HIGH-RESOLUTION HIGH ENERGY X-RAY DIFFRACTION STUDIES OF CHARGE ORDERING IN CMR MANGANITES AND NICKELATES

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High-resolution, high-energy, X-ray diffraction results are presented for the study of weak charge ordering phenomenon. By utilizing X-rays in the 100 keV region the dramatic increase in the penetration depth allows for both bulk-sensitive and high- resolution measurements to be made. The strontium doped La_2NiO_4 system is a prototypical system in the understanding of strong electron-phonon coupling, and the resultant effects on material properties. At doping levels of 1/3 and ½ commensurate charge modulations are observed indicating real-space charge stripes. We have measured the correlation lengths of these charge stripes using both 100 keV X-rays and 8.3 keV X-rays. In comparing our results we have observed that the charge stripes appear to be well correlated in the near-surface region with correlation lengths $\xi \approx$ 2400Å. However, our bulk sensitive measurements show that the charge stripes appear in a possible stripe glass phase with a correlation length of only $\xi \approx$ 300Å. Our measurements on the 3D charge order manganite system $Nd_{0.5}Sr_{0.5}MnO_3$ show that the charge ordering appears to be well correlated in the bulk of the sample in contrast to our nickelate results.

1 Introduction

The strontium doped La_2NiO_4 system is iso-structural with the high T_C super-conducting cuprate La_2CuO_4 and is a prototypical system for the understanding of strong electron-phonon coupling, and the resultant effects on material properties. In the doping regime of $x = 0.333$ and $x = ½$ commensurate charge ordering modulations occur below T_C, characteristic of a charge stripe phase consisting of hole rich anti-phase spin domain boundaries surrounded by anti-ferromagnetic hole deficient regions [1]. In contrast, the strontium doped colossal magneto-resistance oxide $Nd_{0.5}Sr_{0.5}MnO_3$ is a valuable system for the study of the interplay between charge, spin and orbital degrees of freedom and has attracted much interest due to its magneto-resistance properties [2] thought to be due to the metal-insulator transition induced by a magnetic field. At low temperatures regime a charge-ordered state exists with the transition from a ferromagnetic, metallic state to an anti-

ferromagnetic insulating state. In both systems charge ordering is believed to be a critical factor in determining the properties of the ground state.

High-energy X-ray scattering is a technique ideally suited for the study of weak charge density modulations, as it offers both bulk sensitivity and high wavevector resolution. Studies of such phenomena using neutron scattering, while probing the bulk of the sample suffer, as neutrons are not directly charge scattered but are sensitive to the distortions caused by the atomic modulations. X-ray techniques offer a natural solution as they scatter directly of the charge distribution in the sample, however, at energies in the region of approximately 10 keV they are only sensitive to the near surface region. Through the use of a third generation synchrotron radiation sources it is possible to obtain a high flux of high energy X-rays in the region 100 keV – 500 keV which, due to the reduction in sample absorption allow high-resolution bulk sensitive studies [3-5].

In this paper we present studies on the charge ordered phases of both $Nd_{0.5}Sr_{0.5}MnO_3$ and $La_{1.667}Sr_{0.333}NiO_4$ using high energy X-rays. These results display the differing properties between the bulk and near surface region of the samples under study, and as a result we have obtained a clear picture of the charge ordered state in the bulk of single crystal samples.

2   High Energy Diffraction from $La_{0.667}Sr_{0.333}NiO_4$

A single crystalline sample of $La_{1.667}Sr_{0.333}NiO_4$ grown at Bell Labs. measuring approximately 2 mm x 2 mm x 1 mm was mounted on the cold finger of a closed cycle He refrigerator on the 4-circle, triple axis diffractometer [6] on ID15-A at the ESRF, Grenoble France. The sample was mounted with the [111] direction surface normal allowing the (h k l) zone of reciprocal space to be investigated. An incident photon energy of 130 keV was selected by a (113) oxygen precipitated Si crystal monochromator with higher order harmonics rejected electronically by the use of a Ge solid-state detector. Diffraction was performed in the horizontal plane using dispersive Laue geometry with the addition on an analyzer crystal, of the same type as the monochromator, for triple axis measurements.

