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Evidence of Symmetry Breaking in a Gd₂ di-nuclear molecular polymer

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A chiral 3D coordination compound, [Gd₂(L)₂(ox)₂(H₂O)₂], arranged around a dinuclear Gd unit has been characterized by X-ray photoemission and X-ray absorption measurements in the context of density function theory studies. Core level photoemission of the Gd 5p multiplet splittings indicates that spin orbit coupling dominates over j-J coupling evident in the 5p core level spectra of Gd metal. Indications of spin-orbit coupling are consistent with the absence of inversion symmetry due to the ligand field. Density functional theory predicts antiferromagnetic alignment of the Gd₂ dimers and a band gap of the lanthanide dimer array lattice consistent with optical absorption.

1. Introduction

Rare-earth (lanthanide) ions have been of long standing interest in material science because of their luminescence¹⁻³ and magnetic properties.⁴⁻⁶ Many of the rare earth molecular magnets exhibit large magnetic moments and some exhibit large inherent magnetic anisotropy.^{4,7-13} For the lanthanide single molecular magnets with large anisotropy, there is growing evidence of magnetic hysteresis at the molecular level.⁸⁻¹³ For the half-filled 4f⁷ electron configurations, as present in gadolinium(III) and europium(II), the spin momentum is at a maximum, but in the absence of ligand field effects, the orbital angular momentum is minimal. The absence of orbital angular momentum leads to zero spin-orbital coupling, hence a non-degenerate ground state.^{14,15} The electronic structure of Gd and Tb metal is dominated by j-J coupling,^{16,17} but this picture may not be strictly applicable to molecular lanthanide systems.

Studies have been undertaken on di-nuclear gadolinium complexes where the di-nuclear unit shows asymmetry resulting in the loss of inversion symmetry. This loss of symmetry occurs from the interaction between the ligands and Gd ions.¹⁸⁻²⁰ Loss of inversion symmetry is associated with chiral effects and can lead to a large spin orbital coupling. Spin-orbit

coupling can play a key role in spintronics leading to topologically protected spin currents,²¹ while an anisotropy barrier and a large moment can play a role in voltage-controlled quantum computing based on molecular magnets.^{10,18,22-24}

In this study, a 3D coordination compound, [Gd₂(L)₂(ox)₂(H₂O)₂], (where ox corresponds to the oxalate ligand (C₂O₄)²⁻ and L- is a chiral imidazolium ligand bearing two carboxylate groups, Figure 1a), developing from a di-nuclear Gd unit was studied using X-ray photoemission and X-ray absorption spectroscopy techniques. The Gd ions are coupled antiferromagnetically and this type of dinuclear array of lanthanide chains may be suitable²⁵ for voltage control in a continuous readout logic gate based on a solid state Mach-Zehnder interferometer.²⁵⁻³³ In this context, spin orbit coupling would enhance device functionality and performance.^{14,25,34} The strong magnetic anisotropy that can be imposed on the Gd ion, by a ligand field, can give rise to different zero-field splittings and thus provide distinct spin qubits in the [Gd₂] molecular dimer.¹⁸

2. Experiment

The [Gd₂(L)₂(ox)₂(H₂O)₂] compound was synthesized by reacting in solvothermal conditions the imidazolium ligand [HL] (0.530 g, 2.50 mmol) with Gd(NO₃)₃·6H₂O (1.128 g, 2.5 mmol) and oxalic acid H₂ox (0.157 g, 1.25 mmol) in a mixture water/ethanol (6 mL, 1:1 vol) at 393 K for 3 days. Crystalline material was filtered and washed with ethanol (yield: 57 %). Crystal structure was studied by X-ray diffraction on single crystal (for further details, see supplementary information part). Phase purity was confirmed by powder X ray diffraction (see Figure S4 in SI). Elemental analysis for [Gd₂(L)₂(ox)₂(H₂O)₂] (M = 948.5 g.mol⁻¹) Found (Calc.): C 27.28 (27.83), H 2.70 (2.74), N 5.68 (5.90). Infrared (reflectance, cm⁻¹): 3303 (w), 3132 (w), 3087 (w), 2992 (w), 2947 (w), 1698 (m), 1601 (s), 1461 (m), 1415

