Proposal:	5-15-634		**Council:**	10/2022

Title: Oxygen Supercell Ordering¿s Effecton the Magnetism of Charge-stripe Ordered System

Research area: Physics

This proposal is a new proposal

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Samples: La2NiO4.11

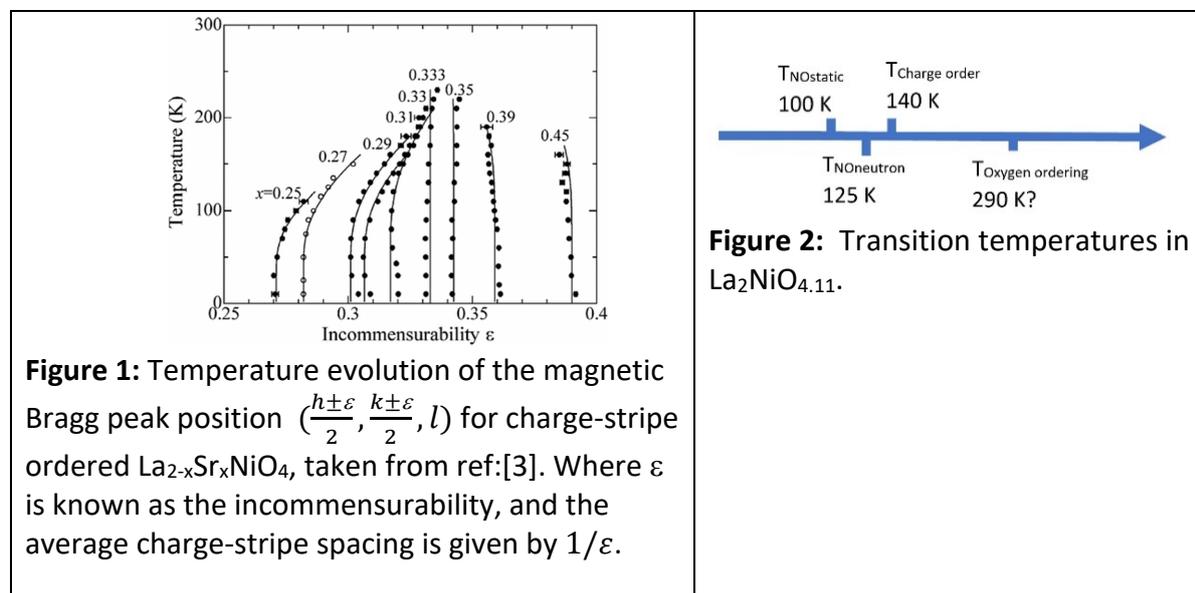| Instrument	Requested days	Allocated days	From	To
D19	10	10	23/06/2023	03/07/2023
ORIENTEXPRESS	1	1	15/05/2023	16/05/2023

Abstract:

How charge-stripe order materials magnetically order remains an open question, despite the near ubiquitous occurrence of charge stripes in cuprate superconductors and the associated magnetic order of La-based cuprates. In studies of non-superconducting $La_{2-x}Sr_xNiO_{4+\delta}$ the ordering processes can be studied without the competing or co-existing phases that cuprates have. In charge-stripe ordered $La_2NiO_{4.11}$ we have evidence that frustration of the magnetic excitations prevents static ordering, frustration due to competition between charge and spin degrees of freedom on the charge-stripe order structure. Once the frustration is removed, the material statically orders. Yet this proposal relies is based on ordering of the excess oxygen ordering that has not been determined for our material. In this proposal we determine the excess oxygen ordering of $La_2NiO_{4.11}$, magnetic and nuclear structure, to test our proposed magnetic

