

## Charge stripe glasses in $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$ for $0.20 < x < 0.25$

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**Abstract.** We present high resolution X-ray measurements characterising the charge stripe order state in the  $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$  system with  $x = 0.20, 0.225$  and  $0.25$ . We find that in the  $x = 0.20, 0.225$  and  $0.25$  systems the charge stripe order exists in a charge stripe glass characterised by weak, poorly correlated incommensurate charge stripes in contrast to the strong well correlated charge stripes in the commensurate  $x = 1/3$  system. No stabilisation of the charge order was observed at the next possible commensurate value of  $\varepsilon = 0.25$ . A comparison with high energy X-ray measurements suggested that the charge order may exist in a charge stripe glass in the bulk in the doping region  $x = 0.20$ – $0.33$ . Finally at low temperature there was an initial increase in the intensity and correlation not observed with neutron measurements and it appears to be an effect that X-rays are sensitive to but neutrons are not.

**PACS.** 61.10.-i X-ray diffraction and scattering – 71.27.+a Strongly correlated electron systems; heavy fermions – 71.30.+h Metal-insulator transitions and other electronic transitions – 71.28.+d Narrow-band systems; intermediate-valence solids

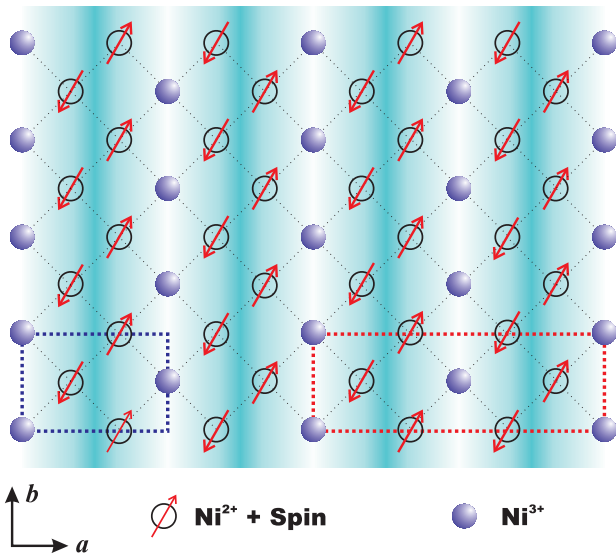
### 1 Introduction

The  $\text{La}_{2-x}\text{Sr}_x\text{NiO}_{4+\delta}$  system has been studied intensively due to its structural similarity with the high temperature superconducting  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  system [1]. However, despite the isostructural nature with the high  $T_C$  cuprates it displays dramatically different properties. The parent compounds  $\text{La}_2\text{NiO}_4$  and  $\text{La}_2\text{CuO}_4$  are antiferromagnetic Mott insulators with the layered perovskite  $\text{K}_2\text{NiF}_4$  structure. By substituting Sr for La holes are doped into the system and these holes are mobile and drastically change the properties of both systems. The cuprate system shows superconductivity for a doping level as low as  $x = 0.05$ , whereas the nickelate system does not show superconductivity for any doping level. However, the nickelate system shows strong, well correlated charge stripes unlike the cuprate system which displays weak dynamic charge stripes. The nickelates are a model system for the study of charge stripe order and any understanding may be beneficial in exploring the relationship between charge stripes and high temperature superconductivity.

Below the charge ordering temperature,  $T_{CO}$ , the holes order to form static charge stripes and below  $T_N$ , the spins order in the region between the charge stripes. The

