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

L. S. Taran[+1)], *V. Y. Elfimova*[*], *S. V. Streltsov*[+*]

[+]*M. N. Mikheev Institute of Metal Physics of Ural Branch of Russian Academy of Sciences, 620137 Yekaterinburg, Russia*

[*]*Institute of Physics and Technology, Ural Federal University, 620002 Yekaterinburg, Russia*

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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**), ($PPh_4$ 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) exchange-correlation 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:

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

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 $[ReF_6]^{2-}$ 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_{2g} 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 ($t_{2g} - e_g$ crystal field splitting parameter 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]:

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

Using estimation of $\lambda = 320$ meV for Re^{4+} [11] and the crystal-field splittings shown in Fig. 1 for $(PPh_4)_2[ReF_6]\cdot 2H_2O$, 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.

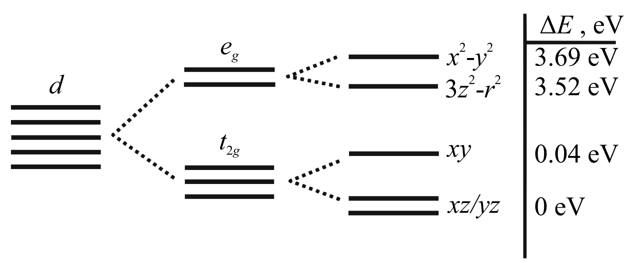

Fig. 1. Results of the Wannier function projection of the non-magnetic DFT Hamiltonian for (**1**). We used the local coordinate system where axes are directed as much as possible to the ligand to calculate on-site energies of different Re $5d$ orbitals

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1)e-mail: taran@imp.uran.ru

1. V. V. Novikov and Yu. V. Nelyubina, Russ. Chem. Rev. **90**, 1330 (2021); 10.1070/RCR5002.
2. K. S. Pedersen, M. Sigrist, M. A. Sørensen, A.-L. Barra, T. Weyhermüller, S. Piligkos, C. Aa. Thuesen, M. G. Vinum, H. Mutka, H. Weihe, R. Clérac, and J. Bendix, Angewandte Chemie International Edition **53**, 1351 (2014); 10.1002/anie.201309981.
3. G. Kresse and J. Hafner, Phys. Rev. B **47**, 558 (1993); 10.1103/PhysRevB.47.558.
4. G. Kresse and J. Furthmüller, Comput. Mater. Sci. **6**, 15 (1996); 10.1016/0927-0256(96)00008-0.
5. G. Kresse and J. Furthmüller, Phys. Rev. B **54**, 11169 (1996); 10.1103/PhysRevB.54.11169.
6. K. Lejaeghere, G. Bihlmayer, T. Björkman et al. (Collaboration), Science **351**, aad3000 (2016); 10.1126/science.aad3000.
7. G. Kresse and D. Joubert, Phys. Rev. B **59**, 1758 (1999); 10.1103/PhysRevB.59.1758.
8. J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **78**, 1396 (1997); 10.1103/PhysRevLett.78.1396.
9. S. L. Dudarev, G. A. Botton, S. Y. Savrasov, C. J. Humphreys, and A. P. Sutton, Phys. Rev. B **57**, 1505 (1998); 10.1103/PhysRevB.57.1505.
10. A. Abragam and B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions*, Clarendon press, Oxford (1970).
11. M. Vijayakumar and M. S. Gopinathan, Journal of Molecular Structure (Theochem) **361**, 15 (1996).