First-Principles study of an $S=1$ quasi-1D quantum molecular magnetic material

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We use density functional theory to study the structural, magnetic and electronic structure of the organo-metallic quantum magnet NiCl$_2$·4SC(NH$_2$)$_2$ (DTN). Recent work has demonstrated the quasi-1D nature of the molecular crystal and its quantum phase transitions at low temperatures. This includes a magneto-electric coupling and, when doped with Br, the presence of an exotic Bose-glass state. We systematically show that, by using the generalized gradient approximation (GGA) with inclusion of a van der Waals term to account for weak inter-molecular forces and by introducing a Hubbard $U$ term to the total energy, our calculations reproduce the magnetic anisotropy, the inter-molecular exchange coupling strength and the magneto-electric effect in DTN, which were observed in previous experiments. Further analysis into the electronic structure gives insight into the underlying magnetic interactions, including what mechanisms may be causing the ME effect. Using this computationally efficient model, we predict what effect applying an electric field might have on the magnetic properties of this quantum magnet.

I. INTRODUCTION

Interest in materials that exhibit sizable magneto-electric (ME) effects has grown considerably within the past decade. New classes of materials exhibiting the phenomena hint at the prospect of applications where it can be harnessed and materials can be designed for use in potential low-power spintronic devices and future computing applications. The ME effect is characterized by a coupling between the magnetization and electric polarization of a material. That is, the application of a magnetic field induces a change in the electric polarization of a material and similarly, the application of an electric field causes a change in the magnetization. Investigations into the ME effect have largely focused on its presence within transition-metal oxides. Recent studies have shown that this coupling between the electric and magnetic properties may also be present within the class of materials known as organo-metallic molecular crystals.

The fundamental building block of these solids is the molecule where individual molecular units are held together by relatively weak inter-molecular interactions. At the center of each molecule is a magnetic, metal ion and the interactions between neighboring magnetic moments dictate the magnetic properties of the crystal. Given the weak interactions between molecules, molecular crystals are often easily strained under external magnetic and electric forces. This soft lattice structure may provide a degree of freedom through which the ME effect may be tuned. The potential to synthesize organic ligands may also allow future flexibility in designing and tuning properties of such materials.

The organic quantum magnetic system NiCl$_2$·4SC(NH$_2$)$_2$ (DTN) which has been studied in experiments and by quantum Monte-Carlo simulations based on model Hamiltonians is the subject of this work. The molecular unit of this system (Figure 1) has a central magnetic cation Ni surrounded by four electrically polar ligands, SC(NH$_2$) (thiourea). DTN and its doped derivatives have been studied extensively due to the rich physics present at low temperatures. The phase diagram of pure DTN shows that, at temperatures below 1.2 K and below a critical magnetic field, $H_{c1}$, it is a quantum paramagnet. As the magnetic field, applied perpendicular to DTN’s $ab$-plane, reaches the first critical field, it experiences a quantum phase transition into an $XY$-antiferromagnetic ($XY$-AFM) state where all spins are now lying within the $ab$-plane. As the field is increased further the spins begin to cant, with a corresponding increase in magnetization. When the second critical field, $H_{c2}$, is reached, the magnetization saturates and the material enters a spin-polarized state where all spins are pointing along the c-axis and parallel to the applied magnetic field. Within this $XY$-AFM region DTN exhibits the ME effect where, along with an increase in magnetization, there is a correlated increase in the electric polarization. In this paper we investigate the structural, electronic and magnetic properties of DTN from first principles. Using an appropriate level of approximation within density functional theory (DFT) we are able to balance accurate structural predictions with computational efficiency to gain insight into DTN’s electronic and magnetic structure, the possible mechanisms responsible for its ME effect and investigate properties of the solid not yet studied in the literature.

