Magnetic anisotropy of single-ion magnet $(PPh_4)_2[ReF_6] \cdot 2H_2O$

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In the present work we studied the magnetocrystalline anisotropy of two related single-molecule magnets [1] with a single rhenium ion in irregular tilted octahedra $(PPh_4)_2[ReF_6]\cdot 2H_2O$, (1), $(PPh_4)_3$ stands for tetraphenylphosphonium, $(C_6H_5)_4P$), and $[Zn(viz)_4(ReF_6)]$, (2), (viz = 1-vinylimidazole) [2].

All density functional theory (DFT) calculations were performed using the VASP code [3–6] with projector-augmented wave method (PAW) [7], employing Perdew–Burke–Ernzerhof (PBE) version of the generalized gradient approximation (GGA) exchangecorrelation functional [8] and taking into account strong Coulomb correlations *via* rotationally invariant DFT + U approach after Dudarev et al. [9].

In order to estimate single-ion anisotropy (SIA) we performed total energy calculations with spin-orbit coupling (GGA + U + SOC) for different spin directions and mapped these results onto the model, where the SIA is described by the following Hamiltonian:

$$\hat{H}_{\rm SIA} = D \cdot \hat{S}_z^2. \tag{1}$$

The obtained results have shown the easy-plane anisotropy for these $5d^3$ systems with large single-ion anisotropy parameters D equal to 11.7 K for (1) and 16.8 K for (2). Magnetic moments for both complexes are less than expected $3\mu_B$. It can be explained by the covalency effects and substantial spin-orbit coupling. Due to irregular tilted $[\text{ReF}_6]^{2-}$ octahedra, there is a strong $t_{2g} - e_g$ crystal-field splitting of the order of 3.5 eV. Since symmetry of the crystal-field is lower than cubic, t_{2q} levels get an additional splitting onto nearly degenerate xz and yz orbitals, that are lower in energy than xy orbital (see Fig. 1). The spin-orbit coupling mixes the ground state singlet Γ_2 with orbital triplet Γ_5 , lying on 10Dq higher $(t_{2g} - e_g \text{ crystal field splitting pa-}$ rameter in spectroscopy) [10]. This triplet is split by the non-cubic crystal-field onto a doublet, characterized by fictitious orbital moment $\tilde{l}_z = \pm 1$ and having energy Δ_1 , and a singlet with $\tilde{l}_z = 0$ and Δ_0 .

In the second order of the perturbation theory one can take into account the mixing of these Γ_5 states with the ground state (Γ_2) due to the spin-orbit coupling. This admixture splits the ground state into two spin doublets and the value of this splitting is proportional to the spin-orbit coupling constant λ [10]:

$$2D = -\frac{8\lambda^2}{\Delta_0} + \frac{8\lambda^2}{\Delta_1}.$$
 (2)

Using estimation of $\lambda = 320$ meV for Re⁴⁺ [11] and the crystal-field splittings shown in Fig.1 for (PPh₄)₂[ReF₆]·2H₂O, one can see that such a consideration gives a reasonable estimation of D = 14.6 K. This agrees with the obtained single-ion anisotropy parameters D presented above.

Fig. 1. Results of the Wannier function projection of the non-magnetic DFT Hamiltonian for (1). We used the local coordinate system where axes are directed as much as possible to the ligand to calculate on-site energies of different Re 5*d* orbitals

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