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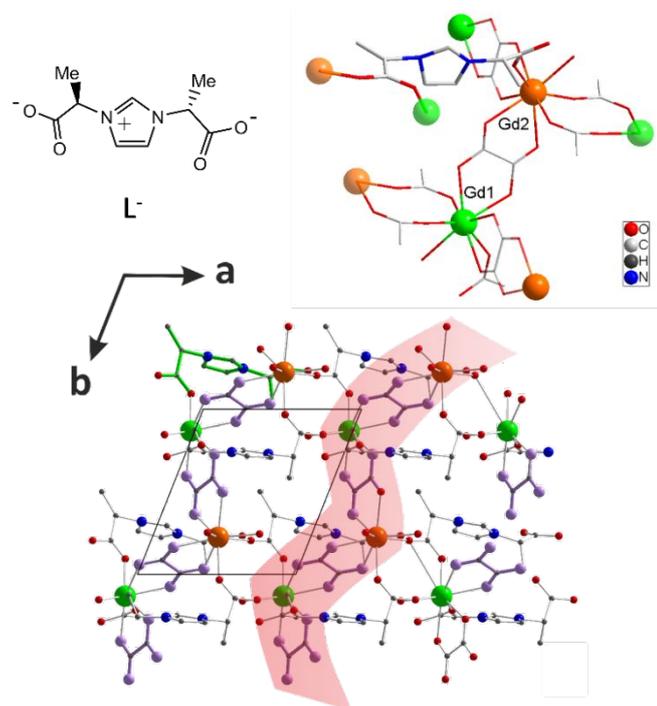


Fig. 1 : The crystal structure of $[\text{Gd}_2(\text{L})_2(\text{ox})_2(\text{H}_2\text{O})_2]$: (top) a schematic of the chiral imidazolium ligand, L^- , and details of the connectivity between the ligands and the Gd ions (only one L^- is fully depicted, for the others only the carboxylic moieties are plotted) where the independent Gd1 and Gd2 sites are shown in green and orange, respectively); (bottom) a view of the 3D organization highlighting the Gd-oxalate chain organization.

(m), 1363 (m), 1313 (m), 1223 (w), 1180 (w), 918 (w), 988 (w), 794 (s), 597 (m), 489 (m).

The X-ray single crystal experiment was carried out on a Rigaku Synergy S four circles diffractometer equipped with an Eiger 1M Dectris detector; a Cu micro focus photonjet X-ray source was used. Low temperature measurements were achieved using an Oxford cryostream 800 system. A schematic representation of the $[\text{Gd}_2(\text{L})_2(\text{ox})_2(\text{H}_2\text{O})_2]$ compound is shown in Figure 1b and details on the crystal structure analysis are given in the supplementary information. The crystallographic information for the structure has been deposited at CCDC with number 2160787.

The elemental analysis for C, H, N was carried out at the Laboratoire de Chimie de Coordination using a Perkin–Elmer 2400 series II instrument. The infrared measurements were done using a Perkin–Elmer spectrum GX 2000 FT-IR spectrometer. The absorption measurements were done using a Perkin Elmer Lambda 950 spectrometer (spectra recorded in reflection mode using a 150 mm integrating sphere with a mean resolution of 2 nm and a sampling rate of 225 nm.min⁻¹).

The X-ray absorption spectroscopy (XAS) measurements was performed at the bending magnet beamline 6.3.1, at Advanced Light Source at Lawrence Berkley National Laboratory and the photon flux was in the region of 1.16×10^4 .photons.sec⁻¹.μm⁻² in the two-bunch mode. The absorption across the Gd N_{2,3} edge was done on electron yield mode. X-ray photoemission spectroscopy (XPS) measurements were taken using non-monochromatized Al Kα x-ray source. The photon

energy of 1486.6 eV and SPECS PHOIBOS 150 energy analyzer with photon energy 10 eV was used. All the measurements were taken on the powder.