The rest of the paper is organized as follows. Section II A introduces the theory behind modelling dispersion interactions, use of Wannier functions to interpret magnetic interactions, and an introduction to the Hubbard model, respectively. Section II B covers the computational details of the calculations as implemented within the software package VASP. In Section III we discuss our results relating to the systematic improvements made to our model, comparing to experiments along the way. Using this model we go on to predict experimentally unverified properties of the material. We summarize our conclusions in Section IV.
II. THEORY AND METHODS

A. Approximations and analysis

Molecular crystals pose a challenge to theorists when trying to predict their structural properties. This has been especially true within density functional theory (DFT) with generalized gradient approximations (GGA) given that exchange-correlation functionals struggle to account for long-range correlations in materials, i.e., Van der Waals (vdW) and hydrogen bonding. Recent advancements in theory have introduced new functionals that attempt to model these dispersive interactions, namely optB88 and DF2 functionals. However, the method frequently cited for successfully predicting molecular crystal structures, and what we use in this paper, is one that augments the DFT total energy with a dispersion correction. This DFT-D3 dispersion correction adjusts the inter-nuclear energy to account for the long-range asymptotic behaviour with little effect in the short range. In this paper we add the dispersion correction to the PBE functional, with an adjustment to the damping parameter, and compare the lattice constants of relaxed structures using the correction scheme to other functionals without the correction. The benefits of applying this method, outside of predicting an accurate structure, includes decreasing the computational cost of calculations and the freedom to choose functionals that allow us to further predict an accurate electronic structure.

In order to gain insight into the magnetic interactions in DTN we calculated maximally-localized Wannier functions (MLWF) using the wannier90 software package. Wannier functions (WF) are an analog of molecular orbitals for solid state materials. Unlike Bloch states which are de-localized and defined by a band index and crystal momentum, Wannier functions are spatially localized and centered on a lattice site. Given the large number of Bloch states in Hilbert space resulting from a groundstate DFT calculation, this transformation to a WF basis can be performed by choosing a subset of Bloch states forming bands near the Fermi level and Fourier transforming them into the new, smaller basis set. The software follows the method of Marzari and Vanderbilt for minimizing the spread of MLWF. Our calculations used eight bands near the Fermi level. Microscopic insights into the relevant orbitals and superexchange paths at work in DTN are given in the results section.

Calculations of WF functions lie in the range of a tight-binding model where the hopping integrals are output as the off-diagonal elements of the Hamiltonian, $H_{TB}$. Within a tight-binding model, however, the Coulomb interaction ($U$) is neglected. This may be a reasonable first approximation given that standard DFT calculations are known to underestimate $U$, neglecting electron-electron interactions. The Ni ion has eight electrons in its outer 3d shell. With the localization of d-orbitals, we expect strong correlation effects and attempt to model the DTN system by adding an additional Hubbard-like term to the groundstate DFT total energy to account for electron-electron interactions.

B. Technical details

First-principles calculations were performed using the Vienna ab initio Simulation Package (VASP) within the density functional theory (DFT) framework. Wavefunctions are expanded in plane waves and an energy cutoff of 520 eV is used for all calculations. The Brillouin zone was sampled on a 6x6x6 Monkhorst-Pack mesh for most calculations. The Projector-augmented wave potentials were used and convergence threshold was set to $10^{-8}$ eV. The DTN structure was relaxed using the PBE functional with the DFT-D3 dispersion correction and damping set to $S_R = 1.5$. Forces were converged to within 0.01 eV/atom. Comparisons between different functionals on the structure are discussed in Section III-A. Calculations of exchange coupling between magnetic Ni ions were performed by creating a supercell composed of two DTN unit cells. In order to compare to experiment we focused on $J$ couplings along the $c$-axis of the unit cell, $J_c$, and coupling between Ni ions within the $ab$-plane, $J_{ab}$. Two different supercells were created to isolate inequivalent Ni ions; one extends two unit cells along the $c$-axis (1x1x2) and the other extends two units along the $a$-axis (2x1x1). The Brillouin zone sampling mesh was 2x6x6 and 6x6x2 for the $ab$ and $c$ supercells, respectively. We fit $J$’s to the Heisenberg model and compare results to experiment for GGA and GGA+$U$ (both with inclusion of the vdW interaction). All GGA+$U$ calculations were performed with a choice of $U_{eff} = 6$. 

