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Embedded cluster calculations on magnetism and spectroscopy of rare-earth high-entropy oxides

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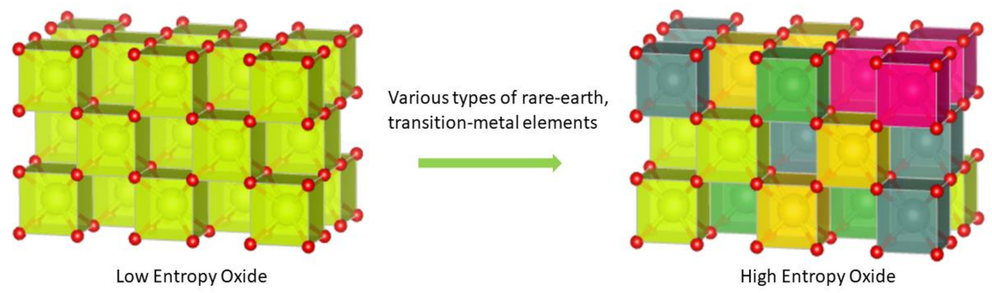
VIRTUAL MATERIALS DESIGN

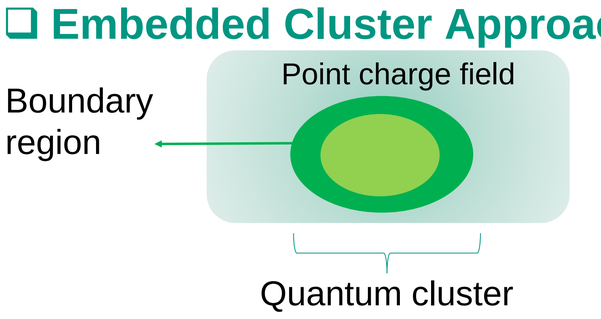
Abstract

High entropy oxides (HEOs) are single-phase oxides with five or more kinds of cations in a near-equiatomic proportion.[1] An increasing attention has been put to the magnetic and spectroscopic properties of HEOs.[2,3] The introduction of open-shell transition-metal and rare-earth elements gives rise to magnetic properties. In our computational approach we start from CeO_2 and investigate the influence of other 4f centers as well as oxygen vacancies. For one and two magnetic centers, the magnetic main axes and temperature dependent magnetic susceptibilities can be calculated with complete active space spin-orbit configuration interaction (CASOCI).[3]



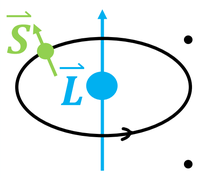
Method

Embedded Cluster Approach

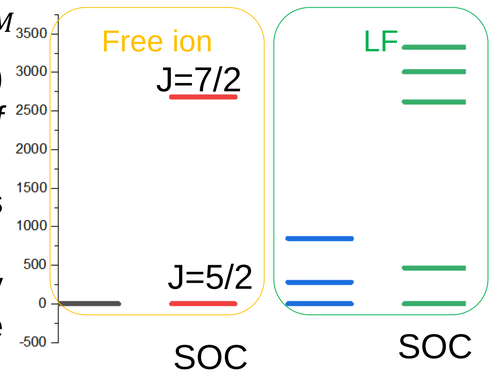


- Long-range electrostatic interactions represented by point charge approximation.
- Positive point charges in the boundary region are equipped with large core electronic core potentials (ECP).

CASOCI $\hat{H} = \hat{H}_{SC} + \hat{H}_{SOC} + \hat{H}_{ZM}$

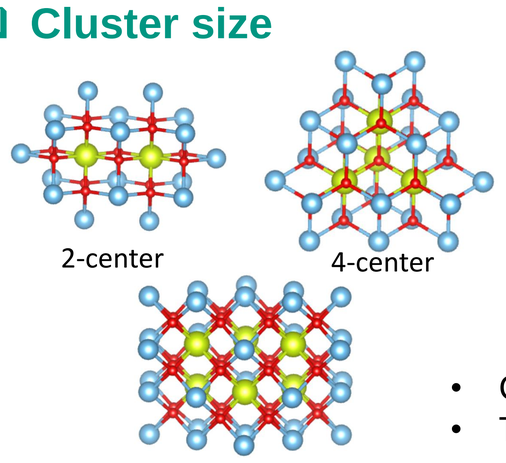


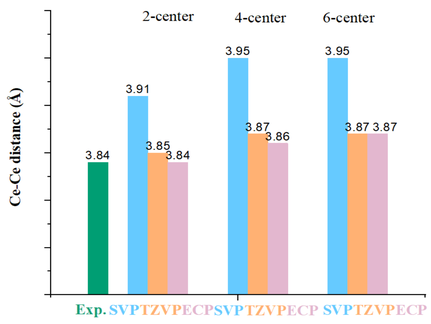
- Spin-orbit coupling (SOC) is considered in the *4f* shell.
- Zeeman interaction is taken into account.
- Magnetic susceptibility and g-tensors can be obtained.