hole rich stripes act as  $\pi$  domain walls for the local anti-ferromagnetic order, existing in the hole deficient regions with nickel moments parallel to the stripe propagation direction. Such charge and spin stripes form within the  $a - b$  plane of the material, and are found to be two dimensional in nature. For comparison with previous data we will index the nickelate system with the  $F4/mmm$  unit cell unit cell as opposed to the tetragonal  $I4/mmm$  unit cell. A schematic of charge and spin stripes in the  $a - b$  plane in the  $F4/mmm$  setting is shown in Figure 1. The wavevectors for the charge and spin stripes are  $Q_{CO} = (2\varepsilon, 0, 1)$  and  $Q_{SO} = (1 \pm \varepsilon, 0, 0)$  respectively where the commensurability  $\varepsilon$  is the splitting from the Bragg peak. The commensurability  $\varepsilon$  approximately follows the hole concentration  $n_h$ , with  $n_h = x + 2\delta$  where  $\delta$  is the amount of excess oxygen and  $x$  the doping. Originally it was postulated that the charge stripes were restricted to commensurate values only such as  $1/2, 1/3$  etc [2] but charge and spin stripes have been confirmed in a wide variety of Sr concentrations from  $x = 0.135$  to  $0.50$  [3–6]. In the  $x = 0.33$  doped sample the charge and spin stripes are coincident in reciprocal space and they are also commensurate with the lattice. It is believed that a coupling between the charge order and the lattice is necessary to stabilise the charge and spin stripes.

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**Fig. 1.** A schematic representation of the charge and spin stripes in  $\text{La}_{1.67}\text{Sr}_{0.33}\text{NiO}_4$ .  $\text{Ni}^{3+}$  ions are shown as filled circles and the  $\text{Ni}^{2+}$  ions are represented as open circles with the associated spin vector. The spins are believed to be canted away from the stripe direction. The dotted lines show the spin and charge supercells respectively and the shading shows the charge density distribution.

Neutron studies by Yoshizawa [7] et al. in the doping range  $0.289 < x < 0.50$  and high resolution X-ray studies by Du et al. [8] and Ghazi et al. [9] on the  $x = 0.33$ , 0.30 and 0.275 samples have shown that the charge order is strongest and most stable in the  $x = 0.33$  doped sample. Moving the doping level away from  $x = 0.33$  in either direction results in the charge ordering temperature decreasing and the charge order becoming weaker, less correlated and incommensurate. In the study by Ghazi et al. [9] the charge order in the  $x = 0.30$  and  $x = 0.275$  samples was weaker than in the  $x = 0.33$  doping and incommensurate but was still intense and highly correlated. In the  $x = 0.33$ , 0.30 and 0.275 compositions the commensurability tended towards the commensurate  $\varepsilon = 0.333$  position as the temperature was increased. Indeed even in the  $x = 0.33$  sample the charge order was slightly incommensurate and on heating moved towards the stable  $1/3$  position and ‘locked in’ to this position resulting in a stabilisation of the charge order evidenced by a decrease in the inverse correlation length. In the  $x = 0.30$  and  $x = 0.275$  samples the change in the commensurability was far more significant. This was in agreement with the X-ray results observed by Ishizaka et al. [10] who studied samples in the doping region  $0.25 < x < 0.45$ . In both samples, the charge order was observed to disappear before reaching this commensurate value. In the  $x = 0.275$  and 0.30 compositions no long range charge order was present above  $T_N$ . However, in the  $x = 0.33$  composition above  $T_N$  the charge order pattern was stabilised by the interaction between the lattice at the commensurate position of  $\varepsilon = 0.33$  even in the absence of the magnetic order.

In this paper we report on high resolution X-ray studies of charge stripes in the nickelate system for  $x = 0.20$ ,

0.225 and 0.25. The  $x = 0.20$  system was previously studied with neutron diffraction by Sachan et al. [3] and the  $x = 0.225$  with neutron diffraction by Tranquada et al. [5] and high energy X-rays of 100 keV by Vigilante et al. [6] which provided direct bulk measurements of the charge stripes. These studies reported the presence of weak, diffuse incommensurate charge stripes contrasting with the intense well correlated charge stripes observed for  $x > 0.275$ . The  $x = 0.33$  sample studied by Ghazi et al. [9] at 12 keV was studied using energies of 130 keV by Wilkins et al. [11] to obtain bulk measurements of the system. There was a considerable difference reported in the properties of the charge order in the bulk compared to that at the surface. In the bulk the charge order was found to exist in a charge glass approximately eight times less correlated than that measured at the surface where the charge order was highly correlated. It was postulated that the reason for this difference was that the charge stripes were pinned at the surface resulting in a stabilisation of the charge stripe order.