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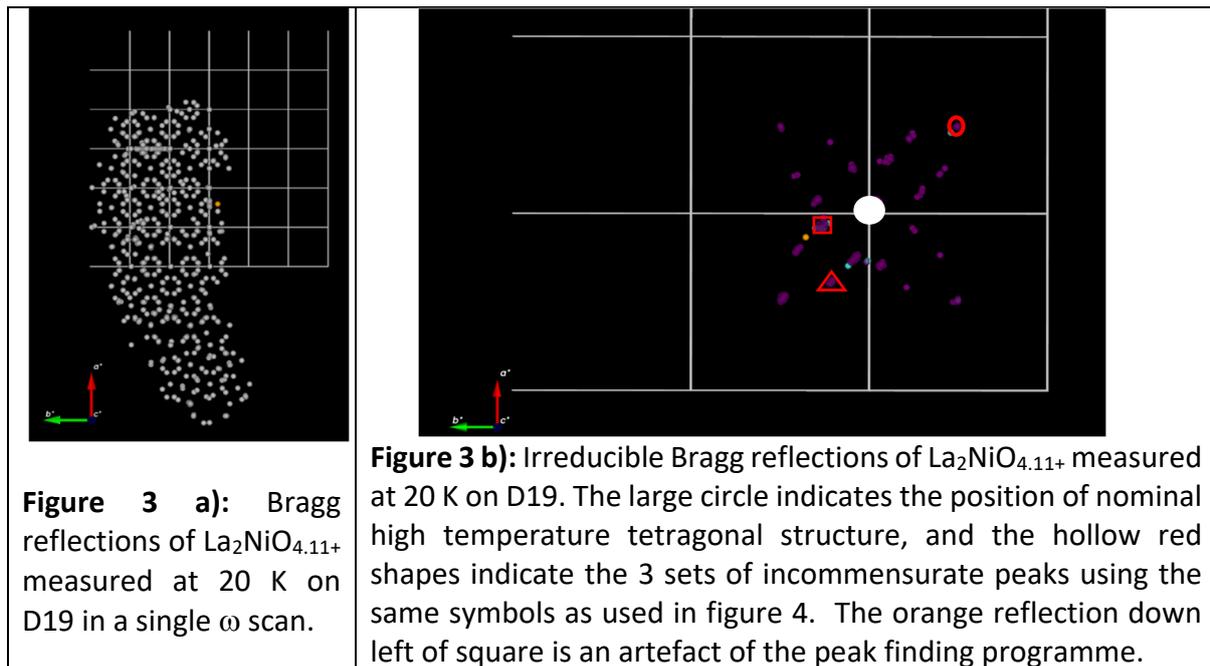
In La-cuprates that magnetically order the ordering is glassy with the spin ordering temperature (TSO) observed by neutron diffraction measured on the picosecond timescale significantly higher than that observed on the microsecond timescale by muon Spin Rotation (μSR) [1]. A similar trend is observed in the related non-superconducting charge-stripe ordered $La_{2-x}Sr_xNiO_{4+\delta}$ (LSNO)[2], where the magnetic ordering is believed to occur due to a slowing down of spin fluctuations over a wide temperature range. We argue from studying $La_2NiO_{4.11}$ that picosecond ordering is instead prevented from static ordering by frustration of the magnetic excitations, but before this proposal on D19 we did not know the structure of the excess oxygen ordering in this material , and that limits our findings on this alternative understanding of LSNO.

Figure 1: Temperature evolution of the magnetic Bragg peak position $(\frac{h\pm\varepsilon}{2}, \frac{k\pm\varepsilon}{2}, l)$ for charge-stripe ordered $La_{2-x}Sr_xNiO_4$, taken from ref:[3]. Where ε is known as the incommensurability, and the average charge-stripe spacing is given by $1/\varepsilon$.

Figure 2: Transition temperatures in $La_2NiO_{4.11}$.

