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Peer-reviewed

### Citation for published item:

Wilkins, S. B. and Hatton, P. D. and Roper, M. D. and Prabhakaran, D. and Boothroyd, A. T. (2003) 'Soft x-ray resonant magnetic diffraction.', *Physical review letters.*, 90 (18). p. 187201.

### Further information on publisher's website:

<http://dx.doi.org/10.1103/PhysRevLett.90.187201>

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## Soft X-Ray Resonant Magnetic Diffraction

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(Received 28 January 2003; published 8 May 2003)

We have conducted the first soft x-ray diffraction experiments from a bulk single crystal, studying the bilayer manganite  $\text{La}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$  with  $x = 0.475$  in which we were able to access the (002) Bragg reflection using soft x rays. The Bragg reflection displays a strong resonant enhancement at the  $L_{\text{III}}$  and  $L_{\text{II}}$  manganese absorption edges. We demonstrate that the resonant enhancement of the magnetic diffraction of the (001) is extremely large, indeed so large that it exceeds that of the nonresonant Bragg diffraction. Resonant soft x-ray scattering of 3d transition metal oxides is the only technique for the atomic selective measurement of spin, charge, and orbital correlations in materials, such as high temperature superconductors, colossal magnetoresistance manganites, and charge stripe nickelates.

DOI: 10.1103/PhysRevLett.90.187201

PACS numbers: 75.25.+z, 61.10.-i, 71.30.+h, 75.47.Lx

X-ray diffraction is a mature technique for studying the crystallographic structure of materials. With the advent of high intensity synchrotron radiation, the technique has broadened to take advantage of the polarization, time structure, low divergence, and coherence. The energy of the monochromatic x-ray beam can be changed to alter the penetration and scattering, particularly close to element absorption edges giving atomic selectivity.

The use of soft x-ray energies in single crystal diffraction experiments has received little attention due to the perception that the absorption by the sample is far too high. Certainly, x rays at such energies are extremely inconvenient to work with. First, air absorption at such energies is severe; the experiment (sample, diffractometer, etc.) must be placed in vacuum. Second, soft x rays have prohibitively long wavelengths, which means that the Ewald sphere is very small and only a very small volume of reciprocal space around the origin is accessible. It is for these reasons that it has been widely believed that soft x rays are inappropriate for diffraction experiments. As a result, there have been no reported experiments of diffraction from single crystals using soft x rays. For this, the first attempt at soft x-ray diffraction, we chose to study the bilayer manganite  $\text{La}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$  [1]. This material crystallizes in a layered structure, as shown in Fig. 1, and has unit cell parameters of  $3.87 \times 3.87 \times 20.1$  Å. The  $c$  axis is sufficiently long to allow us to access the (002) Bragg reflection, even at soft x-ray energies. We find that the diffraction intensity varies strongly with incident x-ray energy when scanned through the  $L_{\text{III}}$  and  $L_{\text{II}}$  absorption edges, and we observe diffraction from the magnetic ordering via a dramatic resonant enhancement at the  $L_{\text{II}}$  and  $L_{\text{III}}$  edges. Our results demonstrate that resonant magnetic diffraction can be extended to the 3d

transition metals and that this technique provides a direct probe of the 3d orbitals of charge, spin, and orbitally ordered oxides such as manganites, cuprates, and nickelates.

The experiments were conducted on station 5U1 at the Synchrotron Radiation Source (SRS) at Daresbury Laboratory. The beam line, situated at the end of a variable gap undulator, produces a tunable monochromatic

