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Meeting-report

Atomic-Resolution Analysis of 2-D and Thin Film Quantum Materials

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The recent discovery of superconductivity in thin-film materials, including nickelates [1], has sparked renewed interest in Ruddlesden-Popper (RP) oxides, $A_{n+1}B_nO_{3n+1}$, where A is an alkaline earth or rare earth, B is a transition metal, and n = 1, 2, 3, …, ∞). Such RP phases contain the structural motif of perovskite-like, *n*-layer slabs that are separated by double rocksalt layers. The RP nickelates $La_{n+1}Ni_nO_{3n+1}$ evolve from insulating, charge- and spin-stripe ordered states for n = 1, to charge and spin-density wave states for n = 2 and n = 3, to a metallic, Pauli paramagnetic state for n = ∞ [2, 3]. High-temperature superconductivity has recently been reported for n = 2 and n = 3 compounds subjected to pressure, with n = 2 $La_3Ni_2O_7$ having a maximum reported $T_c \approx 80$ K at 14 GPa and n = 3 $La_4Ni_3O_{10}$ $T_c \approx 25$ K at 38 GPa [4, 5].

In this contribution, we will discuss our recent discovery of a new polymorphic RP phase in bulk crystals of $La_3Ni_2O_7$. While the well-known n = 2 RP $La_3Ni_2O_7$ polymorph adopts a uniform "2222" stacking of bilayers (Figure 1a), the newly discovered polymorph assumes a novel stacking sequence in which single-layer and tri-layer blocks of NiO_6 octahedra alternate in a "1313" sequence (Figure 1b). Single crystals of $La_3Ni_2O_7$ with the 1313 were grown using the floating zone technique and transport measurements on these RP-phase crystal reveal its metallic character and the signature of a charge density wave (CDW) at T ≈ 134 K [6]. Samples were prepared for STEM analysis using a cryo-FIB/SEM at UIC, the ThermoFisher Helios 5CX, equipped with an Aquilos cryo-stage and a Leica vacuum cryo transfer system. Atomic-resolution STEM and EELS analysis is performed using the aberration-corrected JEOL ARM200CF at UIC. A Gatan double-tilt LN_2 stage is available, allowig for atomic-resolution imaging and spectroscopy analyses at temperatures around 90 K.

Figures 2a) and b) shows atomic-resolution high-angle annular dark field (HAADF) images of both the 1313 and the 2222 $La_3Ni_2O_7$ RP phases with their distinct stacking sequence of perovskite-like and rocksalt layers. Figure 2c) shows EELS data of the O *K*-edge taken from the different layers in the 1313 RP phase. A comparison to standard perovskite oxide nickelates reveals the different Ni valence states as a function of the Ni position within the 1313 stacking sequence. We also note that stacking faults in both the 2222 and 1313 crystals appear to affect the oxygen octahedral tilts in the quasi-perovskite layers.

Atomic-column resolved annular bright-field imaging and EELS will be used to resolve the possible presence of octahedral distortions in the bulk crystal and at the observed stacking faults. In-situ cryo-STEM will be used to characterize the emergence of the CDW at 134 K. We will discuss how the possible competition between the different phases in $La_3Ni_2O_7$, specifically the 13123 and 2222 RP phases, as well as other possible new polymorphs, yet to be discovered, could be a source of superconductivity in such novel nickelate thin-film or bulk materials [7].

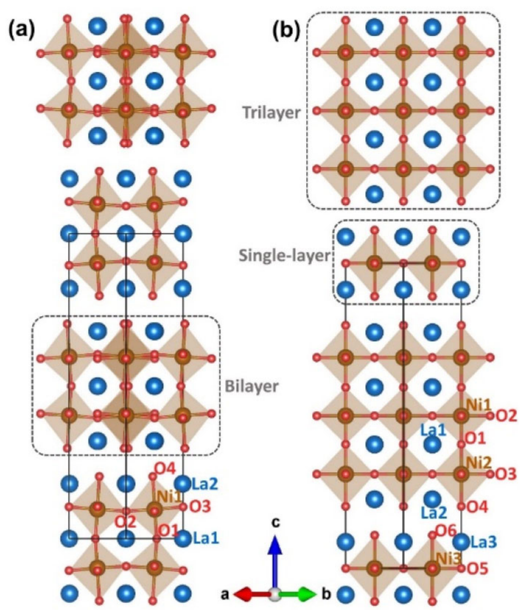

Fig. 1. Model of the crystal structures for the two RP polymorphs a) the $La_3Ni_2O_7$ 2222 and b) the 1313 phase.

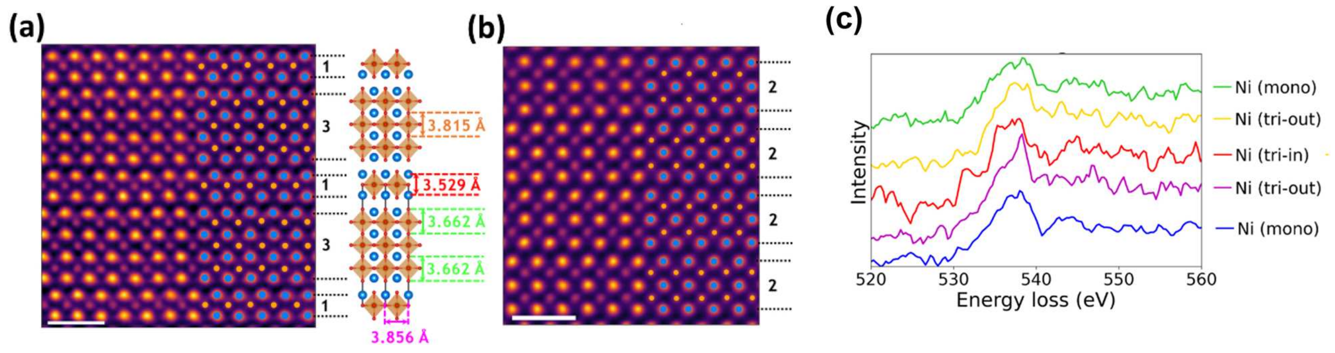

Fig. 2. Atomic-resolution STEM HAADF images of the $La_3Ni_2O_7$ a) 1313 and b) 2222 RP polymorphs. c) Atomic-column resolved EELS data of the O K-edge across a 1313 RP unit-cell, showing distinct near-edge fine-structures, expected for the different Ni valence states.

References

1. D Li *et al.*, *Nature* **572**(7771) (2019), p. 624.
2. CH Chen *et al.*, *Physical Review Letters* **71**(15) (1993), p. 2461.
3. J Xu *et al.*, *Physical Review B* **46** (10) (1992), p. 6382.
4. H Sun *et al.*, *Nature* **621** (7979) (2023), p. 493.
5. M Zhang *et al.*, arXiv:2311.07423 (2023).
6. X Chen *et al.*, *Journal of the American Chemical Society* **146**(**6**) (2024), p. 3640.

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