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First-Principles EFG Calculations and PAC Probing of Octahedral Distortions in AYTiO4 (A = Na, Ag) Layered Perovskites

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The engineering of material properties in perovskite-related oxides is strongly influenced by distortions of the oxygen octahedral framework. In Ruddlesden-Popper (RP) compounds such as $AYTiO_4$ (A = Na, Ag), the interplay between competing octahedral distortions gives rise to functionalities like acentricity and negative thermal expansion (NTE). While octahedral rotations are common in simple ABO_3 perovskites, the emergence of acentric or ferroelectric behavior, via inversion symmetry breaking, is rare except in layered perovskite structures.

A notable example is the A-site ordered RP compound $NaRTiO_4$ (R = rare-earth metal), long considered centrosymmetric for R = Y. However, Akamatsu et al. \cite{akamatsu2014} showed that its low-temperature phase adopts the acentric space group $P\bar{4}2_1m$ (113). In a separate study, Yoshida et al. investigated octahedral distortions in the $AgRTiO_4$ family and revealed biaxial NTE behavior. Unlike typical NTE materials, DFT calculations indicated that this biaxial NTE results from the competition between octahedral rotation and deformation \cite{yoshida2022}.

To probe these effects at the atomic scale, we employed Perturbed Angular Correlations (PAC) spectroscopy on $NaYTiO_4$ and $AgYTiO_4$ across a broad temperature range (10–1200 K). PAC enabled us to follow the evolution of the hyperfine electric field gradient (EFG) at the A-site nuclei, offering detailed insights into local structural distortions and temperature-driven phase transitions.
PAC has recently demonstrated its effectiveness in resolving oxygen distortions in RP systems, providing direct confirmation of the corkscrew-like atomic mechanism underlying NTE in these layered perovskites \cite{rocha2020}.

Furthermore, we performed \textit{ab-initio} calculations of the EFGs in these layered oxides an area still largely unexplored in the literature. The EFG sensitivities to different crystallographic symmetries (P4/nmm (s.g. 129), $P\bar{4}2_1m$ (s.g. 113), Pbcm (s.g. 57)) were assessed and compared with total energies and lattice parameters from previous structural refinements based on synchrotron and neutron diffraction data \cite{akamatsu2014,yoshida2022}. Comparing experimental PAC data with simulated EFGs enables the unambiguous identification of the dominant octahedral distortions in these systems.

In summary, we will show how the comparison between experimental EFG data and ab initio EFG simulations may enable the identification of the dominant octahedral distortion modes across temperature, possibly providing insights into the structural mechanisms driving the functional properties of these layered perovskites.

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