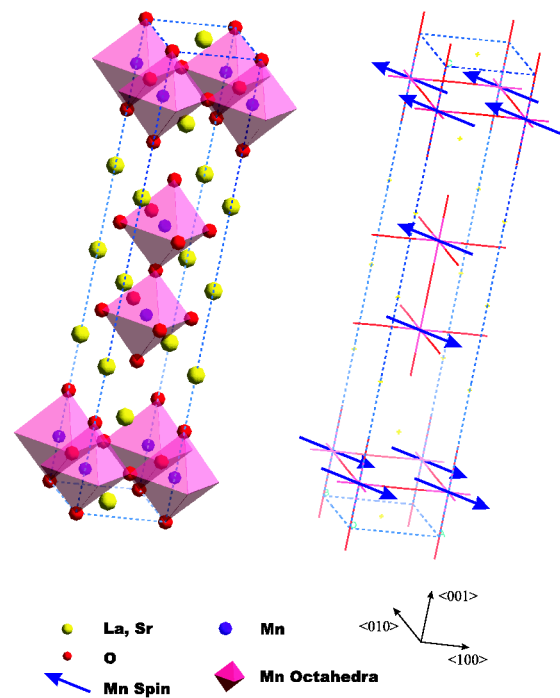


FIG. 1 (color online). The magnetic and crystallographic structure of the Ruddlesden-Popper bilayer manganite  $\text{La}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ .

beam of photons in the energy range 60–1000 eV. A 300  $\mu\text{m}$  post grating exit slit was used resulting in an energy resolution of  $\Delta E = 1$  eV at 640 eV. The incident x rays were approximately 90% linearly  $\sigma$  polarized with an incident flux of the order  $10^{11}$  photons  $\text{s}^{-1}$ . The two-circle diffractometer [2] is in a high vacuum vessel to eliminate air absorption, and a variable temperature stage using liquid nitrogen is located on the sample ( $\theta$ ) axis. The diffractometer was operated with a base pressure in the region  $10^{-6}$  to  $10^{-7}$  torr with the theta and two theta axes both having a mechanical resolution of  $0.0005^\circ$ . A 300  $\mu\text{m}$  slit was placed in front of the detector to increase the experimental resolution, resulting in an angular resolution of  $0.1^\circ$ . The scattered photon flux was estimated from calibration of the drain current of the photodiode detector. Typically, data was collected with an average measurement time of 1–5 s per datum.

The crystal of  $\text{La}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$  with  $x = 0.475$  was grown by the floating-zone method with dimensions of  $8 \times 8 \times 1$  mm. These samples naturally cleave with large faces with [001] surface normal, and it was this untreated surface that was used. The sample was aligned in the diffractometer with the [001] and [110] defining the diffraction plane, giving an azimuthal orientation with the [110] direction being perpendicular to the incident x-ray electric field vector. Initially, experiments were carried out in the nonresonant condition at a photon energy of 900 eV. The inset of Fig. 2 shows a scan through the Bragg (002) diffraction reflection in the [001] direction. At 900 eV, the  $\theta$  angle of approximately  $44^\circ$  that is required to satisfy the Bragg condition is easily accessible. By measuring the peak width in the [001] direction (i.e., parallel to the scattering vector), it is possible to measure the crystal truncation rod, the broadening in reciprocal space due to the finite depth penetration of the incident x-ray beam. Performing such a calculation, we find the inverse correlation length [defined as  $\xi^{-1} = \frac{2\pi}{c} \kappa$ , where  $\kappa$  is the half width at half maximum in reciprocal lattice units (r.l.u.) and  $c$  is the direct space lattice parameter] to be  $2.273 \times 10^{-3} \text{ \AA}^{-1}$ . This is approximately half that of the inverse correlation length measured by us on the same crystal at a photon energy of 12.4 keV and is comparable with the absorption attenuation length,  $\mu^{-1}$ . This demonstrates that the soft x rays are penetrating through many unit cells of the single crystal and that the technique is not particularly surface sensitive.

In the next part of the experiment, we recorded the (002) Bragg peak intensity as a function of the incident x-ray energy. Close to absorption edges the real and imaginary scattering factors are radically altered, giving increased absorption, and also increased scattering. Figure 2 shows the intensity of the (002) Bragg reflection as a function of energy close to the  $L_{\text{III}}$  and  $L_{\text{II}}$  Mn-absorption edges. Dramatic enhancement of the diffraction intensity is observed at  $\sim 640$  and  $\sim 655$  eV,

