

Insight from first principles into the stability and magnetism of alkali-metal superoxide nanoclusters

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ABSTRACT

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METRICS

Molybdenum . Density functional theory . Sodium . Basis sets . Band gap

ABSTRACT

Alkali-metal superoxides are gaining increasing interest as $2p$ magnetic materials for information and energy storage. Despite significant research efforts on bulk materials, gaps in our knowledge of the electronic and magnetic properties at the nanoscale still remain. Here, we focused on the role that structural details play in determining stability, electronic structure, and magnetic couplings of $(\text{MO}_2)_n$ ($M = \text{Li}, \text{Na}, \text{and K}$, with $n = 2-8$) clusters. Using first-principles density functional theory based on the Perdew-Burke-Ernzerhof and Heyd-Scuseria-Ernzerhof functionals, we examined the effect of atomic structure on the relative stability of different polymorphs within each investigated cluster size. We found that small clusters prefer to form planar-ring structures, whereas non-planar geometries become more stable when increasing the cluster size. However, the crossover point depends on the nature of the alkali metal. Our analysis revealed that electrostatic interactions govern the highly ionic $M\text{-O}_2$ bonding and ultimately control the relative stability between 2-D and 3-D geometries. In addition, we analyzed the weak magnetic couplings between superoxide molecules in $(\text{NaO}_2)_4$ clusters comparing model Hamiltonian methods based on Wannier function projections onto π_g states with wave function-based multi-reference calculations.