Our previous X-ray studies of the  $x = 0.33$ , 0.30 and 0.275 compositions showed clear differences from the reported neutron studies. In the neutron measurements by Lee et al. [12] the intensity of the charge order decreased gradually on heating whereas the X-ray measurements showed an initial increase in the charge order intensity on heating. Ghazi et al. [9] suggest possible reasons but no definite explanation has been given for this difference. Synchrotron X-rays measurements have advantages over neutron measurements due to the high flux and high wavevector resolution. This allows weaker features to be observed and smaller inverse correlation lengths to be measured than with neutrons. In this paper we report a detailed systematic study of the charge stripe order in the  $x = 0.20$ , 0.225 and 0.25 doped nickelates.

## 2 Experimental details

High quality samples of  $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$  with  $x = 0.25$ , 0.225 and 0.20 were grown using the floating zone method at Oxford University [13]. The crystal structure was found to be tetragonal with  $I4/mmm$  symmetry at room temperature but for comparison with previous work the samples were indexed with the  $F4/mmm$  setting with lattice parameters  $a \simeq b = 5.4145 \text{ \AA}$  and  $c = 12.715 \text{ \AA}$ . The samples were cut and aligned with the  $\langle 1, 0, 1 \rangle$  direction surface normal and the samples were polished using 1 micron diamond paste. The samples were mounted with the  $\langle 1, 0, 1 \rangle$  direction normal to the scattering vector and the  $\langle 0, 1, 0 \rangle$  corresponding to the beam direction. The samples were found to be of excellent quality with mosaic widths of  $\sim 0.021^\circ$ ,  $\sim 0.032^\circ$  and  $\sim 0.034^\circ$  for the  $x = 0.20$ ,  $x = 0.225$  and  $x = 0.25$  samples respectively. The experiments were carried out on the XMaS CRG beamline, BM28, at the ESRF, Grenoble France [14]. Measurements were carried out at an energy of 12.39 keV ( $1.000 \text{ \AA}$ ) which is close to the peak flux obtainable on the beamline. To increase the wavevector resolution a Ge (111) analyser was used. Both the  $x = 0.225$  and 0.20 samples were slightly oxygen rich

and the excess oxygen concentration.  $\delta$  was measured as  $\delta = 0.01 \pm 0.01$  in the 0.20 sample and  $\delta = 0.01 \pm 0.01$  in the 0.225 doped sample using thermogravimetric analysis.

### 3 Results

The samples were cooled to a base temperature of 20 K and a search was carried out around the (4, 0, 4) Bragg peak. Superlattice reflections from the charge order were located at a modulation of  $(2\varepsilon, 0, 1)$  with  $\varepsilon = 0.255$  in the 0.20 sample and  $\varepsilon = 0.28$  in the 0.225 and 0.25 samples. The positions were the same in both the  $x = 0.225$  and  $x = 0.25$  doped samples as a result of the excess oxygen doping of  $\delta = 0.01 \pm 0.01$  in the 0.225 system.

Scans were carried out in the  $H$ ,  $K$  and  $L$  directions of reciprocal space on the charge order and the data fitted. The charge order peak in all samples fitted the Lorentzian squared lineshape in the  $H$ ,  $K$  and  $L$  directions. The scans for the (4.5, 0, 3) charge order in the  $x = 0.20$  sample are in Figure 2 and as a comparison the scans for the sharp (4, 0, 4) Bragg peak are shown.