3. Theory

The orbital-resolved electronic structure of $[\text{Gd}_2(\text{L})_2(\text{ox})_2(\text{H}_2\text{O})_2]$ was calculated by spin density function theory (DFT) employing the projector augmented wave method (PAW) pseudopotentials³⁵ method as implemented in the VASP package.^{36,37} The electronic exchange and correlation were accounted with the Perdew–Burke–Ernzerhof (PBE)³⁸ functional with the density functional theory DFT-D3³⁹ correction (with and without Hubbard U parameter of 6.8 eV for Gd 4f electron, i.e. PBE+U) and the Heyd–Scuseria–Ernzerhof (HSE06) functional.^{40,41} We used a Gaussian smearing method, with $\sigma = 0.1$ eV, and sampled the Brillouin zone with a $2 \times 2 \times 2$ Γ -centered grid for lattice parameter optimization, structural relaxation and the partial density of states for the PBE and DFT+U, while for HSE a $1 \times 1 \times 1$ Γ -centered grid for the partial density of states was used. Spin-orbit coupling (SOC) effects are included in all electronic structure calculations.

4. Spin-Orbit Coupling

The X-ray photoemission spectrum of $[\text{Gd}_2(\text{L})_2(\text{ox})_2(\text{H}_2\text{O})_2]$ is shown in Figure 2. It shows expected two main Gd 5p core level features of $5p_{3/2}$ and $5p_{1/2}$ at binding energies of around 23 eV and 27 eV. The energy separation between two main features is about 4 eV which is similar to the expected value for the Gd 5p the spin-orbit coupling.^{16,17,42} These two $p_{1/2}$ and $p_{3/2}$ features of the experimental 5p core level photoemission spectrum exhibits a fine structure splitting that can be fitted with six Gaussian peaks (Figure 2), as expected when the p core level photoemission spectra is dominated by either L-S coupling or j-J coupling (as schematically indicated in Figure 2).^{16,17}

While the multiplet splitting of the photoemission spectrum of the Gd 5p levels occurs due to the half-filled 4f level, in fact, what is observed for $[\text{Gd}_2(\text{L})_2(\text{ox})_2(\text{H}_2\text{O})_2]$ (Figure 2) is not the multiplet structure of the 5p core level seen for Gd metal (Figure 2c), in which the multiplets are dominated by j-j coupling.^{16,17} The $[\text{Gd}_2(\text{L})_2(\text{ox})_2(\text{H}_2\text{O})_2]$ experimental 5p core level photoemission peak around 22 eV feature exhibits three components with binding energies 19.0 ± 0.1 eV, 21.9 ± 0.1 eV, and 23.7 ± 0.1 eV. The feature around 28 eV has three peaks with binding energies 26.1 ± 0.1 eV, 27.1 ± 0.1 eV, and 28.9 ± 0.1 eV. For Gd metal, and an isolated Gd atom, the photohole created by exciting an electron at 5p level will have an electrostatic interaction with unpaired electrons in the 4f level. It has been showed that the splitting obtained from photoemission for an Gd atom has a four-fold splitting in the $5p_{3/2}$ feature and concluded that the splitting arises as a result of j-J coupling.^{16,17} For pure gadolinium, the Gd $5p_{3/2}$ envelope can be fitted with four components at 20.3 eV, 20.9 eV, 22 eV and 23.4 eV and the $5p_{1/2}$ envelope can be fitted with two components at roughly 27.5 eV and 28.3 eV. In other words, the

$j = 3/2$ term couples with the $8s_{7/2}$ to form four multiplets under the Gd $5p_{3/2}$ envelope, because of j - J coupling.^{16,17} This is not seen here for $[\text{Gd}_2(\text{L})_2(\text{ox})_2(\text{H}_2\text{O})_2]$.

This is evident in Figure 2 where the Gd $5d$ core level is fitted according to a j - J photoemission final state coupling scheme (Figure 2a), an L-S photoemission final state coupling scheme (Figure 2b) and the observed j - J photoemission final state coupling scheme (Figure 2c) seen for Gd metal.¹⁶ Even with the inclusion of the configuration interactions (Figure 2c), the largest J angular momentum multiplets, that is to say the $J=5$