Previous X-ray and neutron experiments [7-9] have verified that the charge ordering (CO) superlattice reflections are characterized by a modulation wavevector $G_{CO} = (2\varepsilon, 0, 1)$ with $\varepsilon \approx 0.333$. The sample was cooled to below T_{CO} and superlattice reflections were located at (4.667, 0, 5), (3.333, 0, 3), (4.667, 0, 3) and (0, –4.667, 5), the latter occurring due to twinning in the a-b plane of the crystal. The resolution function measured on the (4, 0, 4) Bragg reflection was calculated to be $\delta = 1.6$ x 10^{-4} Å^{-1} in the $Q_{//}$ (longitudinal) direction in reciprocal space. This is a factor of 10 better than the resolution obtained at 8.3 keV in measurements of the near surface region. The temperature dependencies of the super-lattice reflection (4.667, 0, 5) was measured scanning in both the $Q_{//}$ and $Q_{\perp}$ directions in reciprocal space.

The sample was found to be of high quality with a mosaic spread of only ~ 0.01° and showed no lattice strains, as all the Bragg reflections were sharp in the $Q_\parallel$ (2θ) direction. Figure 2 shows a comparison of the CO superlattice peak and the corresponding Bragg peak. The corresponding charge order peaks are clearly very broad and weak which suggests that in the bulk of the crystal the charge stripes are correlated over only a short distance of ~ 40 Å. The intensity of the superlattice reflections was found to be considerably less than in previous high-energy studies [3] suggesting that the number of stripes, or the charge amplitude may be sample dependant. Such results are consistent with previous neutron scattering measurements on $La_{1.667}Sr_{0.333}NiO_4$ and $La_{1.775}Sr_{0.225}NiO_4$ [7, 9-11].
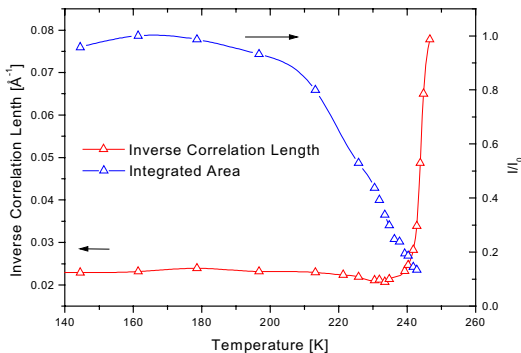

Figure 1 : Temperature dependence of the integrated intensity, and inverse correlation length of the (4.667, 0, 5) CO superlattice peak.
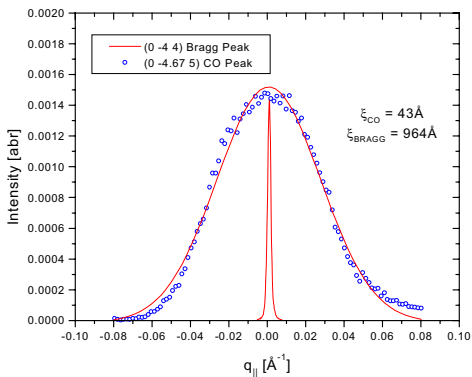

Figure 2 : Longitudinal scan through the (0,-4,4) and (0,-4.66, 5) Bragg and charge order peaks

In our previous work on this sample of $La_{1667}Sr_{0.333}NiO_4$ using X-rays with an incident photon energy of 8.3 keV, probing the near surface region of the sample, we found a much sharper CO reflections corresponding to correlation lengths of ~2400Å [8, 12]. Figure 1 displays the temperature dependence of the inverse correlation length. This shows that the melting of the charge stripes occurs at 240K, and above this transition temperature only very weak CO scattering is observed. This is caused by charge ordered critical fluctuations with the rapidly decreasing correlation length displaying the expected power law dependence. Below T_C the charge stripes are only short range ordered (~ 300 Å) and exist in a disordered glassy state. Figure 1 also shows the integrated intensity of the charge ordered reflection suggesting that the stripes do not reach maximum charge amplitude until below 200K. Figure 3 shows a comparison of the temperature dependence of the correlation length measured in the bulk using high energy X-rays and in the near surface region using conventional X-ray scattering. Both sets of data were obtained from the same sample. It is clear that very different behaviour is being observed. We postulate, that in such high quality crystal the charge stripes are semi-disordered and hence only correlated over very short distances of a few unit cells. However in the near surface region, where the dislocation density and strain energy are much higher the charge stripes are "pinned" to the lattice, causing a much higher degree of correlation.
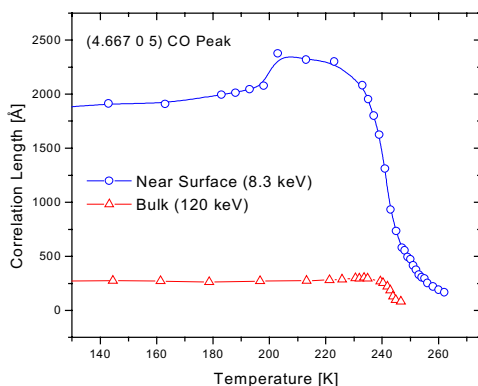

