents a rea-
sonable estimate, and such materials should therefore be
considered moderate to strongly spin-orbit coupled. This
suggestion follows from a key feature of organics: due to
their molecular nature, all relevant energy scales, such as
hopping integrals $t$, Coulomb repulsion $U$, and orbital
energy splittings $\Delta_c$, are often at least an order of magni-
tude smaller than for inorganic materials. Thus SOC, the
scale of which is set in molecular systems by the heaviest
constituent atoms, may play a significant role for the or-
organics despite their being composed of relatively lighter
elements than their $n \geq 5$ inorganic counterparts.

Although light heteroatom ($n = 2, 3$) organic mag-
etic materials have a long history, heavy atom ($n > 3$)
radical magnets have emerged only recently; they sim-
ply were not known before 2006 because of the strong
tendency for the radicals to dimerize and form non-
magnetic singlet ground states. Continued research into
such systems may well provide a rich source of new
SOC related physics. For example, the possibility of
realizing topologically nontrivial phases in organics re-
 mains essentially unexplored.36 Although weaker than in
their selenium-based counterparts, anisotropic exchange
terms have also been implicated in magnetically ordered
sulfur-based organics, such as the spin-canted antiferro-
magnets (BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl$_3$.37–39 p-NC-C$_6$F$_4$-
CNSSN,40 and FBBO.41 A comprehensive study of the
SOC effects in these and other organic materials is of
great interest and importance.

In summary, we have introduced an ab-initio scheme
suitable for calculation of spin-orbit hopping parameters,
$C_{00}^{ij}$, in organic materials. Combining this method with
high pressure FMR measurements has allowed investiga-
tion of the structural aspects of SOC in the Se-based
ferromagnet 1. With increasing pressure, the anisotropy
field measured by FMR increases continuously, consistent
with the theoretical calculations that predict strong en-
hancement of interstack anisotropic exchange with pres-
sure. The large relative magnitude of the SOC terms sug-
gests significant modification of both the magnetic and
electronic excitations in this heavy atom ferromagnet,
prompting reconsideration of the role of SOC in a broad
range of other organics.

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