![Figure 1. The molecular unit making up the DTN molecular crystal. Four thiourea ligands surround the magnetic Ni ion.](Image)
TABLE I. Lattice constants of DTN with optimized structures obtained using different exchange-correlation functionals.

| XC Functional | a (Å) | b (Å) | c (Å) |
|---------------|-------|-------|-------|
| LDA           | 9.29  | 9.29  | 8.44  |
| GGA           | 9.70  | 9.70  | 9.35  |
| GGA-DFTD3     | 9.58  | 9.58  | 8.92  |
| DF2           | 9.77  | 9.77  | 9.02  |
| optB88        | 9.54  | 9.54  | 8.63  |
| PBEsol        | 9.41  | 9.41  | 9.07  |
| hse06         | 9.67  | 9.67  | 9.16  |
| Experiment    | 9.56  | 9.56  | 9.08  |

III. RESULTS AND DISCUSSION

A. Structural relaxation

We first discuss attempts at getting an accurate structure for the DTN molecular crystal. As mentioned in the theory and methods section, modeling molecular crystals is challenging due to the presence of weak inter-molecular interactions between molecular units. We attempt to model the molecular crystal with different exchange-correlation (XC) functionals and list the relaxed lattice constants in Table I.

For LDA and PBE functionals, the $a$, $b$, and $c$ lattice constants are either severely underestimated or overestimated. Attempts at using functionals that inherently include dispersion interactions give mixed results. In the case of the DF2 functional, it obtains an accurate $c$ lattice constant, but overestimates $a$ and $b$. The optB88 functional has the opposite effect, accurately predicting $a$ and $b$ constants but underestimating $c$. The PBEsol and the hybrid hse06 functionals’ lattice constants are within 0.2 Å of the experimental lattice constants. Finally, when using the DFT-D3 dispersion correction we are able to obtain lattice constants that are all within 0.08 Å of the experimental values.

A comparison of bond lengths and bond angles between the DFT relaxed structure using the GGA functional with the DFT-D3 dispersion correction we are able to obtain lattice constants that are all within 0.08 Å of the experimental values.

B. Spin maps and Magnetic anisotropy

With the choice of an XC functional that correctly predicts DTN’s structure we went on to calculate basic magnetic properties of the molecular crystal. We first performed a series of spin-constrained DFT calculations on the DTN molecular unit itself, allowing the total energy, $E(\theta, \phi)$, to be a function of spherical coordinates and producing a spin-map (Figure 2). From the top figure we see the easy-axis is along $\theta = 90^\circ$, with little $\phi$ dependence, and the uniaxial symmetry of the molecule. The bottom figure is the spin map produced using the DTN unit cell that contains two i-equivalent Ni ions. In this bcc unit cell we have a Ni ion at the corner of our box and one body-centered Ni. To produce this spin map we fixed the corner Ni’s spin to lie along the $c$-axis of the cell and sampled different spherical coordinates for the central Ni. This shows the ground state is antiferromagnetic (AFM).

In the results that follow we make comparisons between two different approximations, namely, DFT calculations performed using GGA+DFTD3 and GGA+$U$+DFTD3. Experimentally it is shown that the zero-field splitting, $D$, between $S_z = 0, \pm 1$ is 8.98 K. Our calculation of the magnetic anisotropy (mae) shows that without the Hubbard $U$ term, we underestimate this anisotropy to be 6.26 K. Adding $U$ gives an anisotropy value of 9.10 K, which is within 0.15 K of the experimental results. A full investigation of magnetic anisotropy, including the effects of substitutions of Cl ions and ligands, will be left for future work. Earlier results suggest a decrease in magnetic anisotropy as the substitute ion gets larger.

C. Exchange coupling

A large part of our efforts went into getting a better microscopic understanding of the magnetic interactions at play in DTN. Experimentally it has been shown that the exchange coupling between Ni ions along the $c$-axis is an order of magnitude larger than the coupling between Ni’s within the $ab$-plane, labeled as $J_c$ and $J_{ab}$, respectively. The phenomenological spin-spin Hamiltonian is:

TABLE II. Bond lengths and bond angles of structurally relaxed DTN using the GGA functional with the DFT-D3 dispersion correction compared to experiment.