Figure 3 : Temperature dependence of the correlation length of the (4.667, 0, 5) CO superlattice peak in the near surface, and bulk, of $La_{1.667}Sr_{0.333}NiO_4$.

3   High energy diffraction from Nd$_{0.5}$Sr$_{0.5}$MnO$_3$

A sample of Nd$_{0.5}$Sr$_{0.5}$MnO$_3$ was mounted on the 4-circle triple axis diffractometer at ID-15A as outlined in section 2 with an incident photon energy of 100 keV. The sample was mounted with the (101) direction surface normal allowing the (*h 0 l*) zone of reciprocal space to be investigated.

The sample was cooled to below the transition temperature (~ 140 K) and charge order satellites at (1.5, 0, 2), (2.5, 0, 2), (1.5, 0, 3) and (2, 0, 2.5) were located. Figure 4 shows a comparison between the charge order superlattice peak and the corresponding Bragg peak normalized to the same peak intensity. It is clear that in this sample the charge ordering is long-range, being almost of the same value as the Bragg correlation length.
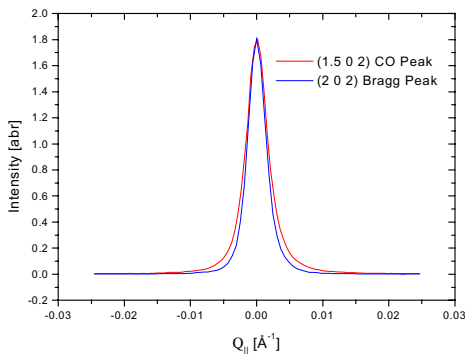

Figure 4 : Comparison of the (1.5, 0, 2) CO superlattice peak and the (2 0 2) Bragg peak in the $Q_{\parallel}$.direction.
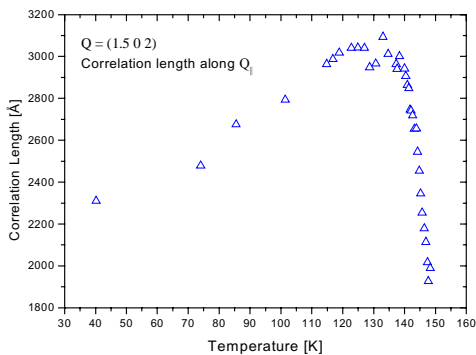

Figure 5 : Correlation length along $Q_{\parallel}$ of the (1.5, 0, 2) charge ordering superlattice peak.

The charge ordering is much stronger in the manganites than in the nickelates and is also 3D rather than 2D in nature. Scans were taken as a function of temperature through the charge order peaks in both the $Q_\parallel$ and $Q_\perp$ (analyzer and sample rocking curves respectively) directions in reciprocal space. The correlation length of the charge ordering was calculated and is shown in Figure 5 as a function of temperature. From the temperature dependence measurements of the correlation length in Figure 5 it is clear that the correlation of the charge ordering improves as the temperature is increased upon warming to T_C.

4   Acknowledgements

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[12] Correlation lengths were calculated from the inverse of the HWHM of the peak in reciprocal space where $d^* = d^{-1}$. Previously correlation lengths were calculated using $d^* = 2\pi.d^{-1}$ underestimating the correlation length by a factor of 2π.