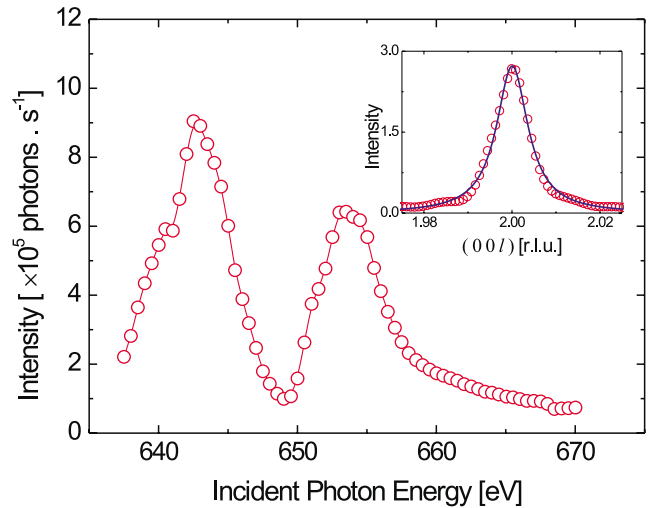


FIG. 2 (color online). An energy scan at constant wave vector at the (002) Bragg reflection through the  $L_{\text{III}}$  and  $L_{\text{II}}$  Mn edges at 300 K. The inset shows a scan in the  $\theta$ -2 $\theta$  direction through the (002) Bragg reflection at 300 K. The solid line is a Lorentzian fit to the experimental data (open circles).

while there was no observed change in the background of the Bragg peak on resonance. These enhancements are so large that potentially extremely weak charge scattering, unobservable at off-resonant energies, could become easily observable via the resonant enhancement effect.

These charge scattering measurements already extend the range of possibilities of x-ray diffraction in the study of crystal structures, but the really exciting prospect is the use of such resonances in the study of magnetic structures. The use of x-ray scattering to probe the magnetic structure of crystalline solids started over 25 years ago with the study of NiO by de Bergevin and Brunel [3]. However, such scattering is an extremely weak phenomenon, typically  $10^8$  times weaker than charge reflections, with the result that most magnetic structure determination has employed neutron diffraction. During the past 15 years, enormous strides have been made in magnetic x-ray scattering using highly intense synchrotron sources. Huge increases in the magnetic cross section of x-ray scattering have been obtained by tuning the x-ray energy near to the absorption edge of the material [4–6]. These resonant enhancements can be so large that resonant magnetic scattering can be employed in the study of thin films and even surface layers. Furthermore, in the resonant regime close to an absorption edge there are other terms that contribute to the total scattering. For an x ray promoting an inner shell electron to an unoccupied outer level, the amplitude for resonant magnetic scattering depends upon the matrix elements that couple the ground and excited states. This means that the energy and polarization dependence of the magnetic scattering probes the fine structure of the magnetic states.

Most experiments have concentrated on the lanthanides (for which the  $L$  absorption edges are around 8 keV) and the actinides (where the  $M$  edges are around 3–4 keV). Such edges are convenient to work with, as the effects of air and sample absorption are not so severe. For example, experiments on the spiral magnetic structure of holmium at the  $L$  edges found a fiftyfold resonant enhancement of the diffraction [4,5]. At the  $M$  edge even larger effects have been observed, e.g., in uranium arsenide (UAs) an enhancement of 7 orders of magnitude was observed at the  $M_{IV}$  edge (3.7 keV) and 5 orders of magnitude at the  $M_V$  edge [6]. Until now, the highest resonant enhancement obtained was discovered in UAs where the magnetic scattering signal was found to be 1% of the charge scattering.