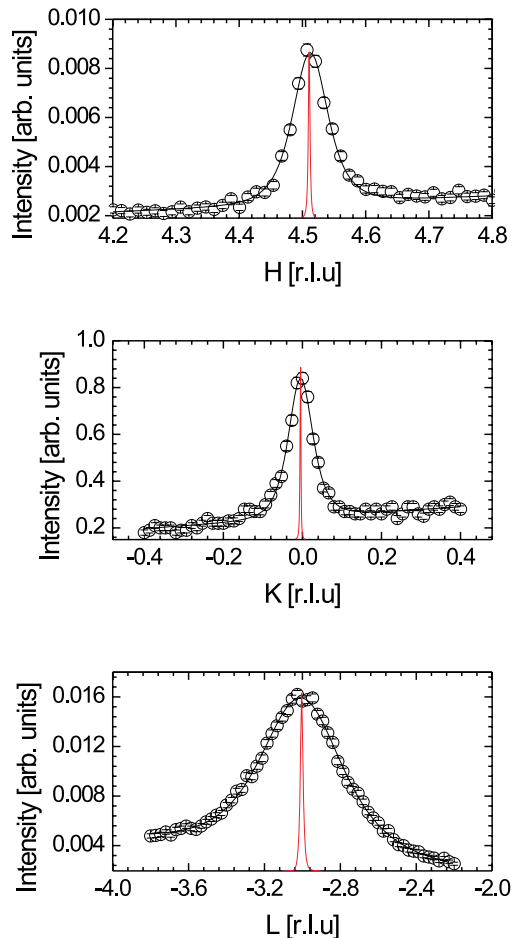
The inverse correlation length,  $\xi^{-1}$ , of the Bragg and superlattice reflections was calculated using the equation

$$\xi_d^{-1} = \frac{2\pi}{d} w, \quad (1)$$

where  $w$  is the half width at half maximum of the reflection and  $d$  is the Bragg plane spacing normal to the scattering vector.

Consistent with the higher doped samples [9] the charge order was measured to be two dimensional indicated by a greater inverse correlation length in the  $L$  direction. However, unlike the  $x = 0.33$  doped samples the charge order in the  $x = 0.20$  doped sample was not only poorly correlated between planes but within the plane as well. The strongest charge order reflection in the  $x = 0.20$  sample was the (4.5, 0, 3) which had an intensity of approximately 200 counts per second (c.p.s) at 20 K which is very weak compared to the charge order in the  $x = 0.33$  sample which was approximately 20,000 c.p.s, at 20 K. In contrast to the charge stripe ordering in the  $x = 0.33$  sample where the charge stripes are intense and well correlated in the  $x = 0.20$  the charge ordering exists in a charge stripe glass state characterised by weak, short range ordered and incommensurate charge stripes similar in some ways to the charge order observed in the half doped cobaltate  $\text{La}_{1.5}\text{Sr}_{0.5}\text{CoO}_4$  [15]. The charge order in the  $x = 0.25$  and 0.225 samples was stronger and more correlated than that in the 0.20 sample with it being strongest and most correlated in the  $x = 0.25$  doped sample but still weaker than in the higher doped samples.

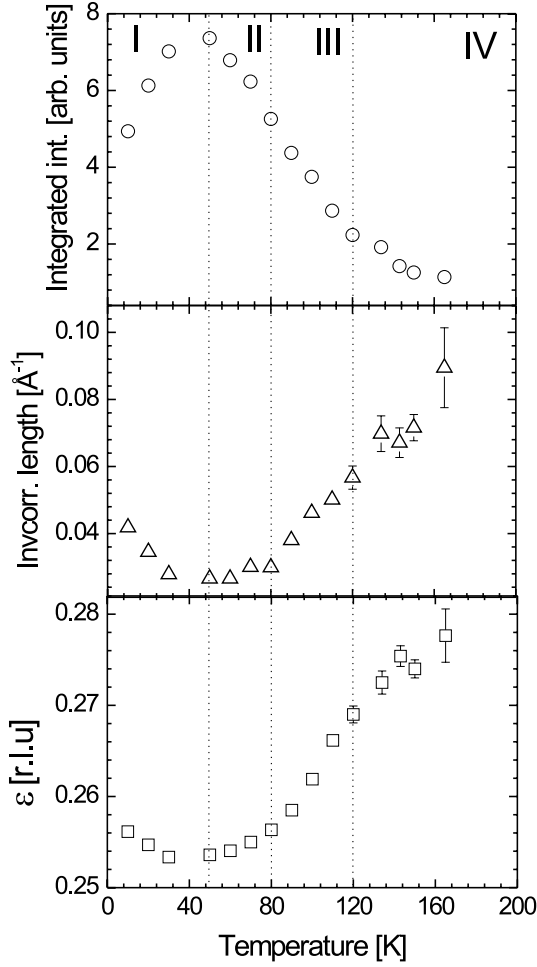
In each of the samples the strongest charge order peak was measured as a function of temperature in the  $H$ ,  $K$  and  $L$  directions. Figure 3 shows the temperature dependence of the integrated intensity, inverse correlation length and incommensurability in the  $x = 0.20$  sample for the (4.5, 0, 3) reflection in the  $H$  direction and Figure 4