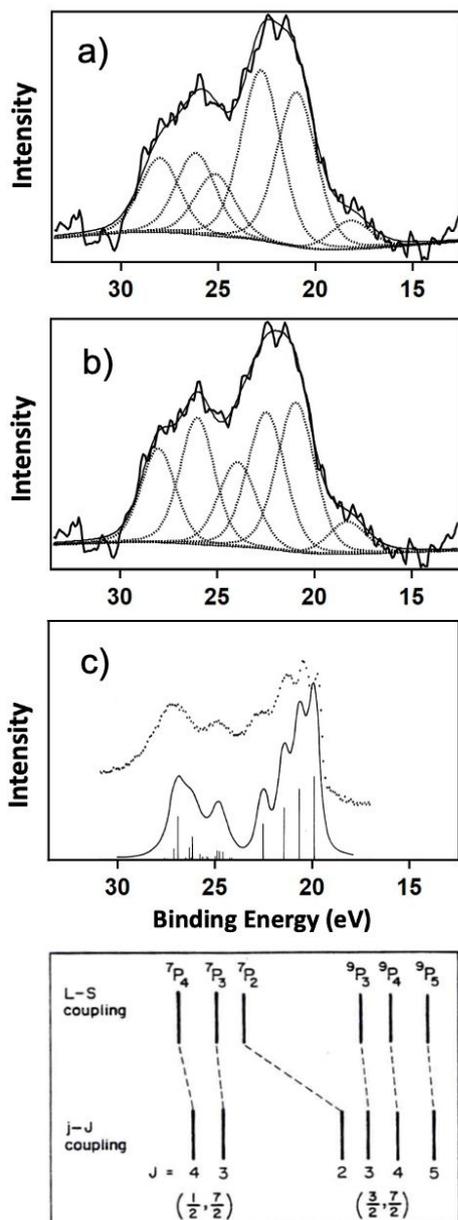


Fig. 2 The X-ray photoemission spectroscopy of Gd, showing the components of the $5p$ core level components at binding energies of 19.3 eV, 21.9 eV, 23.7 eV, 26.1 eV, 27.1 eV and 28.9 eV, based on an LS coupling scheme (a), compared to a fitting scheme more in-line with j - J coupling (b) for $[\text{Gd}_2(\text{L})_2(\text{ox})_2(\text{H}_2\text{O})_2]$. The $5p$ core level spectra for Gd metal, combined with the multiplets based on configuration interaction calculations, are shown for comparison in (c), taken from reference [16]. Binding energies are with respect to the chemical potential (the Fermi level) in terms of E_F .

multiplet in the $5p_{3/2}$ Gd core level envelope and the $J=4$ multiplet in the $5p_{1/2}$ Gd core level envelope, should be the most intense in the j - J photoemission final state coupling scheme.¹⁶ This is true for Gd metal (Figure 2c),¹⁶ but not for $[\text{Gd}_2(\text{L})_2(\text{ox})_2(\text{H}_2\text{O})_2]$, as is evident when we attempt to fit the $5p$ core level spectra to an L-S coupling scheme, as done in Figure 2b. In this context, we cannot reconcile the j - J photoemission final state coupling scheme to the observed the $5p_{3/2}$ and $5p_{1/2}$ Gd core level photoemission features for $[\text{Gd}_2(\text{L})_2(\text{ox})_2(\text{H}_2\text{O})_2]$.

The ground state configuration of Gd is $5s^25p^64f^75d^16s^2$, but since in the valence state of gadolinium is nominally $3+$, the already weak interaction of the $5d$ and $6s$ with the Gd $4f^7$ and $5p^6$ can be ignored. Photoemission from the Gd $5p$ core leave $5p^54f^7$, thus resulting in the 7P_4 (28.9 ± 0.1 eV), 7P_3 (27.1 ± 0.1 eV), and 7P_2 (26.1 ± 0.1 eV) multiplets under the Gd $5p_{1/2}$ envelope and 9P_3 (23.7 ± 0.1 eV), 9P_4 (21.9 ± 0.1 eV) and 9P_5 (19.0 ± 0.1 eV) under the Gd $5p_{3/2}$ envelope, as seen in the fitting of Figure 2. The j - J photoemission final state coupling scheme is not excluded as the multiplets for any large Z system cannot be completely described by L-S coupling or j - J coupling alone. Clearly the situation here, for $[\text{Gd}_2(\text{L})_2(\text{ox})_2(\text{H}_2\text{O})_2]$, is that L-S coupling dominates if only because the the $J=5$ multiplet in the $5p_{3/2}$ Gd core level envelope has a ver weak intensity compared to the other multiplets. We note that this analysis here does not include all the various configuration interactions,^{16,43-45} which are indeed expected for gadolinium.¹⁶ While some of the components have binding energies that overlap with the O $3s$ core level,⁴⁶ the cross-section for this oxygen core level is very weak and the O $3s$ core level components are much broader than the features seen here. Even if there are C $3s$ and O $3s$ contributions to the Gd $5p$ core level spectra seen here (Figure 2), the multiplets still must be dominated by L-S rather than j - J in the final state of photoemission. If the features at 19.0 ± 0.1 eV and 28.9 ± 0.1 eV are wholly due to C $3s$ and O $3s$ contributions, the results still are easier to reconcile with L-S coupling. While in the scenario the 9P_5 multiplet would be assigned to the 23.7 ± 0.1 eV component, but in this case the Gd $5p_{3/2}$ envelope has equal width to the Gd $5p_{1/2}$ envelope, which only occurs if L-S coupling dominates.