Geometry and electronic structure

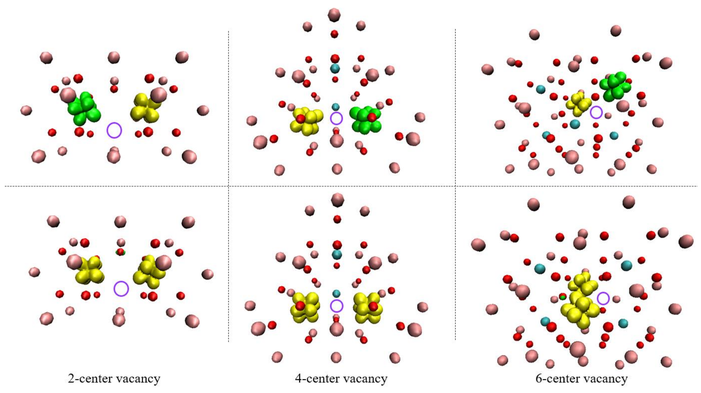
Cluster size





- Cluster size converges quickly.
- TZVP level basis set and ECP give reasonable descriptions.

Oxygen vacancy



Calculated oxygen vacancy formation energy (eV) at B3LYP-DJB3/x2c-TZVPall level based on PBE0-D3BJ/TZVP optimized structure.

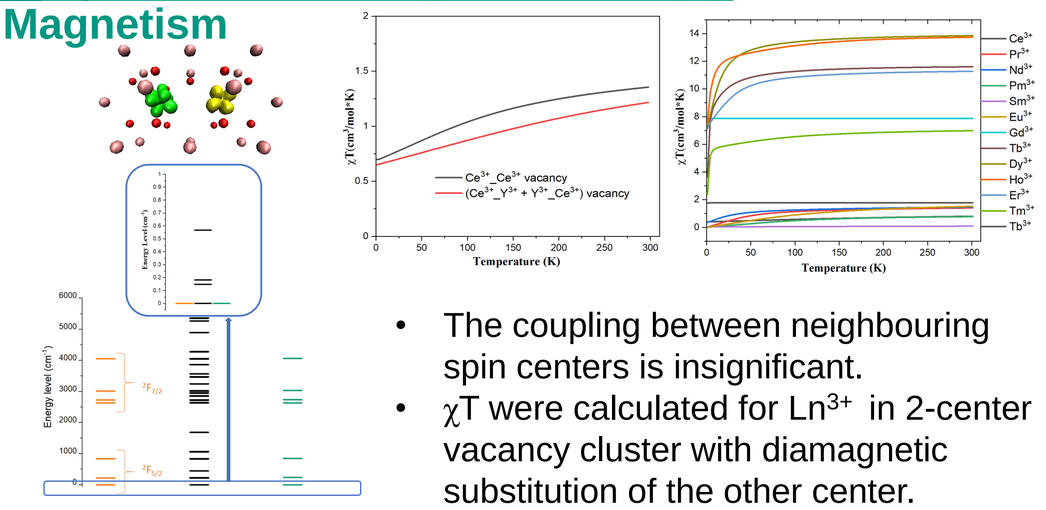
	Closed-shell	singlet	triplet
2-center	7.44	3.92	3.90
4-center	4.89	2.47	2.48
6-center*	4.60	1.88	1.87

*: for 6-center cluster, the structures were optimized at PBE0-D3BJ/ECP.

- Electrons are localized on Ce centers with the creation of oxygen vacancy.

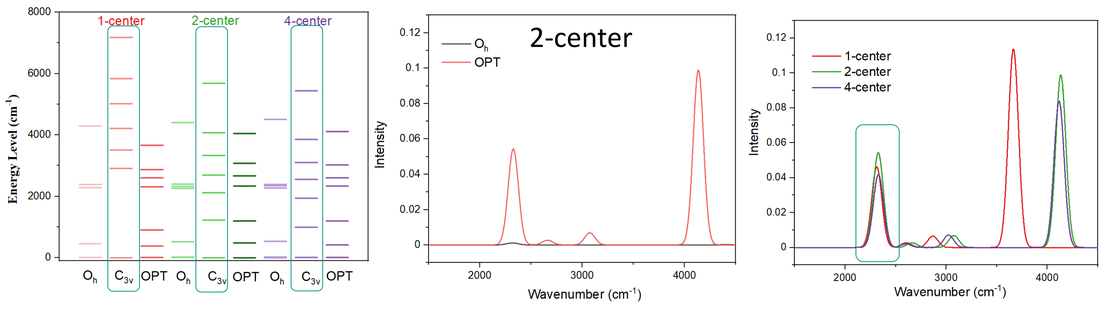
Magnetism and Spectroscopy

Magnetism



- The coupling between neighbouring spin centers is insignificant.
- χT were calculated for Ln^{3+} in 2-center vacancy cluster with diamagnetic substitution of the other center.

Spectroscopy



- Geometry relaxation is essential for a reasonable energy description in the model cluster.
- Laporte-forbidden transitions become optically active upon symmetry reduction.
- Successful prediction of the signature adsorption band.

Conclusion and outlook

- For geometry optimizations large core ECPs for Ce can give satisfactory results.
- Oxygen vacancy structures were optimized resulting in different electronic states.
- In case of oxygen vacancies, the remaining unpaired electrons go to nearby Ce 4*f* orbitals forming Ce^{III}.
- Magnetic coupling between two Ce centers is very small.
- Due to the small coupling of the spin centers, the magnetic susceptibility of the entire cluster can be obtained by a straightforward summation of the susceptibilities of the individual center.

Reference

1. Yeh, J.-W. et al. J. Mater. Res. 33, 3129–3137 (2018).
2. Sarkar, A. et al. Dalton Trans. 50, 1973–1982 (2021).
3. S. Afrin et al. J. Phys. Chem. C 127, 234-247 (2023).
4. Bodenstein, T et al. ChemPhysChem 23, e202100648 (2022).