Strain effects and anomalous x-ray scattering in tetragonal manganites

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Abstract. Using an ab initio pseudopotential approach, we examine the effect of variations in the c/a ratio on the Mn K-edge anomalous x-ray scattering tensor in La_0.5Sr_0.5MnO_3 films coherently strained by growth on several different perovskite substrates. The calculations agree well with the results of recent Mn K-edge interference scattering measurements on these systems. Comparison with experiment supports the interpretation that the anomalous scattering signal is determined by the Jahn–Teller distortion, as opposed to the effect of the Mn 3d–4p onsite Coulomb interaction proposed earlier.

Contents

1. Introduction 2
2. Method 3
3. Results and discussion 5
4. Summary 7
Acknowledgments 7
References 7
1. Introduction

The interplay between spin, orbital, charge and lattice degrees of freedom is a key factor in determining the properties of strongly correlated transition-metal oxides, such as colossal-magnetoresistive manganites [1]. Unlike spin, charge and structural order, which can be monitored by conventional neutron, electron and x-ray diffraction techniques, direct experimental observation of orbital ordering has proven quite challenging. In recent years, resonant elastic x-ray scattering (RXS)—also known as anomalous x-ray scattering—has emerged as a powerful tool for the analysis of structural, magnetic and electronic ordered phases. RXS techniques have been exploited to investigate orbital ordering in manganites and related transition-metal compounds [2]–[9]. It has been shown, in particular, that the use of hard x-rays tuned to the transition-metal K edge considerably enhances the sensitivity of the x-ray probe to the anisotropy of the electron distribution related to orbital order. Several different mechanisms, however, have been invoked to explain this effect, and its origin remains rather controversial.

In the case of manganites, it is generally accepted that the Mn K-edge scattering process derives from virtual electric dipole excitations to empty Mn 4p states. Two conflicting descriptions, however, have been proposed to explain the anisotropy of the Mn 4p states and the resulting RXS data. On the one hand, on the basis of multi-electron MnO₆ cluster calculations, it has been proposed that the measured anisotropy is determined by the Mn 3d orbital ordering via onsite 3d–4p Coulomb interaction [6, 10]. On the other hand, \textit{ab initio} local-density-based band-structure and multiple-scattering calculations have indicated that the RXS intensity derives from the Jahn–Teller distortion of the MnO₆ octahedra that accompanies the orbital ordering, rather than from the orbital ordering itself [11]–[16]. The relative importance of orbital ordering versus Jahn–Teller distortion in determining the RXS signal is still a debated issue.

Very recently, an RXS technique making use of interferences between $\sigma$ and $\pi$ polarization components of the scattered beam has been applied to epitaxially strained La₀.₅Sr₀.₅MnO₃ films to discriminate between the two mechanisms [17]. The idea is that the two competing mechanisms should differ in the sign of the splitting they induce between Mn 4pₜ and 4pₓ,ᵧ states [6]: an information that can be extracted from the analysis of interference spectra, as opposed to conventional RXS spectra,³ in systems exhibiting ferro-orbital ordering. Such an ordering occurs in La₀.₅Sr₀.₃MnO₃ under tetragonal strain [18] (see also [19] for an extensive local-density-based study of the orbital and magnetic ordering properties of tetragonal La₁₋ₓSrₓMnO₃ films [19]). Measurements were performed on La₀.₅Sr₀.₃MnO₃ films pseudomorphically grown on three different perovskite substrates: LaAlO₃ (LAO), (LaAlO₃)₀.₃₋(SrAl₀.₅Ta₀.₅MnO₃)₀.₇ (LSAT), and SrTiO₃ (STO). The analysis indicated that the Mn 4p₂, 4pₓ,ᵧ energy ordering is systematically opposite to that predicted by the 3d–4p Coulomb-interaction mechanism [6], and the data were interpreted as evidence that the Jahn–Teller distortion has a dominant effect on the anomalous scattering signal [17]. The spectra were fitted using differences between rigidly shifted Mn atomic scattering factors [17]: $f(E + \Delta) - f(E)$, where $f(E)$ is the Mn K-edge atomic scattering factor obtained from fluorescence data averaged over the strained films and $\Delta$ is the fitting parameter measuring the Mn 4p₂−4pₓ,ᵧ splitting: $\Delta = E(4p_2) - E(4p_{x,y})$. The fits yielded $\Delta$ values of $-1.72 \pm 0.21$, $0.25 \pm 0.07$, and $1.01 \pm 0.13$ eV for La₀.₅Sr₀.₃MnO₃ on LAO, LSAT, and STO, respectively.