**Fig. 2.** Scans of the (4.5, 0, 3) charge order peak. The black line shows the fit and the grey line shows the corresponding scans of the sharp (4, 0, 4) Bragg peak.

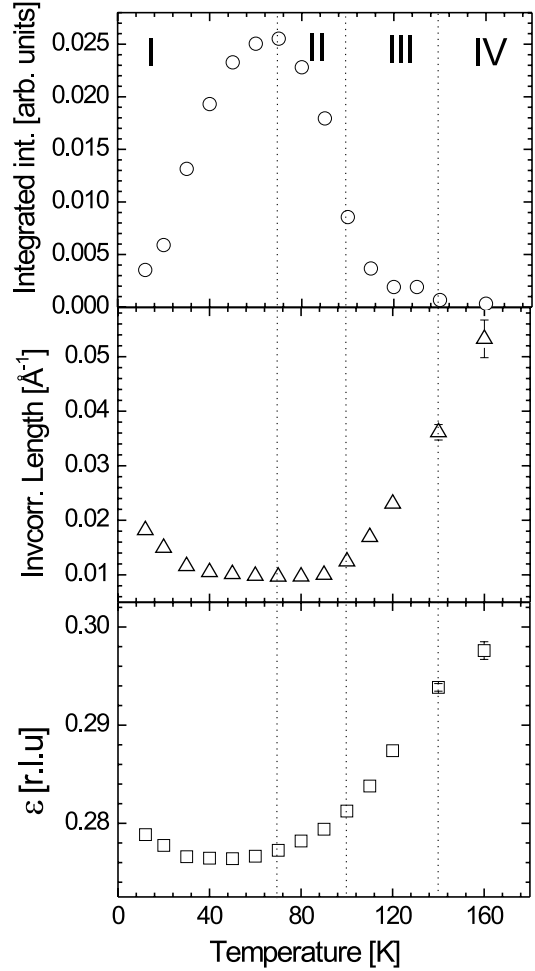
shows the temperature dependence of the (4.56, 0, 5) reflection in the  $x = 0.25$  doped sample. The  $x = 0.225$  doped sample displayed similar behaviour.

Consistent with the behavior observed in  $x = 0.30$  and  $x = 0.275$  doped samples by Ghazi et al. [9] the charge ordering can be divided into 4 clear regions and for discussion we refer the reader to Figure 3. In region I at 10 K the charge ordering is relatively strong, has a relatively small inverse correlation length and exists at a position with  $\varepsilon = 0.255$ . As the temperature was increased the integrated intensity began to increase and maximised at 50 K. This was accompanied by a decrease in the inverse correlation length and the incommensurability. The intensity and position of the (4, 0, 4) Bragg peak was checked at regular temperature intervals to ensure there was no change in the intensity or position with temperature. This behaviour was not observed in the neutron measurements by Sachan et al. [3] for the  $x = 0.20$  system or by Tranquada et al. [5] for the  $x = 0.225$  doped system. This is consistent with the X-ray measurements by Ghazi et al. [9] in the higher doped samples. In region I the commensurability shows a clear decrease towards a stable value of approximately  $\varepsilon = 0.254$  and the inverse correlation length shows a decrease. This indicates that at the same



