Abstract.

The magnetic Bragg reflections of charge-stripe ordered La$_{1.725}$Sr$_{0.275}$NiO$_4$ where investigated by neutron diffraction to determine the intensity ratio of first to third order harmonics. The third harmonic Bragg reflections were not observed at temperatures across that magnetically ordered phase, creating an upper bound for their intensity of 0.16% of the first harmonic intensity.

1. Introduction

The charge stripe interpretation of La-based cuprates has been under investigation since the discovery of charge stripe order in a non-superconducting La-Nd based cuprate[1]. A great advance on the magnetic structure of La-Nd cuprates was achieved by polarized neutron diffraction, confirming a co-linear spin arrangement at 1/8 doping level that is consistent with charge stripe order[2]. The striking hourglass magnetic excitation spectrum of the cuprates can also be understood within a charge stripe ordered picture[3, 4]. Despite this effort, the centring of the charge stripe order remains a undesirable free parameter for modelling the magnetic excitations of cuprates[5].

Recently calculations were made of the relative intensity of first to third harmonic magnetic Bragg reflections for both site (Cu or Ni) and bond (O) centred charge stripes measured by neutron diffraction, and the ratio is found to be significantly larger for site centred charge stripes[6]. Due to a small Cu moment in the magnetically ordered cuprates, resolving the third harmonics will be very challenging in the cuprates. The relative intensity of magnetic third harmonic Bragg reflections in charge stripe ordered La$_2$NiO$_{4.13}$ was determined to be 1.7%[7]. The measured value can be compared to the calculated values of 1.1% for site centring or 11.8% for bond centring, implying site centred charge stripes[6]. But as the charge-stripe structure of La$_2$NiO$_{4.13}$ locks into an oxygen ordering supercell, this supercell could be the cause of site centred charge order[7]. It is therefore desirable to investigate the third harmonics in charge-stripe ordered La$_{2-x}$Sr$_x$NiO$_4$, where there is no Sr ordering, to further test the calculation and determine the effect of the oxygen supercell on the charge stripe structure of this material.
2. Experimental details

A single crystal of La$_{1.725}$Sr$_{0.275}$NiO$_{4+\delta}$ was grown by the floating-zone technique[8]. The sample was cut from the crystal used in our earlier neutron studies of La$_{1.725}$Sr$_{0.275}$NiO$_{4+\delta}$ [9], and is a rod of 8 mm diameter and 15 mm length used in our recent diffraction measurements[10]. Thermo-Gravimetric Analysis (TGA) of an as-grown crystal determined the oxygen excess to be $\delta = 0.02 \pm 0.01$. Data on the bulk magnetization of an as-grown crystal are published elsewhere[11]. As our previous studies showed the excess oxygen has little effect on the properties of this material, we label the sample $x = 0.275$.

Neutron diffraction measurements were performed on the cold Triple-Axis Spectrometer (TAS) RITA II at the P.S.I., and the experimental setup has been described in detail previously[10]. The neutrons initial and final energy were selected from Bragg reflections off a vertically focusing pyrolytic graphite (PG) monochromator, and a flat PG analyzer. The sample was oriented so that ($h, h, l$) positions in reciprocal space could be accessed. In this work we refer to the body centred tetragonal unit cell of LSNO, which has unit cell parameters $a \approx 3.8 \, \text{Å}$ and $c \approx 12.7 \, \text{Å}$.

3. Results

In figure 1(a) we show the charge stripe ordered model for site/Ni centred charge stripes in $x = 0.275$, which produces magnetic Bragg reflections indicate in Fig. 1(b) in the $(hk0)$ reciprocal plane, and in the $(hhl)$ reciprocal plane in Fig. 1(c). First order magnetic Bragg reflections are observed at $(h + \frac{1}{2}, k + \frac{1}{2}, l) \pm (\varepsilon/2, \varepsilon/2, 0)$ with $\varepsilon = 0.300 \pm 0.001$ at base temperature, and third harmonic magnetic Bragg reflections should be observed at $(h + \frac{1}{2}, k + \frac{1}{2}, l) \pm (3\varepsilon/2, 3\varepsilon/2, 0)$. The magnetic ordering temperature of the $x = 0.275$ is $T_{SO} = 140 \pm 5 \, \text{K}$[10].

