Theoretical Analysis of Magnetism, Orbital, and Lattice Distortions in the Magnetoelectric Candidate Material RbO_2

E. Yamaguchi[1], R. ono[2] and P. Krüger[1]

[1]*Graduate School of Science and Engineering, Chiba university, Chiba, Japan,*

[2]*IAdvanced Science Research Center, Japan Atomic Energy Agency, Japan*

Alkali superoxides such as rubidium superoxide (RbO_2) are ionic crystals composed of alkali metal cations andO_2^-molecules. At low temperatures, a single electron occupies the π^*orbitals of O_2^-, giving rise to S = 1/2 magnetic moments and orbital degrees of freedom associated with the π_x^* and π_y^* orbitals. The interplay between these orbital degrees of freedom, molecular orientations, and lattice distortions leads to complex low-temperature properties, whose magnetic and orbital states remain incompletely understood.

I performed first-principles calculations including crystal-field effects and spin-orbit coupling using the GGA-PBE functional. For the crystal structure, I used the experimentally determined lattice constants and atomic positions. By constructing Wannier functions from the band structure, I extracted hopping parameters and derived a two-orbital Hubbard model. Assuming a Mott-insulating state, I introduced superexchange interactions and analyzed the magnetic and orbital properties using a low-energy effective model.

The results show that the low-temperature structure exhibits antiferromagnetic (AFM) interactions for the nearest- and next-nearest-neighbor bonds within the ab plane, accompanied by uniform orbital ordering along the $(1\bar{1}0)$ direction. Lattice distortions generate two types of interlayer bonds: a short bond ($3'$) with a strong FM out-of-plane exchange component $\mathcal{J}_3^z$, and a long bond (3) with an in-plane AFM interaction $\mathcal{J}_3$ that is about 1.4 times stronger than $\mathcal{J}_1$. The resulting ground state is an AFM structure with antiparallel spin alignment between layers.

I reveal that structural changes between the room-temperature and low-temperature phases—namely, an approximately 4% lattice contraction and a monoclinic distortion of the angle γ by about $0.57°$—significantly affect the exchange interactions. In particular, bond angle variations are found to be more influential than bond-length changes, indicating that the magnetism of RbO_2 is highly sensitive to subtle lattice distortions.

References

[1] M. Miyajima, Ph.D. thesis, Okayama Univ. (2021).