**Fig. 3.** Integrated intensity, inverse correlation length and incommensurability of the  $(4.5, 0, 3)$  charge order peak in the  $H$  direction. Unless shown the error bars are smaller than the data symbols.

time the charge stripes are becoming more correlated. The charge order enters region II at 50 K and as the temperature is increased the charge stripes gain more thermal energy and this enables them to overcome the Coulomb repulsion and move towards the favored  $\varepsilon = 1/3$  value and thus the commensurability wavevector increases. It is evident from this that  $\varepsilon = 0.33$  is still the stable position for the charge ordering with no apparent stabilisation at the commensurate position of  $\varepsilon = 0.25$ . There is a decrease in the integrated intensity as the temperature is increased into region II. As the temperature is increased the holes gain thermal energy allowing them to overcome the interactions with the lattice which fix them on the charge stripe. This lowers the hole concentration on the charge stripes and as a result the integrated intensity decreases. The boundary of regions II and III at 80 K corresponds to the spin ordering temperature  $T_N$ . The charge stripes are no longer stabilised by the spin stripes and coupled with the increased thermal energy begin to vibrate, resulting in a sharp increase in the inverse correlation length. In region III there is a continuation of the decrease in integrated intensity and increase in the incommensurability as



**Fig. 4.** Integrated intensity, inverse correlation length and incommensurability of the  $(4.56, 0, 5)$  charge order peak in the  $H$  direction for the  $x = 0.25$  sample. Unless shown error bars are smaller than the data symbols.

the holes continue to gain thermal energy. In region IV at 120 K only critical scattering exists and this is very weak, virtually uncorrelated, and  $\varepsilon$  continues to move towards the 0.33 position. The charge ordering disappears before  $\varepsilon$  reaches the stable  $1/3$  value. The  $x = 0.25$  and 0.225 doped samples display similar behaviour but because the charge order is more stable in the higher doped samples they have higher transition temperatures into each of the 4 regions.

## 4 Discussion

When discussing the results we refer to the results from Ghazi et al. [9]. Our results demonstrate that there is an initial increase observed in the integrated intensity in all samples in the doping region 0.20–0.33. The charge order observed in the  $x = 0.20$  and 0.225 doped samples show an initial increase in intensity that was not observed in the neutron measurements by Sachan et al. [3] for  $x = 0.20$  doped sample and Tranquada et al. [5] for  $x = 0.225$  where the intensity decreases in the low temperature region. This

**Table 1.** Inverse correlation lengths for the charge stripe order in the doping region  $0.20 < x, 0.33$  at 20 K. As a comparison the  $(4, 0, 4)$  Bragg peak in the  $x = 0.2$  sample is shown.

Sample	Inverse correlation length [ $\times 10^{-3} \text{ \AA}^{-1}$ ]		
	$H$	$K$	$L$
$x = 0.33$	$6.10 \pm 0.07$	$2.66 \pm 0.03$	$54.2 \pm 0.4$
$x = 0.30$	$7.56 \pm 0.08$	$4.69 \pm 0.09$	$18.8 \pm 0.4$
$x = 0.275$	$8.01 \pm 0.14$	$4.89 \pm 0.04$	$24.7 \pm 0.3$
$x = 0.25$	$18.2 \pm 0.1$	$14.6 \pm 0.1$	$66.4 \pm 0.1$
$x = 0.225$	$28.8 \pm 0.7$	$18.5 \pm 0.1$	$79.1 \pm 4.2$
$x = 0.20$	$41.8 \pm 1.2$	$46.7 \pm 1.3$	$209 \pm 8$
Bragg	$2.00 \pm 0.04$	$1.80 \pm 0.02$	$4.70 \pm 0.10$