For the Gd compound studied here, $[\text{Gd}_2(\text{L})_2(\text{ox})_2(\text{H}_2\text{O})_2]$, the three-fold splitting obtained for both the $5p_{3/2}$ and $5p_{1/2}$ features indicates the $5p$ core level photoemission is dominated by L-S coupling.^{16,17} Strong L-S coupling, resulting in the $5p$ core level ${}^7P_{2,3,4}$ and ${}^9P_{3,4,5}$ final states, seen here in Figure 2, is consistent with the local structure around each Gd atom, summarized in more detail in the supplementary materials. Strong spin-orbital coupling, as indicated by the XPS multiplet structure, will arise from symmetry breaking associated with the bonding environment. If there is no inversion symmetry, spin-orbit coupling is turned on and can be seen in photoemission. In compounds, especially with more ionic bonds, the core level photoemission multiplets can be more dominated by L-S coupling than j - J coupling.^{45,47} So the trend towards L-S is expected, especially if inversion symmetry is lost, as indicated by the crystal structure of Figure 1. This is also consistent with the much broader Gd $5p$ envelope seen in core level photoemission of $[\text{Gd}_2(\text{L})_2(\text{ox})_2(\text{H}_2\text{O})_2]$ compared to Gd

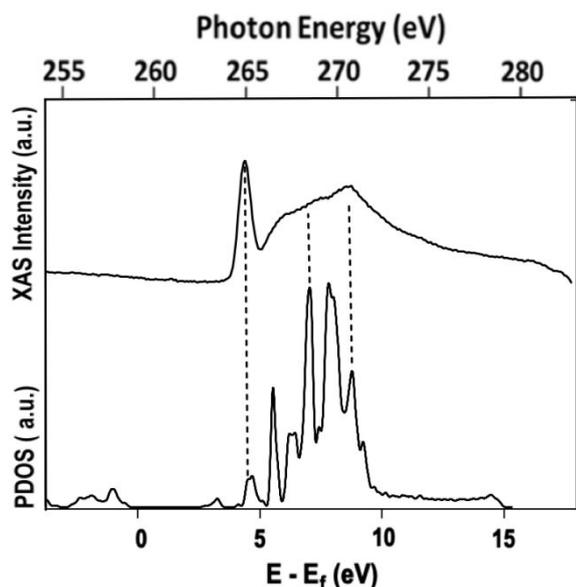


Fig. 3 a) X-ray absorption spectroscopy measurement taken for Gd N_3 edge. b) Partial density of states (PDOS) calculated for the Gd 5d contributions to the unoccupied molecular orbitals of $[\text{Gd}_2(\text{L})_2(\text{ox})_2(\text{H}_2\text{O})_2]$.

metal, as seen in Figure 2. The anisotropy of the multiplet intensities indicates some preferential selection of the specific m_l states indicative of large magnetic moment anisotropy within the ligand field, in agreement with theoretical expectations discussed below. Realistically, because this is a dinuclear complex, exchange coupling matters and quantitatively accurate values of J need to include dynamic correlation effects, which have been neglected as inclusion would require a more extensive consideration of configuration interactions.⁴⁸⁻⁵⁰

