

## MS15-P5 Lattice distortions in PrNiO<sub>3</sub> across the metal-to-insulator transition analyzed using the “amplimodes” approach

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The most significant feature of the RNiO<sub>3</sub> perovskite family ( $R=Y$  or rare earth  $\neq La$ ) is a metal to insulator phase transition at a critical temperature ( $T_{MIT}$ ) which systematically increases by decreasing the size of the  $R$ . The electronic localization at  $T_{MIT}$  is associated with a subtle structural phase transition, which involves the splitting of the single Ni site of the high temperature metallic phase (SG  $Pbmm$ ) into two non-equivalent sites, and decreases the symmetry of the unit cell from orthorhombic to monoclinic (SG  $P2_1/n$ ). The mechanism(s) at the origin of the MIT in this system is presently subject of an intense debate. However, several experimental results such a gigantic <sup>16</sup>O,<sup>18</sup>O isotope effect on  $T_{MIT}$  point out towards a strong coupling between the lattice and the electronic degrees of freedom.

Here we report a detailed neutron powder diffraction study aimed to re-investigate the evolution of the crystal structure of the first member of the series (PrNiO<sub>3</sub>). For this purpose we collected high resolution data at the constant- $\lambda$  diffractometer D2B (ILL, Grenoble, France), and high-Q data at the time-of-flight diffractometer SEPD (IPNS, Argonne National Laboratory, USA). The two sets of data were simultaneously refined using a common structural model and the novel “amplimodes” formalism [2,3] implemented in the Rietveld analysis suite FullProf [4]. Instead of describing the asymmetric unit with fractional atomic coordinates, this formalism involves a parametrization of the structural distortions in terms of symmetry-allowed distortion modes, defined as correlated atomic displacements which transform according to the irreducible representations of parent SG. The amplitudes of the different breathing, rotation and distortion modes are obtained directly in Å from the fit, allowing the identification of the main distortion modes involved in the transition. In the case of PrNiO<sub>3</sub> we could successfully identify such modes, their amplitudes, and the magnitude of the anomalies that they undergo at  $T_{MIT}$ . We could also observe the appearance of an additional breathing mode below  $T_{MIT}$  directly related with the Ni positions splitting and the concomitant charge redistribution.

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## MS15-P6 Role of lithium diffusion on thermal expansion of Li<sub>0.4</sub>WO<sub>3</sub> bronze

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Diffusion of interstitial cations in ionic conductors plays roles on the thermal expansion [1,2], which is of prime importance for the functionality of the materials at a given temperature. Herein we report the anomalous lattice thermal expansion of Li<sub>0.4</sub>WO<sub>3</sub> bronze. The polycrystalline sample was produced by solid state synthesis in a silica tube at low pressure and 973 K. The sample was characterized by in-house X-ray and time-of-flight neutron powder diffraction (NPD) as well as Raman spectroscopy. The as-synthesized Li<sub>0.4</sub>WO<sub>3</sub> crystallized in the  $Im\bar{3}$  space group [3], where the  $6b$  position (8-fold) is partially occupied by lithium and the  $2a$  (12-fold) is found to be vacant. In the  $6b$  site four planar oxygen atoms construct a smaller aperture of 26.7 pm, and the  $2a$  site a larger cavity of 39.5 pm for possible lithium diffusion. Temperature-dependent NPD data Rietveld refinement showed that the Li<sup>+</sup> cations preferentially diffuse from the  $6b$  into  $2a$  site between 300 K and 500 K, which supports the ionic conductivity of some LiWO<sub>3</sub> bronzes at high temperatures [4] and diffusion based phase transition at ambient condition [3]. Thus at this temperature regime a statistical equilibrium (dynamic disorder) exists between two occupancy possibilities for Li<sup>+</sup> cations, leading to increase the LiO<sup>n</sup> coordination as well as the averaged Li-O distance from 245 pm ( $6b$ , shortest distance 219 pm) to 265 pm ( $2a$ ). A sharp minimum was observed at 425 K for the temperature-dependent lattice thermal expansion coefficient (TEC) which does not show high temperature saturation. The low-temperature metric expansion could be modeled using a single Debye temperature. The observed data clearly depart from this model line once in the mid-range due to lithium diffusion and again at high-temperatures due to strong anharmonicity. Using an additional Debye spectrum with a low perturbed quantum anharmonicity term the high-temperature anomaly could be successfully modeled [5]. The change of the bulk modulus for the lithium diffusion was also discussed.

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