

Direct Visualization of The Jahn–Teller Effect Coupled to Na Ordering in $\text{Na}_{5/8}\text{MnO}_2$

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The cooperative Jahn-Teller effect (CJTE) is the correlation of distortions arising from individual Jahn-Teller (JT) centers in complex compounds. The effect usually induces strong coupling between the static or dynamic charge, orbital and magnetic ordering, which has been related to many important phenomena such as colossal magnetoresistance and superconductivity. Here we report a $\text{Na}_{5/8}\text{MnO}_2$ superstructure with a pronounced static CJTE which is coupled to an unusual Na vacancy ordering [1]. We visualize this coupled distortion and Na-ordering down to the atomic-scale by scanning transmission electron microscopy (STEM) as shown in Figure 1. The Mn planes are periodically distorted by a charge modulation on the Mn stripes measured by atomic resolution STEM-EELS (electron energy loss spectroscopy) as shown in Figure 1, which in turn drives an unusually large displacement of some Na ions through long-ranged Na-O-Mn³⁺-O-Na interactions into a highly distorted octahedral site. At lower temperatures, magnetic ordering appears, in which Mn atomic stripes with different magnetic couplings are interwoven with each other. Our work demonstrates the strong interaction between alkali ordering, displacement, and electronic and magnetic structure, and underlines the important role that structural details play in determining electronic behavior.

NaTMO_2 ($TM = 3d$ transition metal ions) compounds with alternating Na and TM layers have been studied extensively for their potential application in rechargeable batteries or as the parent materials of the superconductive cobaltate. Na can be electrochemically and reversibly removed from these materials creating Na_xTMO_2 ($0 < x < 1$) compounds in a process called de-intercalation. Superstructures due to Na-vacancy (V_{Na}) ordering have been observed and identified to be dominated by the electrostatic interactions in Na_xVO_2 and Na_xCoO_2 . However, Na_xMnO_2 is expected to be more complicated as it mixes Mn³⁺ ions, which display one of the largest JT distortions in transition metal compounds, and forms antiferromagnetic (AF) Mn³⁺ atomic stripes, with Mn⁴⁺ ions, which are not JT active and can form ferromagnetic (FM) or AF nearest neighbor couplings, depending on the competition between different direct and indirect exchange mechanisms. As such, Na_xMnO_2 is well suited to study the interplay between the V_{Na} ordering, CJTE and the magnetic properties.

There have been continuous efforts to directly visualize the CJTE utilizing S/TEM. Here, electron diffraction, synchrotron XRD, density functional theory (DFT) and aberration-corrected atomic resolution STEM imaging are used to determine the superstructure of electrochemically formed $\text{Na}_{5/8}\text{MnO}_2$, and to visualize in sodium intercalation compounds the cooperative distortion of the Mn JT centers and their coupling to Na ordering. Rather than being dominated by electrostatic interactions, we show direct experimental evidence from STEM imaging that the superstructure in $\text{Na}_{5/8}\text{MnO}_2$ is mainly controlled by Jahn-Teller distortions which induce specific long-ranged Na— V_{Na} interactions through Mn charge and d -orbital orderings. We use neutron powder diffraction, magnetic susceptibility measurements and density functional theory (DFT) computations to demonstrate that a “magnetic stripe sandwich” structure is formed at low temperatures, which causes a dramatic change of the magnetic properties.

References:

[1] Li, X. *et al.* Direct visualization of the Jahn–Teller effect coupled to Na ordering in $\text{Na}_{5/8}\text{MnO}_2$. *Nat. Mater.* **13**, 586–592 (2014).

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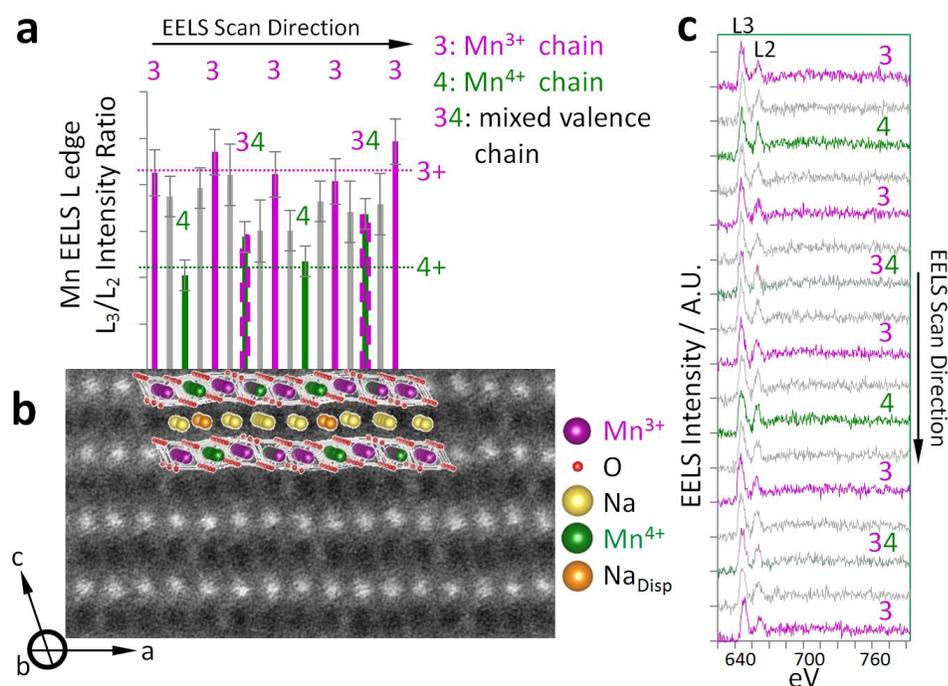


Figure 1. Atomic resolution STEM image visualizes CJTE and STEM-EELS shows Mn charge ordering. a) The Mn EELS L₃/L₂ peak ratio at each Mn [010] atomic column site along the STEM-EELS scanning direction of [100]. The dashed lines show the ratios corresponding to the standard samples of Mn₂O₃ and MnO₂. b) STEM image along [010] shows the periodic distortion of the Mn *ab* plane and the intensity modulation of the Na plane that agrees quantitatively with the superstructure model. c) The 17 Mn L₂₃-edge EEL spectra after background subtraction that give the L₃/L₂ ratios shown in (a).