These new interference measurements are very interesting not only because they offer the possibility of discriminating between the two mechanisms, but also as a critical test of the

³ The latter show a quadratic dependence on the anomalous atomic scattering factor.
existing theoretical schemes to simulate Mn K-edge anomalous scattering in manganites; this concerns, in particular, *ab initio* calculations and their inherent approximations for correlated systems. Furthermore, it should be noted that interpretation of the interference data relies on semiempirical arguments, which are expected to apply well in the case of localized atomic-like Mn 4p orbitals [6]. It is, however, somewhat surprising that the effects of strain may be simulated by rigidly shifted atomic scattering factors in a system where the Mn 4p-type electronic states are delocalized and extend over a bandwidth of at least 70 eV [17]. Confirmation of the splittings by *ab initio* band-structure calculations would certainly strengthen the argument in favour of a band-structure Jahn–Teller effect [17].

In this paper, we investigate by means of *ab initio* local-density-functional calculations the effect of lattice distortion on the Mn K-edge anomalous scattering properties in La$_{0.5}$Sr$_{0.5}$MnO$_3$ coherently strained to LAO, LSAT and STO. We successfully explain the observed interference spectra and their dependence on strain $c/a$. Strain has a rather complex, energy-dependent effect on the Mn 4$p_z$, 4$p_{x,y}$ density of states—difficult to reconcile with a rigid energy shift. The spectral changes, however, exhibit a linear dependence on the distortion $c/a$, and comparison with experiments confirms the dominant influence of the Jahn–Teller distortion in determining the RXS signal.

2. Method

The calculations have been performed within the local-density functional framework, using the pseudopotential plane-wave method. We employ the Perdew–Zunger exchange-correlation potential [20] and Troullier–Martins pseudopotentials [21] in the Kleinmann–Bylander non-local form [22]. The Troullier–Martins pseudopotentials have been generated in the ground-state configuration of the non-spin-polarized atom, using as core-cutoff radii (in a.u.): $r_{4s} = 1.94$, $r_{4p} = 2.61$ and $r_{3d} = 1.94$ for Mn; $r_{5s} = r_{5p} = 1.61$, $r_{5d} = 1.82$ and $r_{4f} = 2.60$ for La; $r_{4s} = r_{4p} = 1.62$ and $r_{4d} = r_{4f} = 2.02$ for Sr; and $r_{2s} = r_{2p} = 1.52$ for O. As the local part, we use the s-component for Mn and O and the p-component for La and Sr. For Mn, we include the non-linear core correction to the exchange-correlation potential to account for the overlap between valence and core charge [23].

The Sr/La doping in La$_{0.5}$Sr$_{0.5}$MnO$_3$ is modelled with an ordered arrangement of Sr/La, using a ten-atom crystal unit cell. We have performed calculations for several different arrangements of Sr/La using larger supercells (up to 40 atoms), but observed negligible influence of the Sr/La distribution on the computed RXS spectra in the energy range considered (i.e., up to 6.6 keV, see figure 1). In our calculations, we neglect the tilting of the MnO$_6$ octahedra, which is rather small in La$_{1-x}$Sr$_x$MnO$_3$ manganites for $x > 0.2$. This approximation has also been used in previous theoretical studies of La$_{1-x}$Sr$_x$MnO$_3$ [18, 19], which describe well the $c/a$ versus $x$ phase diagram of La$_{1-x}$Sr$_x$MnO$_3$ in the range 0.2 $\leq x \leq$ 1.5.

