

Supporting Information

EXAFS evidence for the spin-phonon coupling in monoclinic PrNiO₃ nickelate perovskite

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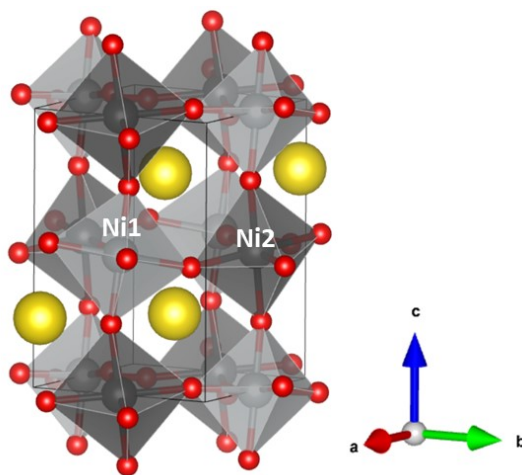
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EXAFS model for PrNiO₃ nickelate

Structural aspects from XRD

PrNiO₃ nickelate is described at 10 K by the monoclinic space-group $P2_1/n$, being characterized by the charge disproportionation between Ni1 (Ni^{+3+ δ}) and Ni2 (Ni^{+3- δ}) sites, with the factor $\delta \neq 0$ (see Fig. S1). When we evaluated the distances Ni–O, three sets of pair-distances for both Ni1 and Ni2 elucidating the occurrence of two octahedra with average distances $\langle \text{Ni1–O} \rangle = 1.912(7)$ Å and $\langle \text{Ni2–O} \rangle = 1.983(7)$ Å could be discriminated from high-resolution synchrotron X-ray diffraction.¹ The same data acquisition protocol was repeated at 295 K to characterize the orthorhombic $Pbnm$ phase, showing instead three sets of Ni–O distances for the single Ni within the structure (average distance $\langle \text{Ni–O} \rangle = 1.942(3)$ Å), due to the loss of the charge disproportionation above $T = 130$ K. In addition, the octahedral unit [NiO₆] does not have appreciated distortion, being more symmetric in the orthorhombic phase when compared to those from the monoclinic phase.

Monoclinic unit-cell at 10 K



<i>Monoclinic</i> $P2_1/n$			
Ni1–O distance (R, Å)		Ni2–O distance (R, Å)	
2 × Ni1–O1	1.875(7) Å	2 × Ni2–O1	2.011(7) Å
2 × Ni1–O2	1.974(7) Å	2 × Ni2–O2	1.947(7) Å
2 × Ni1–O3	1.887(7) Å	2 × Ni2–O3	1.990(7) Å
$\langle \text{Ni1–O} \rangle$	1.912(7) Å	$\langle \text{Ni2–O} \rangle$	1.983(7) Å

Fig. S1: Representation of the monoclinic unit cell of PrNiO₃ at 10 K together with the list of pair-units Ni–O extracted from the structural refinement¹.

Orthorhombic unit-cell at 295 K

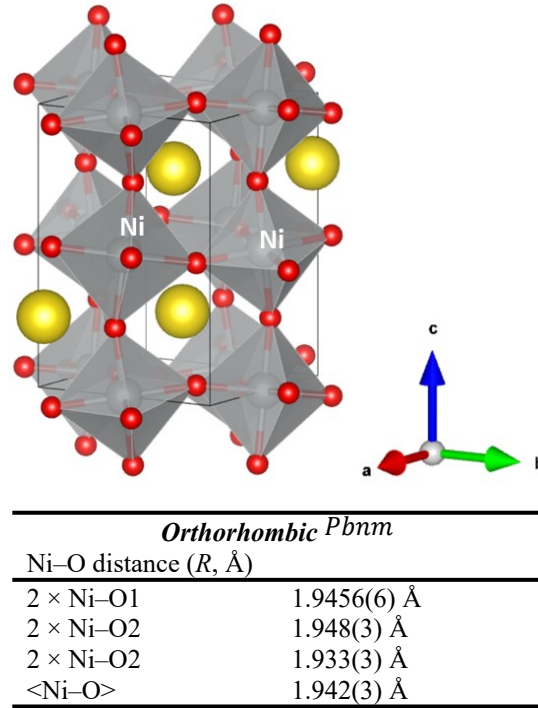


Fig. S2: Representation of the orthorhombic unit cell of PrNiO_3 at 295 K together with the list of pair-units Ni–O extracted from the structural refinement ¹.