![Figure 1](image_url)

**Figure 1.** (a) A model of the Ni sites of a single Ni-O layer of LSNO $x = 0.275$ for site centred charge order. (b) The first harmonic magnetic Bragg reflections of $x = 0.275$ in the $(hk0)$ reciprocal plane. There are two sets of reflections creating a quartet of magnetic Bragg reflections, two for the order in (a) and two for the charge stripe twin with stripes rotated 90° to those in (a). (c) The structural Bragg reflections and magnetic Bragg reflections of the $(hhl)$ reciprocal plane. Solid squares indicate structural Bragg reflections, solid circles are first harmonic magnetic Bragg reflections and hollow circles indicate the position of third harmonic magnetic Bragg reflections. For the purpose of clarity we have omitted the positions of charge order Bragg reflections. (d) An example of a scan parallel to $(hh0)$ of a first harmonic Bragg reflection in charge stripe ordered $x = 0.275$. The solid line is the result of a fit of a Gaussian lineshape on a flat background.
To avoid the high intensity structural Bragg reflections we decided to search for the third order magnetic Bragg reflections around (001) and (003). In Fig. 1(d) we show a scan through the first harmonic reflection centred at (0.35, 0.35, 1) measured at 1.5 K. In figure 2(a) we show a scan through the position of the third harmonic at (0.05, 0.05, 1). At this position the background is tilted with no definite observation of a magnetic Bragg reflection. Using the position of the first order harmonic and the width of this reflection as fitted by a Gaussian lineshape, we fitted the amplitude of the expected reflection in Fig. 2(a). The fit determined an amplitude of $113 \pm 27$ counts compared to a statistical error of 41 counts of the background. In figure 2(b) we show how we repeated this search for third order harmonics near (0.35, 0.35, 3) at $T = 110$ K, having also measured the first harmonic at this temperature.

In Table 1 we compare the amplitude of the fit of the scans of Fig. 2, the statistical error of background for each point, and relative percentage of the fitted amplitude to the first harmonics intensity. Although the fitted peak amplitude is positive, it is never large than three times the standard deviation of the background. We therefore take these values as upper limits on the relative intensity of the third harmonic Bragg reflection, that is the third harmonic has less than $0.16 \pm 0.03\%$ the intensity of the first harmonic magnetic Bragg reflection of $x = 0.275$. 

**Table 1.** Fitted amplitude of peaks at the (0.05, 0.05, l) position of third harmonic magnetic Bragg reflections of charge-stripe ordered La$_{1.725}$Sr$_{0.275}$NiO$_4$.

| l | Temperature (K) | Amplitude Counts of Third Harmonic | Background Noise | Intensity Compared to First Harmonic (%) |
|---|-----------------|------------------------------------|------------------|-----------------------------------------|
| 1 | 1.5             | $113 \pm 27$                       | 41               | $0.22 \pm 0.05$                         |
| 3 | 1.5             | $54 \pm 26$                        | 37               | $0.12 \pm 0.06$                         |
| 3 | 40              | $69 \pm 26$                        | 36               | $0.16 \pm 0.06$                         |
| 3 | 110             | $35 \pm 24$                        | 35               | $0.13 \pm 0.09$                         |

**Figure 2.** Scans of reciprocal space parallel to ($h00$) at the position of third harmonic magnetic Bragg reflections, (a) 1.5 K, $l = 1$, and (b) 110 K, $l = 3$. The solid lines are the result of fits of a Gaussian lineshape on a sloping background, where centre is determined from the position of first harmonic reflections, and the width is fixed to be the same as that of the first harmonic.
4. Discussion and Conclusions

We have searched for, and failed to observe, third order harmonic magnetic Bragg reflections in charge stripe ordered La$_{2-x}$Sr$_x$NiO$_4$ $x = 0.275$, at temperatures across the magnetically ordered phase. Our results differ from the observation of higher harmonic reflections in charge stripe ordered La$_2$NiO$_4$.133$.[7]

Analysis of the scans indicates an upper limit on the strength of the third order magnetic Bragg reflections in $x = 0.275$ of 0.16 % of the first harmonic. Our results indicate the model of the spin structure proposed in ref. [6] does not fully encompass the characteristics of the charge ordered site, that is indicated by the energy dependence of resonant soft x-ray diffraction of La$_{1.8}$Sr$_{0.2}$NiO$_4$[12]. Alternatively the model may require mixing of bond and site centred charge ordering, as observed by transmission-electron-microscopy (TEM) at the surface of this material[13]. In La$_2$NiO$_4$.133 the magnetic domain walls have been determined to be narrow, consistent with the square wave profiles used in the third harmonic calculation[6], and the observed ratio of third to first harmonic reflections is close to the predicted value for site centred charge order. We ascribe the presence of higher harmonics in La$_2$NiO$_4$.133 as due to the distortion caused by the oxygen supercell ordering, that may play an important role in causing the anomalous magnetic excitation spectrum of La$_2$NiO$_{4.11}$[14].

Resonant soft x-ray diffraction and TEM results remain the strongest experimental evidence for predominantly site centred charge order in La$_{2-x}$Sr$_x$NiO$_4$[12, 13]. Searching for third harmonic magnetic Bragg reflections in the cuprates may determine the centring of the charge order in these materials, but it is likely that third harmonics are only observed in materials in which structural distortions stabilise charge order, i.e. La-Nd based cuprates near 1/8 doping[1]. However, in systems where structural distortions stabilise the charge order, the order may not represent that of the undistorted systems.

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