5. Electronic Structure and Moment Ordering

X-ray absorption measurements were taken at the Gd N_3 edge, as shown in Figure 3 together with the calculated partial density of states for the 5d orbitals. X-ray absorption spectroscopy is a partial measure of the unoccupied orbitals of the Gd weighted energy levels of interest. In this case it gives an idea about the unoccupied orbitals with strong Gd weight, but as noted elsewhere, there will be both ligand and metal contributions to the unoccupied molecular orbitals. Indeed, in dinuclear molecular systems, the role of the ligand is significant.⁵¹ To ascertain which unoccupied molecular orbitals contain both metal and ligand weight, XAS has to be combined with other spectroscopies,⁵² which has not been done here. The pre-edge feature of the XAS is around 265 eV which can be identified as one sharp peak and this is followed by a broad spectral signal at higher binding energy region, centered around 270 eV. Since this is a Gd 4p adsorption edge, selection rules are restricted to 4p - to 5d and 4 to 6s excitations. As the latter is unlikely and cannot be reconciled with the data in Figure 3, effectively the XAS in this case is probing the unoccupied density of states with strong 5d weight. This is in qualitative agreement with the calculated

Gd 5d partial density of states that contribute to the $[\text{Gd}_2(\text{L})_2(\text{ox})_2(\text{H}_2\text{O})_2]$ unoccupied molecular orbitals, as shown in Figure 3b.

The antiferromagnetic coupling between the two local-moment Gd spins was experimentally confirmed by vibrating sample magnetometry using a DynaCool Physical Properties Measurement System (Quantum Design). Figure 4 shows the saturation magnetization, inverse DC susceptibility, and product of susceptibility and temperature for the warming cycle of $[\text{Gd}_2(\text{L})_2(\text{ox})_2(\text{H}_2\text{O})_2]$. No difference between warming and cooling curves was observed. The saturation magnetization increases significantly with the bias field and decreasing temperature. At around 10 K, the curvature of the $M(H)$ curves changes from positive (paramagnetism) to negative (ferro-/antiferromagnetism) with decreasing temperature indicating a magnetic phase transition. A closer look at the inverse DC susceptibility and the product of susceptibility and temperature allows us to differentiate between paramagnetism, ferromagnetism and antiferromagnetism leveraging the Curie-Weiss law $\chi = C/(T-T_0)$. For paramagnetism the inverse DC

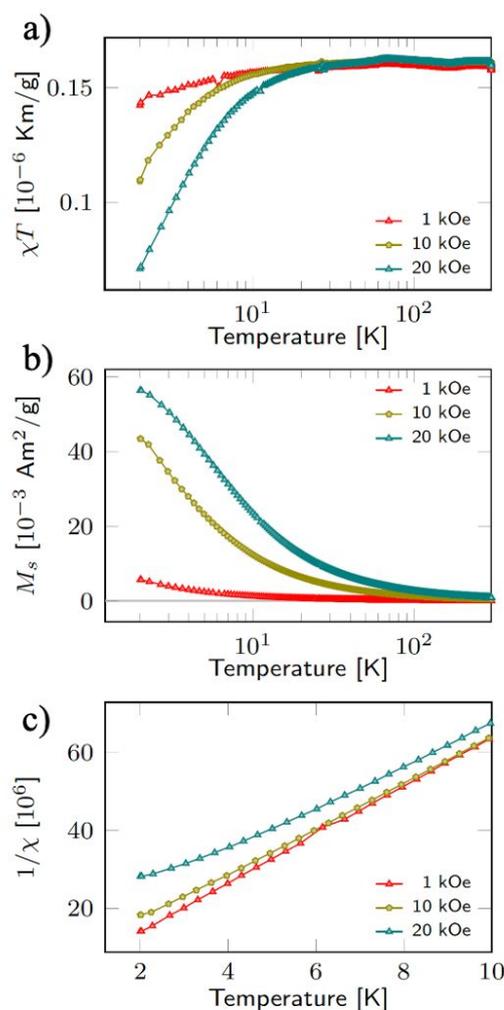


Fig. 4 a) The product of susceptibility and temperature (a), the saturation magnetization (b), and the inverse DC susceptibility (c) for the warming cycle of 17.9 g of $[\text{Gd}_2(\text{L})_2(\text{ox})_2(\text{H}_2\text{O})_2]$.