| Bond Length | Experiment (Å) | Calculated (Å) |
|-------------|----------------|----------------|
| Ni-Cl(1)    | 2.40           | 2.41           |
| Ni-Cl(2)    | 2.52           | 2.54           |
| Ni-S        | 2.46           | 2.44           |
| S-C         | 1.73           | 1.72           |
| C-NH$_2$(1) | 1.34           | 1.34           |
| C-NH$_2$(2) | 1.32           | 1.33           |

| Bond Angle  | Experiment (°) | Calculated (°) |
|-------------|----------------|----------------|
| S-Ni-Cl(1)  | 96.7           | 96.8           |
| S-Ni-Cl(2)  | 83.3           | 83.2           |
| Ni-S-C      | 113.9          | 114.2          |
| S-C-NH$_2$(1)| 116.9         | 119.4          |
| S-C-NH$_2$(2)| 122.3         | 121.3          |
| NH$_2$(1)-C-NH$_2$(2) | 120.8         | 119.2          |
where \( \langle i,j \rangle \) and \( \langle l,m \rangle \) are the out-of-plane and in-plane neighbors, respectively. Both experiments and theory show that \( J_c \) is negative and an order of magnitude larger that \( J_{ab} \), making DTN a quasi-1D antiferromagnetic chain along the \( c \)-axis direction. Using the GGA functional as our first approximation we see that we can calculate \( J \) values that are mostly AFM, indicated by the negative sign. We label six \( J \) values in Table III corresponding to the supercell extended along the \( c \)-axis (Figure 5). Our initial focus, for the approximation using GGA+DFTD3 and using this supercell, is to extract \( J \)'s corresponding to coupling along the \( c \)-axis, namely, \( J_{12} \) and \( J_{34} \). Averaging we get \( \langle J \rangle_{ab} = -1.73 \), where the couplings of interest were those parallel to the \( ab \)-plane, \( J_{12} \) and \( J_{34} \) (Table IV). What we see is that although the magnitude of the coupling is overestimated for both, using GGA+DFTD3 correctly predicts the AFM state and that the coupling along the \( c \)-axis is an order of magnitude larger than those in the \( ab \)-plane. To account for what we expect to be strong correlations of 3d electrons on the Ni ion, we introduce the Hubbard \( U \) and re-calculate the \( J \) values. What we see is that the magnitudes of the \( J \) couplings are within 0.25 K of the experimental couplings (Table V). We also list a coupling not reported experimentally, \( J_{\text{diag}} \), which connects the corner Ni with the body-centered Ni ion (Figure 5).

It has been suggested that strong exchange-coupling along the \( c \)-axis is via the Ni-Cl-Ni-Cl chain. The density of states (DOS) is shown in Figure 3. It can be seen that DTN is insulating with a wide band gap of about 2.5 eV. The Ni(3d) orbitals \((d_{3z^2-r^2} \text{ red}) \text{ and } d_{x^2-y^2} \text{ blue}) \) in the spin-majority channel are fully occupied and those in the spin-minority channel are almost fully empty, indicating the \( S = 1 \) spin state of the Ni\(^{2+} \) cation.
The splitting between Cl-Cl bonding and anti-bonding states labeled in Figure 3(d) is about 2.0 eV, which reflects strong inter-molecular interactions through the Cl-Cl chain. Just below the Fermi level (panels (c) and (d)), the Ni\((d_{3z^2−r^2})\) hybridizes with the Cl-Cl anti-bonding state and Ni\((d_{z^2−r^2})\) hybridizes with S\(_x(p_x)\) and S\(_y(p_y)\).

To understand that hybridization and the magnetic interaction pathway, we performed a unitary transformation on Bloch states to construct Wannier orbitals and the tight-binding Hamiltonian using the energy window shown in Figure 3 with 8 Wannier functions. The isosurface in Figure 4 shows one of the Wannier orbitals which has the features of Cl\((p_x)\), S\((p_x/p_y)\) and Ni\((e_g)\). These characteristics signal strong hybridization. The corresponding matrix elements, in units of eV, including nearest-neighbor hopping \(t\) and the on-site energy \(\varepsilon\) in the WF basis, is:

