Resolving dynamic JT distortion with EXAFS in NaNiO2 – experimental report

2023/09/18, Liam A. V. Nagle-Cocco

Key points

- We had previously collected neutron Pair Distribution Function data which showed that the local Jahn-Teller distortions in NaNiO2 disappeared at the same temperature where there is a monoclinic->rhombohedral transition with heating. This result is surprising due to previous literature [1] on LaMnO3 which implies that Jahn-Teller distortions typically persist locally even when they vanish from the average structure.
- To explain this discrepancy, we hypothesized that in the rhombohedral phase the Jahn-Teller distortion is dynamic at a timescale rendering it invisible to neutron Pair Distribution Function. The aim of this EXAFS experiment was to test this hypothesis.
- Our findings are not consistent with our hypothesis, as our EXAFS data appears entirely consistent with our neutron Pair Distribution Function data (see Fig. 1). We therefore conclude that the Jahn-Teller distortion in $NaNiO_2$ vanishes locally as well as in the average structure.
- This result is interpreted in terms of the triangular lattice in NaNiO2, as compared with the square lattice in LaMnO3. The configurational entropy is subextensive for orbital disorder on a triangular lattice [2], and so a "displacive" transition (by analogy with ferroelectrics) is favoured over an "order-disorder" transition in which Jahn-Teller effects persist locally.
- A publication is in preparation but will require further beamtime under pressure to show that this effect is intrinsic to the lattice, as we have shown with variable-pressure diffraction obtained in other beamtime at I15, Diamond Light Source [2] that the Jahn-Teller distortion disappears in the average structure above 22 GPa of pressure

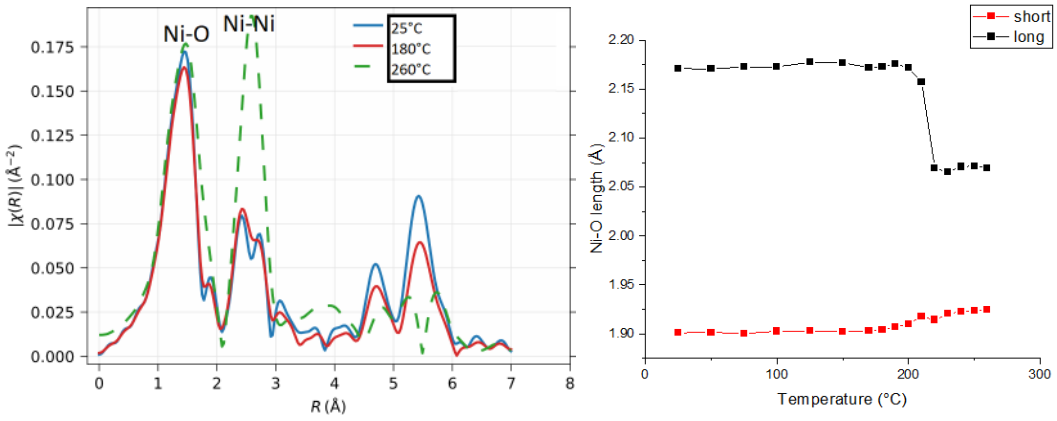

Fig. 1: EXAFS data at some temperature points showing the difference in Ni-O and Ni-Ni peak-shape in the Jahn-Teller-distorted and undistorted temperature regimes (left). A plot of Ni-O bond length from FEFF fitting with temperature using a JT-distorted monoclinic model; above ~210°C, the distorted model shows overlap between long and short bonds and is no longer a better fit compared with an undistorted model (right).

Data analysis

The data was analysed using XRayLarch [3].

Below the Jahn-Teller transition, the distortion changes the NiO_6 octahedra by splitting the Ni-O bond lengths such that there are 4 short and 2 long bonds, and also splitting of the bond lengths of the Ni-Ni bonds in the Ni sublattice. This was modelled using a monoclinic space group in Larch.

The high-temperature structure was modelled using a rhombohedral space group with a single Ni-O and single Ni-Ni length. We also tested a pseudo-orthorhombic structure with an undistorted Ni sublattice (a single Ni-Ni length) but two different Ni-O bond lengths, which would be consistent with a dynamic Jahn-Teller distortion, and a fully monoclinic structure.

We found that at low temperatures the monoclinic structure fit the data well. At higher temperatures, the rhombohedral structure was perfectly capable of giving an adequate fit to the data, although we see a highly asymmetric Ni-O bond length distribution consistent with our neutron PDF and with the expectations for a displacive Jahn-Teller effect. We show the results of a fit with a monoclinic model [Fig. 1, right], which shows significant reduction in the gap between long and short Ni-O bond lengths at higher temperatures, although due to the asymmetry of the Ni-O peak (as in the PDF) we do not see the two lengths converge.

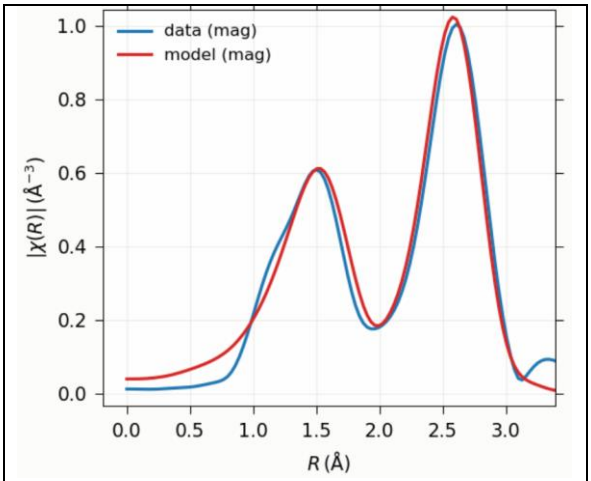

Fig. 2: a fit to the data (in the region of Ni-O and Ni-Ni bonds) at 260°C using a rhombohedral model using only a single Ni-O and Ni-Ni bond length. We can see this fits the data entirely reasonably, indicating a monoclinic model with two different bond lengths is not needed and so disfavouring our initial hypothesis of dynamic, rapidly-oscillating Jahn-Teller distortions at high-temperatures.

Next steps

Having shown that the Jahn-Teller transition is displacive with temperature, we have attributed this behaviour to the triangular lattice owing to our calculated configurational entropies of orbital disorder on a triangular vs a square lattice [2]. To test this hypothesis, we are studying the transition under pressure which, if the hypothesis is correct, should resemble the variable-temperature transition and show a local disappearance of the Jahn-Teller distortion.

To this end, we have identified the monoclinic->rhombohedral transition as 22 GPa [2] using variable-pressure diffraction at Diamond Light Source, and we now hope to study this transition using EXAFS in a future beamtime at ESRF.

References

[1] R. A. Souza, *et al*. Physica Scripta 2005. T115 (2005): 428.

[2] L. A. V. Nagle-Cocco *et al. In preparation.*

[3] M. Newville, Larch: An Analysis Package For XAFS And Related Spectroscopies. Journal of Physics: Conference Series, 430:012007 (2013)