We use a kinetic-energy cutoff of 80 Ryd for the plane-wave expansion of the electronic states. Integrations in reciprocal space are performed using a (4, 4, 6) Monkhorst–Pack $k$-point grid [24], together with a Gaussian electronic-level smearing [25] with a full width at half-maximum of 0.01 Ryd to determine the Fermi energy. The densities of states are computed using

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4 We verified that including the O 3d component has a negligible influence on the RXS spectra.

5 In these systems, the calculated ferro-orbital ordering is induced by the tetragonal strain, which splits the Mn 3d-$e_g$ orbital states.
Figure 1. The calculated (——) anisotropic component of the Mn K-edge atomic scattering tensor, \(\text{Re}[f_c(E) - f_a(E)]\), in La\(_{0.5}\)Sr\(_{0.5}\)MnO\(_3\) coherently strained to the lattice parameter of LAO (top panel), LSAT (middle panel) and STO (bottom panel). The fits obtained using the differences between rigidly shifted atomic scattering factors of the unstrained system (see text), \(\text{Re}[f_a^0(E + \Delta) - f_a^0(E)]\), are also shown (--).  

A (6, 6, 8) \(k\)-point grid; increasing the grid size to (10, 10, 14) results in virtually no change in the computed spectra. The two inequivalent components of the Mn atomic scattering tensor, \(f_c(E) \equiv F_{zz}(E)\) and \(f_a(E) \equiv F_{xx}(E) = F_{yy}(E)\), are evaluated as a function of photon energy \(E\), as follows [26]:

\[
F_{\alpha,\beta}(E) \propto \int_{E_F}^{\infty} \frac{d\varepsilon \, D^{\beta\alpha}_{a}(\varepsilon)}{E + E_0 - \varepsilon - i\Gamma/2}.
\]
where $D_{a}^{4p}(\epsilon)$ is the projected Mn 4$p_{a}$ atomic density of states and $E_F$ the Fermi energy. $E_0$ is the Mn 1s core-level energy (not computed here); this value is adjusted to align the main peak of the calculated and experimental RXS spectra [26]. $\Gamma$ is the broadening corresponding to the inverse lifetime of the Mn 1$s$–4$p$ excitation; we use for $\Gamma$ a value of 2.5 eV.

3. Results and discussion

The interference measurements of [17] are expected to yield, to the first order in the anisotropic components of the Mn atomic scattering tensor, a signal proportional to $\text{Re}[f_c(E) - f_a(E)]$ [17]. In figure 1, we show the calculated Mn K-edge anisotropic scattering amplitude $\text{Re}[f_c(E) - f_a(E)]$ for $\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ coherently strained to the lattice parameter of (a) LAO, (b) LSAT and (c) STO. We have used, in these calculations, the experimental values of the in-plane lattice parameter and tetragonal distortion of $\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ pseudomorphically grown on LAO, LSAT and STO, namely $a = 3.792, 3.870$, and $3.905 \text{ Å}$ and $c/a = 1.052, 0.993$, and 0.973, respectively [17, 18]. The experimental Mn K-edge interference data of [17] are reported in figure 2 for comparison.

The calculations provide a good description of the three main low-energy features of the experimental spectra, in figure 2, and also reproduce quite well the changes in the sign of the resonant interference signal as a function of the photon energy. The relative intensities of the LAO, LSAT and STO spectra in figure 1 are also in good agreement with the experimental data.
We note that, for the systems considered here, the computed intensity of the two main lowest-energy features scales essentially linearly with the distortion \( c/a \), consistent with the observed experimental behaviour. This behaviour indicates that the measured interference spectra are mostly determined by the linear-order term in the Mn anisotropic atomic scattering components, i.e., by \( \text{Re}[f_c(E) - f_a(E)] \), with only a minor influence of higher-order contributions, at least in the low-energy part of the spectra.