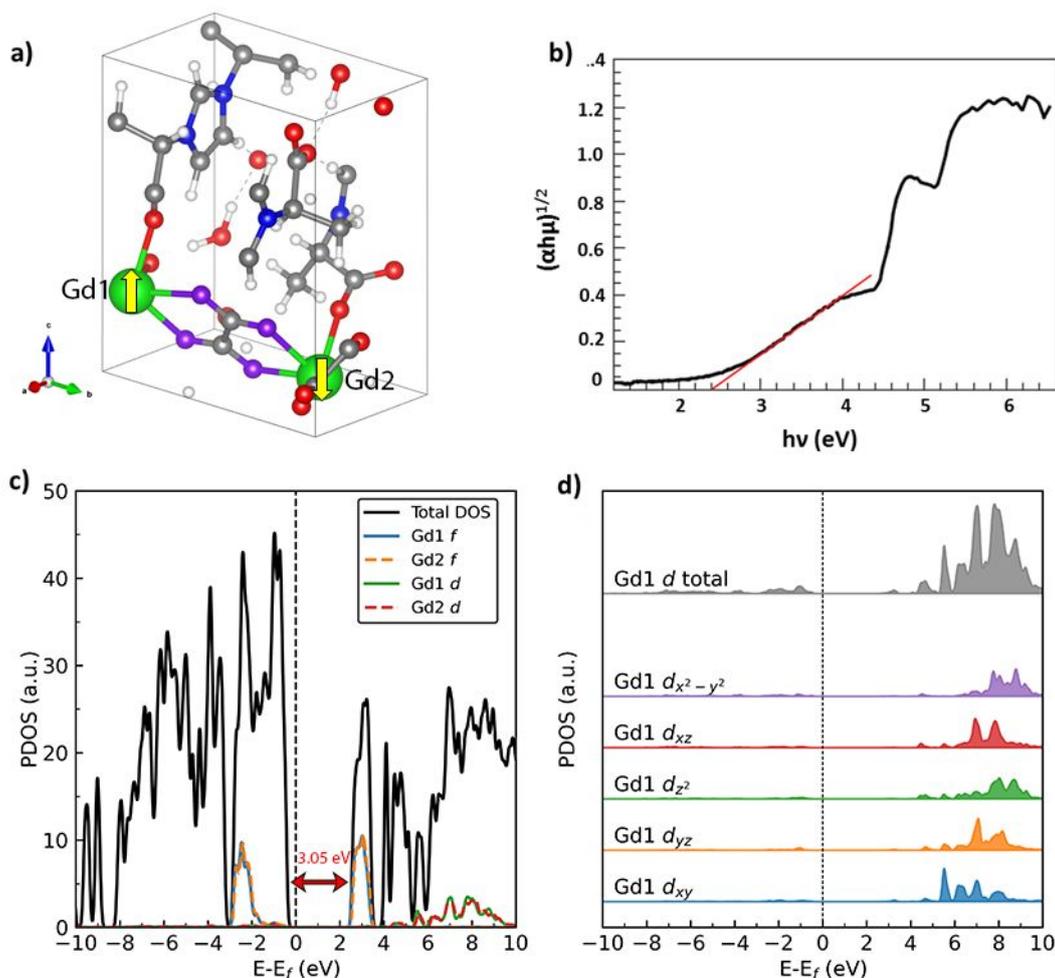


Fig. 5 a) Geometry structure of $[\text{Gd}_2(\text{L})_2(\text{ox})_2(\text{H}_2\text{O})_2]$ with antiferromagnetic ordering. b) Tauc plot obtained from the optical absorption measurements to calculate the optical bandgap. c) Calculated band gap values. d) Partial Gd density of states calculated for Gd 5d contributions to the

susceptibility goes to zero at $T=0$, for ferromagnetism the inverse DC susceptibility goes to zero at finite temperatures ($T>0$), and for antiferromagnetism the plot of the inverse DC susceptibility extrapolates to zero at a negative temperature ($T<0$) leveraging the Curie-Weiss law $\chi = C/(T-T_0)$. The antiferromagnetism causes a stark decline in χT with decreasing temperature at low-temperature and a positive offset of $1/\chi$. Interestingly, the antiferromagnetic contribution appears to become stronger in larger fields and is expected since presumably they align at high temperature with the field.

