

## Poster Presentation

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#### *1D to 2D Na-ion Diffusion Linked to Structural Transitions in Na<sub>0.7</sub>CoO<sub>2</sub>*

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One of the most important scientific problems faced by our society is how to convert and store clean energy. In order to achieve a significant progress in this field we need to understand the fundamental dynamical processes that govern the transfer of energy on an atomic scale. For many energy devices such as solid-state batteries and solid-oxide fuel cells, this means understanding and controlling the complex mechanisms of ion diffusion in solid matter. Because of the unusual evolution of correlated electronic properties (frustrated magnetism and superconductivity), the layered Co-oxide family Na<sub>x</sub>CoO<sub>2</sub> (0 < x < 1), object of this work, has been extensively studied during the last decade. More recently it has also attracted the attention of applied sciences, mainly because of its structural similarity with Li<sub>x</sub>CoO<sub>2</sub>, one of the most common Li-ion battery electrodes. In view of the larger abundance of Na in the earth crust with respect to Li, Na-ion batteries enjoy an increased attention. Hence we decided to investigate the Na-ion diffusion in this material, whose possible use as cathode for solid-state rechargeable batteries has recently been proposed [1]. The present study reports the observation of a crossover from quasi-1D to 2D Na-ion diffusion in Na<sub>0.7</sub>CoO<sub>2</sub>. High resolution neutron powder diffraction data indicate the existence of two structural transitions at T<sub>1</sub>=290K and T<sub>2</sub>=400K [2]. We present here evidence indicating that both transitions are closely related to changes in the Na-ion mobility. Analysis of the anomalies in the Na-Na distances, the Debye-Waller factors and the scattering density in the paths connecting neighbouring Na sites strongly suggest that Na-ion diffusion starts at T<sub>1</sub>, although for T<sub>1</sub><T<T<sub>2</sub> it occurs preferentially along quasi-1D paths. A fully isotropic diffusion is only observed for T>T<sub>2</sub>, coinciding with the equalization of all first-neighbor Na-Na distances in the structure [2]. These findings provide new insight on the subtle mechanisms controlling the Na-ion diffusion in the Na<sub>x</sub>CoO<sub>2</sub> family and could be used for the design of related energy materials with improved functional properties.

Fig. 1. Fourier difference maps of the z = 0.25 Na planes at T = 50, 320 and 450 K showing the evolution of the residual scattering density in the paths connecting the Na<sub>1</sub> and Na<sub>2</sub> sites (from ref.[2]).

[1] A. Bhide et al., *Solid State Ionics* 192, 360 (2011), [2] M. Medarde et al. *PRL* 110, 266401 (2013)

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