Holes are doped into LSNO by substitution of La by Sr, or the addition of excess oxygen into the material. These holes go into the Ni-O layers and form semi-regular spaced lines of charges, charge-stripes, which act as antiphase domain walls to antiferromagnetic spin stripes of the Ni sites. Charge-stripe order in $La_2NiO_{4.11}$ changes from a structure with charge-stripes separated by ~4 Ni-Ni spacing at 2 K, to nearer to 3 Ni-Ni spacings on warming to the charge ordering temperature, see Fig. 1 and [3], determined from the position of magnetic spin stripe Bragg reflections. We have strong evidence that supports the crossover to the base temperature periodicity for the magnetic excitations is the transition to static magnetic order,

however without having characterised the excess oxygen structure in this material it has been highlighted that we do not fully understand the material.

A series of crystals were prepared for this proposal, and after neutron Laue checking of several samples of $La_2NiO_{4.11\pm0.01}$, our highest quality sample with no observable twinning was selected, with a flat cylinder geometry. **UPDATE after a D10 experiment 04/2024: The sample studied on D19 was determined to be at a higher doping level than $La_2NiO_{4.11}$, which we label $La_2NiO_{4.11}+$ in this updated report.** On D19 we mapped reciprocal space to determine the oxygen supercell structure of $La_2NiO_{4.11}+$, with the expectation that the structure would match that $La_2NiO_{4.125}$ as indicated in published studies[4]. A neutron wavelength of 0.95 Å was select to both give a large reciprocal space coverage, and have a clean neutron beam without higher harmonic neutrons present.

Figure 3 a): Bragg reflections of $La_2NiO_{4.11}+$ measured at 20 K on D19 in a single ω scan.

Figure 3 b): Irreducible Bragg reflections of $La_2NiO_{4.11}+$ measured at 20 K on D19. The large circle indicates the position of nominal high temperature tetragonal structure, and the hollow red shapes indicate the 3 sets of incommensurate peaks using the same symbols as used in figure 4. The orange reflection down left of square is an artefact of the peak finding programme.

In $La_2NiO_{4.125}$ the O ordering supercell produces incommensurate satellite Bragg reflections, that can be referenced by two orthorhombic (45° rotated to tetragonal unit cell with $a\sqrt{2}$ lattice parameter) wavevectors: $g_{O1} = (1/3,0,1)$ and $g_{O2} = (0,4/5,4/5)$ from a supercell of dimensions 3a×5b×5c[4]. Figure 3 a) shows the Bragg reflections of a ω scan of $La_2NiO_{4.11}+$ at 20 K, on a mesh of the nominal high temperature tetragonal structure, that clearly indicates vast number of additional reflections. An irreducible set of reflections from a scan is shown in Figure 3 b), where the high temperature tetragonal structural Bragg reflections are under the central dot. Three additional incommensurate sets of peaks are observed and associated with an O ordering supercell due to their presence in the electronically disordered phase at 170 K. The sets of peaks are in tetragonal notation Set 1 $g_{O1} = (0.2,0.4,1)$, Set 2 $g_{O2} = (0.3,0.1,0.5)$ and set 3 (0.5, 0.5, 0.5). Initial consideration of peaks of set 1 and set 2 highlights similarities and differences to the 2 O ordering peaks in $La_2NiO_{4.125}$, hence our preliminary labelling of them. Set 1 is commensurate with the crystal lattice in the c direction, whereas set 2 is not and has a doubling of the unit cell length, so each set could similarly come from excess O sitting above one of the two NiO layers within the overall undistorted crystal structure. Unlike $La_2NiO_{4.125}$, sets 1 and 2 observed in $La_2NiO_{4.11}+$ are not orthogonal, a significant difference. We are unaware of any observed set of peaks like (0.5, 0.5, 0.5), which are structural in origin due to their temperature

dependence. Analysis of the full mapping of reciprocal space of all structural reflections at 20 K is foreseen to solve the O ordering supercell structure.