Building the EXAFS model

To build our EXAFS model at 10 K (for the monoclinic phase), we have observed that 6 paths of Ni–O (multiplicity of 2 for each one) are needed for a precise structural description; however, such a description is not reasonable for a conventional EXAFS analysis in view of few factors, including spectral resolution, and available windows in k and R spaces. To overcome it, we considered that among the 6 paths (CN = 2 for each), we may define two sets of Ni–O distances, namely: $\text{Ni}_a\text{–O}_{1a} \approx 1.89$ Å (CN = 2) and $\text{Ni}_a\text{–O}_{2a} \approx 1.97$ Å (CN = 4) (see Table above for monoclinic unit-cell). We named both paths as $\text{Ni}_a\text{–O}_{1a}$ and $\text{Ni}_a\text{–O}_{2a}$ (see the main text), respectively. The definition of the coordination numbers (CN) was based on the distribution of pair-distances, e.g. the monoclinic phase has 4 pairs with $R < 1.89$ Å, while 8 pairs have $R > 1.89$ Å from the 12 pairs available. Then, after the insulator-metal transition, one may expect that both paths became equal with CN = 6, which is the feature of the orthorhombic phase $Pbnm$. Fig. S3 shows a sketch of the local structure around the Ni absorber for both monoclinic and orthorhombic phases, which culminated in the EXAFS model used here.

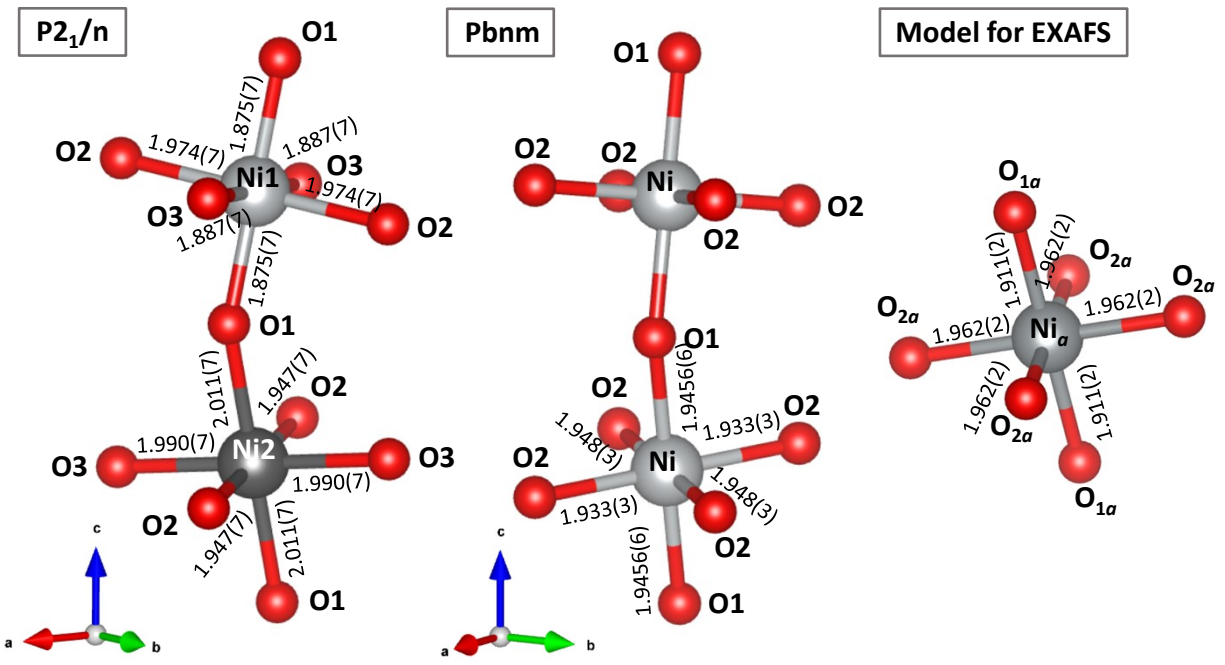


Fig. S3: Sketches of the local structure of PrNiO₃ nickelate in both monoclinic and orthorhombic crystal structures, highlighting the all the pair-units Ni–O. From this, an average octahedral unit was used as initial parameters to describe the EXAFS oscillations in PrNiO₃.

References

¹ J. E. Rodrigues, A. D. Rosa, G. Garbarino, C. Dejoie, Y. Mijiti, T. Irifune, N. M. Nemes J. L. Martínez, M. Mezouar, J. A. Alonso, O. Mathon. *In preparation*, 2022.