To date, it has not been possible to exploit fully resonant magnetic diffraction to study  $3d$  transition metal compounds, the largest class of magnetic materials in technological applications and fundamental research. This is because  $3d$  ions contain no strong resonances in the hard x-ray region. Scattering at the  $K$  edge resonances of  $3d$  ions has been observed [7,8], but the enhancement is small (factor of 3–5) because the transition probed is the  $1s - 4p$  while the spins responsible for the magnetic ordering belong to the  $3d$  band. To study magnetism in transition metal compounds directly, one needs to access the  $L_{III}$  and  $L_{II}$  edges, which exist in the region 500–900 eV. However, the value of utilizing soft x-ray resonance experiments has been demonstrated by related experiments on thin films which have employed resonant soft x-rays to probe the magnetic alignment of coupled layers in metallic multilayers [9] and magnetic stripe domain structures in FePd alloys [10]. Other studies have used soft x-ray absorption edges for x-ray magnetic circular dichroism [11]. Very recently soft x-ray resonant scattering on thin films of  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  at the oxygen  $K$  edge has been observed giving information on the carriers [12].

$\text{La}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$  ( $x = 0.475$ ) undergoes a transition into a charge and orbitally ordered state at 220 K followed by a transition into an  $A$  type antiferromagnetic (AFM) structure at 180 K. The magnetic structure has been previously determined by neutron scattering experiments [13,14]. The right side of Fig. 1 shows the magnetic structure which is ferromagnetic in the  $a$ - $b$  plane but antiferromagnetic along the  $c$  axis previously solved by neutron scattering techniques [15]. Therefore below 180 K a magnetic diffraction peak due to the AFM structure should occur at the (001) position, even though the (001) Bragg reflection is systematically absent because of the crystal symmetry.

The sample was cooled down to 83 K and the incident x-ray energy tuned to the  $L_I$  absorption edge (769 eV). No resonance of the AFM (001) at this energy was observed. The incident photon energy was set to 639 eV corresponding to the  $L_{III}$  absorption edge. Such an edge causes a

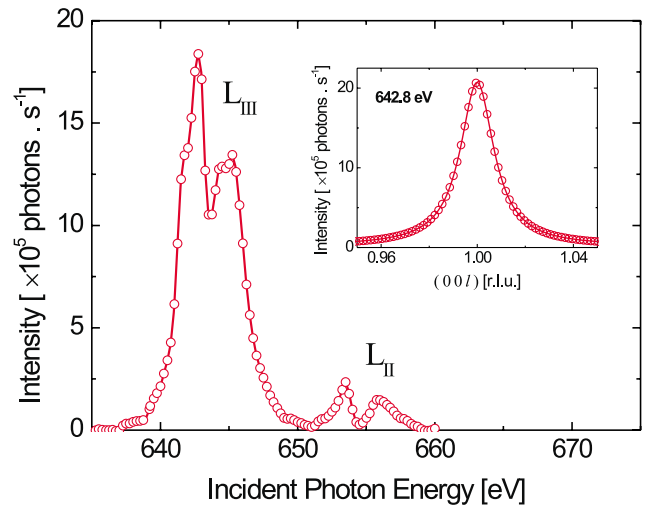


FIG. 3 (color online). An energy scan at fixed wave vector through the (001) antiferromagnetic ordering reflection at 83 K. The inset shows a scan through the same peak in the (00 $l$ ) direction, with the solid line being a Lorentzian fit to the experimental data (open circles).

dipole transition from the  $2p_{3/2}$  to  $3d$  levels directly probing the split electronic structure due to the magnetism. Appreciable intensity of the (001) was found at this wave vector, and a scan is shown as the inset of Fig. 3. A scan of incident photon energy versus the integrated intensity of the (001) diffraction was measured. The result, shown in Fig. 3, indicates two noticeable peaks showing an extremely large resonant enhancement at the  $L_{III}$  edge. In addition, magnetic diffraction was also observed at the  $L_{II}$  edge. Away from the  $L_{II}$  and  $L_{III}$  resonances, the magnetic peak was unobservable due to its very low intensity. Such a large resonant enhancement has been predicted qualitatively [16]. The different spectral shape observed in this resonance as opposed to that of the Bragg peak is most probably due to the electronic structure of the  $3d$  band being split due to the effects of Jahn-Teller distortions of the Mn octahedra and the structure factor of the (001) being only sensitive to the Mn ions. To confirm the origin of the reflection, the sample was warmed to 300 K, past the Néel temperature of 180 K and the energy scan repeated. No resonance was found at high temperature. Measuring the inverse correlation length of the (001) reflection in the [001] direction gives a value of  $5.31 \times 10^{-3} \text{ \AA}^{-1}$ , twice that of the (002) Bragg peak off resonance. This increase is most likely due to the increase in absorption at the edge.