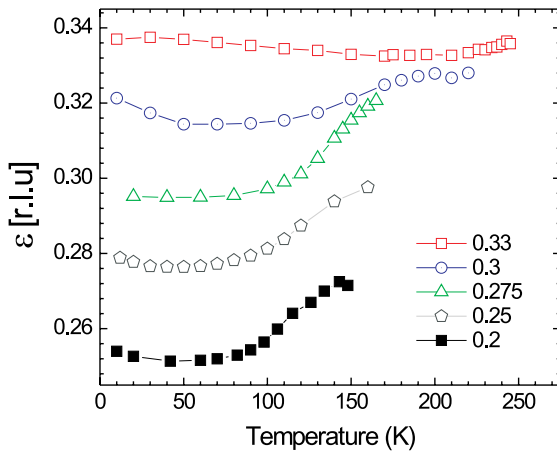
is consistent with the X-ray results on the  $x = 0.275$  and  $x = 0.30$  doped samples which showed an initial increase in the intensity at low temperatures. It could be argued that the initial increase in the low temperature region is due to a surface effect in the nickelates. However, an initial increase in the integrated intensity was observed in the 100 keV high energy X-ray measurements by Vigilante et al. [6] although it is not as dramatic as observed in our measurements. We postulate that it is not a surface effect but is an effect that X-rays are sensitive to and neutrons are not. In region I for  $x < 0.25$  there is a decrease in both the inverse correlation length and in the commensurability that was not observed in the neutron measurements by Sachan et al. [3] and Tranquada et al. [5]. In the  $x = 0.225$  high energy X-ray measurements [6] there was evidence of a decrease in the inverse correlation length but it was a smaller effect than observed in our measurements and there was no decrease observed in  $\varepsilon$ . We can offer no definite explanation for the discrepancy between the neutron and X-ray techniques. Both techniques are sensitive to long range correlations in the electron density and reflect distortions in the electron density and would be expected to show similar results with respect to the integrated intensity. There has been some discussion as to whether a movement of holes from the nickel atoms (site centered stripes) to the oxygens (bond centered stripes) could be responsible. However, Tranquada et al. [16] in a study of  $\text{La}_2\text{NiO}_{4+\delta}$  for  $\delta = 0.133$  determined that the movement of the holes from the Ni sites to the oxygens only became significant above the magnetic ordering temperature. This does not explain the low temperature behaviour which occurs well below the magnetic ordering temperature. Further study is required to clarify the discrepancy between the X-ray and neutron measurements.

The inverse correlation length for all samples in the doping region is shown in Table 1 with the results for the higher doped samples taken from Ghazi et al. [9]. As the doping is reduced from  $x = 0.33$  the charge stripe order becomes progressively less correlated. The charge stripe order in the  $x = 0.20$  and  $0.225$  doped samples exists in a charge stripe glass characterised by weak, diffuse charge stripes. This contrasts with the intense, well correlated charge order observed for  $x > 0.275$ . The charge order in the  $x = 0.25$  doped sample can be characterised as existing in an intermediate state between the two regimes. A difference in the behaviour of the inverse correlation

length was observed in region I between the low doped samples and the samples with  $x > 0.275$ . In the high doped samples the inverse correlation length stays relatively constant in region I. However, in the low doped samples a decrease in the inverse correlation length is observed that accompanies the increase in intensity and decrease in commensurability. We postulate a reason for this is that in the lower doped samples because the charge order is less stable it is more sensitive to Coulomb effects. As the commensurability decreases the Coulomb repulsion decreases resulting in a stabilisation of the charge stripe order shown by the smaller inverse correlation length. In the higher doped samples the Coulomb repulsion is larger because the stripes are closer together but this is countered by the significantly stronger coupling between the charge stripes and the lattice.