Density functional theory (DFT) predicts that the antiferromagnetic interaction between the two adjacent Gd atoms has a slightly lower total energy (roughly 3 meV/Gd atom) than a ferromagnetic interaction, as indicated in the schematic Figure 5a. This is consistent with the product of susceptibility and temperature data just discussed. The Gd moment is about the same in both cases, i.e. ferromagnetic and antiferromagnetic with similar calculated moments of approximately 6.8, 7.0, and 6.9 μ_B per Gd atom as predicted by various PBE, PBE+U, and HSE exchange correlation functionals,

respectively. Although these values for the calculated moments are smaller than that of Gd metal (7.3 μ_B), these calculated moments are consistent with the local moment of 6.7 μ_B per Gd atom in the compounds $\text{GdGa}_{35}\text{N}_{36}$, $\text{Gd}_2\text{Ga}_{34}\text{N}_{36}$ and $\text{GdCGa}_{35}\text{N}_{35}$ ⁵³ and consistent with a spin moment resulting from 7 unpaired 4f electron spins. We also found that the total number of 5d electrons is much less than 1e in the isolated Gd atom. The total number of 5d electrons calculated with PBE, PBE+U, and HSE06 are 0.60e, 0.58e, and 0.55e, respectively, and total magnetization contributed from d electrons (projected on m_z) are 0.035, 0.034, 0.025 μ_B , respectively.

From the Tauc plot^{54,55} of the optical absorption shown in Fig. 5b, we estimated the optical gap for $[\text{Gd}_2(\text{L})_2(\text{ox})_2(\text{H}_2\text{O})_2]$ to be indirect and in the region of 2.4 eV (taking $r = 2$ in $(\alpha h\nu)^{1/r}$ in the fitting to the optical absorption plot).^{50,51} The band gap is smaller than the value calculated from DFT, i.e. 3.05, 3.81, and 5.15 eV calculated with PBE, PBE+U, and HSE06 exchange-correlation functional (supplementary Figure S5). The direct gap (when use $r = 1/2$ in $(\alpha h\nu)^{1/r}$),⁵⁴⁻⁵⁶ from optical absorption is however larger at about 4.5 eV.

DFT has provided a basis for assigning the XAS spectra of other molecular magnets to various unoccupied molecular orbitals.⁵² While the comparison of experiment and theory, *vis-a-vis* the band gaps, provide some minor validation of the efficacy of the density functional theory, from a comparison of theory to the X-ray absorption, as seen in Figure 3, it is clear that the excitation from the $4p_{3/2}$ to unoccupied Gd 5d weighted unoccupied orbitals (plotted in Figure 5d) is dominated by $p_{x,y}$ to 5d d_{xz} , $d_{x^2-y^2}$ and d_{xy} . The strong spectral weight in XAS, at the adsorption edge is well resolved and separated from the broad Gd 5d weighted unoccupied orbitals contribution. If all Gd 5d weighted unoccupied orbitals, the edge feature would not be so pronounced. If the broad XAS feature is then the result of transitions to the Gd 5d d_{xz} and $d_{x^2-y^2}$ or 5d d_{xz} and d_{z^2} . The edge then must arise from the Gd 5d d_{xy} , based on the DFT (Figure 5). With this assignment of the XAS edge, the broad XAS feature is more likely coming from the Gd 5d d_{xz} and $d_{x^2-y^2}$ unoccupied molecular orbitals given the XAS line shape.

6. Conclusions

Large spin orbit coupling is inferred from the 5p core multiplets seen in X-ray photoemission and distinguishes $[\text{Gd}_2(\text{L})_2(\text{ox})_2(\text{H}_2\text{O})_2]$ from the gadolinium atom and gadolinium metal^{16,17} where *j*-*J* coupling dominates. The origin of the unusual L-S coupling in the Gd atoms of $[\text{Gd}_2(\text{L})_2(\text{ox})_2(\text{H}_2\text{O})_2]$ is indicative of a loss of inversion symmetry due to the local bonding about each Gd atom and is consistent with the local structure. Theory suggests that antiferromagnetic interactions are favoured while a comparison of theory with experiment indicated that the X-ray absorption at the $4p_{3/2}$ core is dominated by excitations from $p_{x,y}$ to 5d $d_{x^2-y^2}$ and d_{xy} . We anticipate that $[\text{Gd}_2(\text{L})_2(\text{ox})_2(\text{H}_2\text{O})_2]$ will exhibit chiral optical effects where incident circularly polarized light could generate topologically protected spin photocurrents.

Conflicts of interest

There are no conflicts to declare.

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