\[
\begin{array}{cccccccc}
H_{mn}(eV) & |1^o_{3z^2−r^2}\rangle & |1^o_{x^2−y^2}\rangle & |2^u_{3z^2−r^2}\rangle & |2^u_{x^2−y^2}\rangle & |3^o_{3z^2−r^2}\rangle & |3^o_{x^2−y^2}\rangle & |4^u_{3z^2−r^2}\rangle & |4^u_{x^2−y^2}\rangle \\
\hline
1^o_{3z^2−r^2} & -5.540 & 0.000 & -0.031 & 0.000 & 0.000 & 0.023 & 0.000 & 0.000 \\
1^o_{x^2−y^2} & -0.287 & 0.000 & 0.001 & 0.002 & 0.004 & 0.001 & 0.000 & 0.000 \\
2^u_{3z^2−r^2} & 2.570 & 0.000 & 0.005 & -0.006 & 0.005 & -0.008 & 0.000 & 0.000 \\
2^u_{x^2−y^2} & 2.405 & -0.008 & -0.002 & -0.004 & 0.000 & 0.000 & 0.000 & 0.000 \\
3^o_{3z^2−r^2} & -5.547 & 0.000 & -0.031 & 0.000 & 0.000 & 0.016 & 0.000 & 0.000 \\
3^o_{x^2−y^2} & -0.287 & 0.000 & 0.001 & 0.000 & 0.000 & 0.000 & 0.000 & 0.000 \\
4^u_{3z^2−r^2} & h.c. & 2.570 & 0.000 & 0.000 & 0.000 & 0.000 & 0.000 & 0.000 \\
4^u_{x^2−y^2} & & 2.405 & & & & & & \\
\end{array}
\]

The position labels, 1 to 4, of the WFs are the same as those in Figure 5. The subscripts \(3z^2−r^2\) and \(x^2−y^2\) represent the \(3z^2−r^2\)-like and \(x^2−y^2\)-like WFs. Subscripts \(o\) and \(u\) refer to occupied and unoccupied WFs, respectively.

In particular, the largest hopping \(t\) between occupied and unoccupied WFs is -0.031 eV (bold in Eq. 2), which comes from two \(3z^2−r^2\)-like WFs, of neighboring unit cells, along the c-axis. Considering the difference in on-site energies, \(\Delta\), of associated WFs on Ni ions on the c-axis, we can estimate the magnitude of their exchange interaction by \(J_e \sim 4t^2/\Delta\), to be about 5.5 K. Other hopping elements between WFs centered on Ni ions with distinct occupied states are much smaller (around -0.001 eV or less), indicating a smaller exchange interaction along the diagonal direction. Overall, our results show that, although our estimate is of the right order of magnitude using a tight-binding model in the Wannier basis, using energetics and fitting to a Heisenberg model provides better \(J\) coupling values compared to experiment. What we gain from our Wannier analysis is more insight into the orbital contributions to the superexchange pathway.

\[
\mathcal{H}_{TB} = - \sum_{i>j, \sigma} t_{ij}(\hat{c}_i^\dagger \hat{c}_{j\sigma} + \hat{c}_{j\sigma}^\dagger \hat{c}_i) - \sum_{i, \sigma} \epsilon_i \hat{c}_i^\dagger \hat{c}_{i\sigma} \quad (3)
\]

FIG. 4. Panel(a): Isosurface of a Wannier function for the AFM c-axis supercell indicating hybridization of Ni and Cl orbitals leading to a superexchange path along the Ni-Cl-Cl-Ni chain; panel (b) Wannier orbital value in a cross section containing two Ni ions along a diagonal line of the bcc lattice; and (c) in 100 plane of the lattice.

D. Magneto-electric effect

With a model for DTN that is able to predict the structural and magnetic properties of the molecular crystal, we went on to investigate the magneto-electric properties to see whether we could capture any effects. Our ap-
TABLE III. Specific exchange coupling constants for the c-axis supercell using GGA and GGA+U, with the inclusion of the D3 correction.

| $J_{ij}^c$ (K) | GGA   | GGA+U$_{eff}$ |
|--------------|-------|---------------|
| $J_{12}$     | -13.9 | -2.44         |
| $J_{13}$     | -1.44 | -0.09         |
| $J_{14}$     | 0.31  | -0.09         |
| $J_{23}$     | -1.44 | -0.09         |
| $J_{24}$     | 0.31  | -0.09         |
| $J_{34}$     | -10.4 | -2.44         |