The anisotropic atomic scattering term \( f_c(E) - f_a(E) \), derives from the difference induced by strain between the Mn 4p\(_z\) and 4p\(_{x,y}\) densities of states. In figure 3, we show the calculated Mn 4p\(_z\) and 4p\(_{x,y}\) density of states for La\(_{0.5}\)Sr\(_{0.5}\)MnO\(_3\) coherently strained to LAO (\( c/a = 1.052 \)). We also show in figure 3 (inset) the calculated Mn 4p density of states of the unstrained (cubic) La\(_{0.5}\)Sr\(_{0.5}\)MnO\(_3\) system, for comparison. Considering the effect of the ligand field on localized Mn atomic-like orbitals, a tensile (contractive) strain \( c/a > 1 \) (\( c/a < 1 \)) is expected to shift the Mn 4p\(_z\) level to a lower (higher) energy with respect to the 4p\(_{x,y}\) levels. Inspection of figure 3 indicates that there is indeed a general shift in the ‘weight’ of Mn 4p\(_z\) density of states to a lower energy with respect to the Mn 4p\(_{x,y}\) density of states. This occurs, however, with significant changes in the energy dispersion of the 4p\(_z\) and 4p\(_{x,y}\) densities of states—not well accounted by rigidly shifting identical curves with respect to one another. Having in mind, however, the comparison with the experimental splitting \( \Delta \), an estimate of the corresponding theoretical value may be obtained (in the low-energy part of the spectrum) using a fitting procedure analogous to that employed in the experimental study, i.e., by fitting the expression \( \text{Re}[f_a^0(E + \Delta) - f_a^0(E)] \) to our data, using for \( f_a^0(E) \) the calculated Mn K-edge scattering factor of the unstrained La\(_{0.5}\)Sr\(_{0.5}\)MnO\(_3\) system.

In figure 1, we have reported the best fits to our data in the energy range 6.535–6.575 keV (a range which includes the three main spectral features), which were obtained using the
above procedure. As expected from the behaviour of the 4p, and 4p, density of states in the strained La0.5Sr0.5MnO3 system, displayed in figure 3, the fits obtained using differences between rigidly shifted Mn 4p densities of states cannot account in detail for the calculated interference spectra. Nevertheless, they provide a reasonable description of the relative intensity and energy position of the three main lowest-energy features in the spectra. From the best fits, we find that $\Delta = -1.5, 0.2$, and $0.8$ eV for La0.5Sr0.5MnO3 on LAO, LSAT, and STO, respectively, compared to the experimental values of $-1.72 \pm 0.21, 0.25 \pm 0.07$, and $1.01 \pm 0.13$ eV [17]. The good general agreement between calculated and experimental interference spectra and the comparable values we obtain from the fits for the splitting demonstrate that local-density-based band-structure calculations have the capability of providing a rather accurate description of Mn K-edge RXS properties, even though correlation and excitation effects are treated in an approximate way. Moreover, given that, in such calculations, the onsite 3d–4p Coulomb interaction has a negligible effect on the 4p density of states when compared to the Jahn–Teller effect [11, 12, 26], comparison with experiments supports the claim [17] that the Jahn–Teller distortion is the dominant mechanism that determines the observed K-edge RXS signal.

4. Summary

We have examined by means of ab initio pseudopotential calculations the anisotropic component of the Mn K-edge anomalous scattering tensor induced by strain in La0.5Sr0.5MnO3 films pseudomorphically grown on LAO, LSAT and STO. Our results successfully explain recent RXS interference spectra and their dependence on strain, and confirm the dominant effect of the Jahn–Teller distortion in determining the RXS signal.

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New Journal of Physics 6 (2004) 165 (http://www.njp.org/)