The 12 keV surface X-ray measurements by Ghazi et al. [9] of the correlation length agreed approximately with the neutron measurements by Lee et al. [17] and Yoshizawa et al. [7]. However, 130 keV X-ray studies by Wilkins et al. [11] measured a significantly smaller correlation length than that measured by neutrons. Both techniques measure the bulk properties of the sample and it is not known why there is a difference in the correlation length measured by the two techniques. By comparing the results of this study for  $x = 0.225$  with the high energy results from Vigilante et al. [6] it was hoped to determine if a similar difference was observed in the low doped samples between the surface and bulk X-ray measurements. In the  $x = 0.225$  doped sample we measured an inverse correlation length of  $\xi^{-1} = 0.029 \pm 0.001 \text{ \AA}^{-1}$ . The inverse correlation length measured by Vigilante et al. [6] was estimated from the HWHM of the high X-ray energy and neutron measurements as approximately  $\xi^{-1} = 0.03 \text{ \AA}^{-1}$  with both techniques. In all studies the width of the charge order peaks was significantly larger than the resolution of the system. This result suggests that in the  $x = 0.225$  the charge exists in the same glassy state in both the bulk and at the surface. To allow a comparison the inverse correlation length in the  $H$  direction was calculated for the  $x = 0.33$  doped sample at 130 keV. The inverse correlation length in the  $H$  direction was  $\xi^{-1} = 0.028 \pm 0.001$  and this is approximately the same as the Vigilante [6]  $x = 0.225$  bulk measurements. This may suggest that the charge order exists in a glassy state within the bulk for all samples in the  $x = 0.20 - 0.33$  doping range. However, to clarify this would require high energy X-ray studies of all samples in the doping regime.

The behaviour of the commensurability with temperature for the  $x = 0.33, 0.30, 0.275, 0.25$  and  $0.20$  samples is shown in Figure 5. The results from the  $0.225$  sample have been omitted due to the excess oxygen doping. In the  $x = 0.33$  system there is a small change in the incommensurability as it tends towards the  $\varepsilon = 1/3$  value and when it reaches this position a stabilisation of the charge order pattern occurs. In all the lower doped samples the change in position is much more significant as the charge order attempts to move towards the stable position of  $1/3$  but the charge order disappears before the



**Fig. 5.** Comparison of the commensurability as a function of temperature in the 0.20, 0.25, 0.275, 0.30 and 0.33 doped samples.

stable position is reached. In the 0.20 doped sample the charge order is very close to the next commensurate value of  $\varepsilon = 0.25$  but there appears to be no stabilisation of the charge order pattern at this position. In all the samples the inverse correlation length shows a sharp increase in the region above  $T_N$  because long range order cannot exist in the absence of magnetic order. In the  $x = 0.33$  sample the charge order is stabilised by the interactions between the lattice and the charge order state even above  $T_N$ .

To summarise we have shown that the charge order exists in a charge stripe glass state in the  $x = 0.20$  and 0.225 doped nickelates. When the results for the  $x = 0.225$  sample are compared with the high energy X-ray scattering results it suggests that the charge stripes in the bulk and at the surface may exist in the same state. This contrasts with the X-ray measurements on the  $x = 0.33$  doped system where there is a dramatic difference between the charge order in the bulk and at the surface when measured with X-rays. In all samples there are clear differences at low temperature between the X-ray results and the neutron results.

## 5 Conclusions

In the nickelate system we have shown that the charge order for samples with  $x < 0.25$  is weak, incommensurate and poorly correlated i.e. it exists in a charge stripe glass. This differed from the intense, highly correlated charge order observed in the  $x = 0.275$  doping level and above. The study showed that as the doping was increased from 0.20 towards 0.33 the charge order became more intense and stable. The commensurability showed the same behaviour in all samples with it moving towards the stable  $\varepsilon = 0.33$  position and no stabilisation was observed at the next commensurate position of  $\varepsilon = 0.25$ . The charge order in all samples showed an initial increase in the integrated intensity at low temperatures that was not observed with the neutron measurements but is observed with X-ray measurements. The comparison with the high

energy results from the  $x = 0.225$  sample and those in the  $x = 0.33$  sample suggests that the charge order may exist in a glassy state within the bulk across the 0.20–0.33 doping range. The charge order is pinned at the surface in the nickelates but as the doping is decreased from 0.33 the stabilisation of the charge order at the surface decreases until in the  $x = 0.225$  doped sample and below it exists in a charge glass in the bulk and at the surface. However, this requires further investigation as there are discrepancies between the neutron and high energy X-ray measurements in the  $x = 0.33$  sample.

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