TABLE IV. Specific exchange coupling constants for the ab-plane supercell using GGA and GGA+U, with the inclusion of the D3 correction.

| $J_{ij}^{ab}$ (K) | GGA   | GGA+U$_{eff}$ |
|------------------|-------|---------------|
| $J_{12}$         | -1.73 | -0.42         |
| $J_{13}$         | -0.57 | -0.09         |
| $J_{14}$         | -0.57 | -0.09         |
| $J_{24}$         | -0.57 | -0.09         |
| $J_{23}$         | -0.57 | -0.09         |
| $J_{34}$         | -1.73 | -0.42         |

The approach was to sample different magnetic configurations by constraining the spins to lie at different polar angles, relative to the c-axis.

For each angle we calculate the electric dipole moment within the modern theory of polarization framework. What we see is that as the angle $\theta$ increases and the spin approaches the ab-plane there is a correlated decrease in the electric dipole moment of the unit cell along with the expected decrease in $M_z$. This was done for the GGA and GGA+U approximations, with the inclusion of the D3 correction. The effect was present in both, but largest when using GGA (Figure 6).

Finally, experiments have shown that the application of a magnetic field has an effect on the electric polarization so it was natural to wonder whether the application of an electric field can effect the magnetic properties of the system. Our calculations indicate that by applying an electric field in a direction parallel to the ab-plane and perpendicular to the 1D-chain, we can gradually increase the magnetic anisotropy of bulk DTN (Figure 7).

As a mechanism for the ME coupling, the literature suggests magnetic field induced strain, i.e. magnetostriction, changes the unit cell and a re-orientation of the electrically polar ligands results in a change of the polarization. In what follows we explore strain effects on the DTN unit cell. In our calculation sampling different canted spin configurations (Figure 6) what we see is the presence of the ME coupling in the absence of internal ionic relaxation. This indicates that what is responsible for the effect are more subtle changes in the electronic degrees of freedom. To examine this idea further, to see what added contribution structural changes in the lattice have, we apply a tensile strain on the unit cell along the c-axis up to 0.1% while allowing the ions to...
relax and minimize the total energy. We correspondingly compress the $a$, $b$ lattice constants to keep the volume constant. Similarly, we apply a compression to the $c$ lattice constant and expand the $a$, $b$ constants and repeat the calculations. A look at the orientation of the ligands shows little variation in the Cl-Ni-S bond angles or bond lengths.

Further investigations (Figure 8) shows little change in polarization due to changes in the ionic structure and that the main contribution comes from subtle changes in electronic degrees of freedom. This result is an indication that re-orientation of the ligands in fact does not happen.

IV. CONCLUSION

Our aim in this paper has been an attempt to model DTN within a DFT framework. This approach not only provides a way to gain insight into the mechanisms responsible for structural, electronic and magnetic properties but also allows us to make accurate predictions while minimizing the computational cost. We were able to show that the inclusion of the DFT-D3 correction substantially improves the structure of the DTN molecular crystal, providing accurate lattice constants, bond lengths and bond angles. Including the Hubbard term to the standard GGA functional allowed us to improve our modelling of the magnetic interactions in DTN, accurately predicting the magnetic anisotropy and exchange coupling constants and providing an additional $J_{\text{diag}}$ coupling. The quasi-1D nature of DTN was indicated by the hybridization of Ni($d_{3z^2-r^2}$) and Cl-Cl anti-bonding orbitals via a virtual superexchange path along the c-axis. Finally, we showed the presence of the ME coupling and predict an increase in magnetic anisotropy with the application of an electric field. The results of this study are a first step towards understanding the detailed mechanisms involved in the magneto-electric coupling in DTN. Its presence in functional organic quantum magnets suggests the possibility of future applications where the magnetic properties of materials may be fine-tuned through more feasible structural and electronic means. Yet to be explored in detail is the nature of Bose-Einstein condensates (BEC) in organic quantum magnets and the important role the ME effect plays in this state. We hope this work puts forward the idea that these fundamental properties may be investigated from First-Principles.

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