| Figure 4: The temperature evolution of the three sets of incommensurate structural reflections observed in $La_2NiO_{4.11+}$. An ordering temperature of 280 K is observed for all 3 sets of reflections. | |
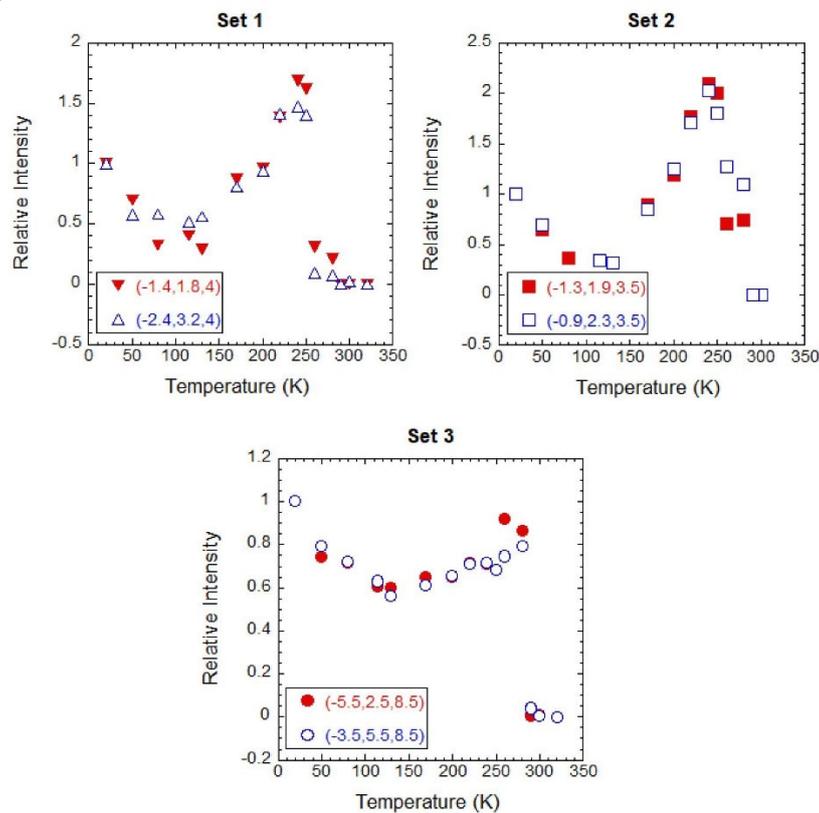
The temperature dependence of the Set 1-3 peaks was measured over a limited range of reciprocal space, see fig. 4. All 3 sets of peaks gain intensity below 280 K, although set 3 rapidly gains full intensity, sets 1 and 2 only obtain full intensity by 250 K. Without a change in wavevector, all 3 sets of peaks lose intensity on further cooling and having a minimum in intensity between 100-150 K, where charge ordering and magnetic ordering occurs. The intensity of the peaks then recovers (set 3) or partially recover by 20 K. This highly unusual temperature dependence demands a further joint investigation of the CSO magnetic Bragg reflections, charge-stripe order Bragg reflections, and O ordering peak sets 1-3.

Additional data was taken at $\lambda = 1.45$ Å at 20 K to confirm the magnetic structure of the as studied sample matches that of the large crystal used in inelastic studies. The open geometry, lowest accessible scattering angle, and the vast quantity of higher order harmonic peaks present in the data, is proving challenging to analyse the data. Data from D10 however have confirmed the doping level of this sample is higher. Finally on the last day of the experiment tests on the effect of the thermal history on the observed signal was tested, as earlier studies have indicated the thermal history is important for O ordering[5]. A strict thermal cycle had been employed for the rest of the measurements of this proposal at the not insignificant cost of heating and cooling time. We do not yet have preliminary findings to report on any thermal history effects on the excess O ordering in $La_2NiO_{4.11+}$.

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[3] K. Ishizaka et. al., Phys. Rev. Lett. **92**, 196404 (2011).
[4] P. Wochner, et. al., Phys. Rev. B **57**, 1066 (1998).
[5] P. G. Freeman, et. al., Phys Rev B **80** ,144523 (2009)