We measured the integrated intensity of the AFM (001) peak as a function of temperature upon warming. The results are shown in Fig. 4. The sample displays charge ordering below 220 K resulting in additional charge supercell reflections at a wave vector of  $(\frac{1}{2}, \frac{1}{2}, 0)$ . Separately, we have measured the charge ordering satellite intensity as a function of temperature [17] using

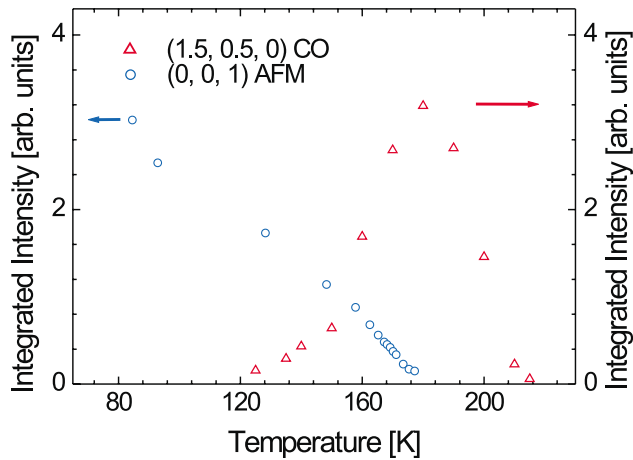


FIG. 4 (color online). Integrated intensity of the antiferromagnetic (001) peak measured by resonant soft x rays at the manganese  $L_{III}$  edge (open circles) and the (0.5, 1.5, 0) charge order superlattice reflections measured by high-energy non-resonant x-ray diffraction (open triangles).

nonresonant high-energy x-ray diffraction at beam line BW5 at HASYLAB, Germany [18]. Here the same sample was mounted on a four-circle diffractometer with an incident photon energy of 94.8 keV. As found by others [15], the charge ordering reaches a maximum at 180 K before reducing in intensity and disappearing below 120 K. In Fig. 4, we can see that the onset of the AFM ordering at 180 K exactly coincides with the maximum intensity of the charge ordering. It is the onset of the ferromagnetic order in the  $a$ - $b$  plane that causes a collapse of the charge order.

Our results demonstrate the unique features of resonant magnetic diffraction as a probe of the magnetic state of a material. By tuning to the different edges, it is possible to provide elemental specific measurements, separating the spin and orbital components on each chemical species. Second, the absorption edge, and thus the energy of the core-electron transitions, is dependent on the valence state of the ion. Therefore the resonant energy of the magnetic transition is dependent on the valence state. Resonant magnetic x-ray scattering is the only technique which provides this degree of both element and valence state specificity. These new results obtained using soft x rays show that we are in a new regime where resonant magnetic scattering is substantially larger than nonresonant charge scattering. In a future paper, we will demonstrate the use of soft x rays to probe orbital correlations. Resonant soft x-ray diffraction at the  $L$  edges of  $3d$

transition metal oxides is the only technique for the direct observation of spin, charge, and orbital correlations in strongly correlated electron systems. Soft x-ray resonant techniques may be used to study layered cuprates such as  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  (with periods greater than 6.6 Å) which display charge and spin ordering. This work has shown that soft x-ray diffraction will become an exciting technique in the future for the study of magnetism in  $3d$  materials with extensions to systems such as copper based high temperature cuprate superconductors, colossal magnetoresistance manganites, and charge striped nickelates.

We gratefully acknowledge experimental support and discussions with P.D. Spencer, T.A.W. Beale, T.P.A. Hase, B.K. Tanner, S.P. Collins, and G. van der Laan. We are grateful to the director of the Laboratory for access to the beam line and to EPSRC and CLRC for financial support. S.B.W. would like to thank EPSRC for support, and P.D.H. thanks also the University of Durham Sir James Knott foundation for support.

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