Has charge ordering actually been observed in manganites by resonant X-ray scattering?

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The comparison between X-ray resonant scattering experiments and X-ray absorption data shows that no real Mn^{3+}/Mn^{4+} charge ordering occurs in manganites with $Mn^{3+}/Mn^{4+}=1$ ratio. However, these experiments demonstrate the presence of two different types of manganese atoms with a different local geometrical structure. A structural model, which accounts for both X-ray absorption and resonant scattering experiments, is proposed.

Keywords: Manganites, Charge-ordering, XANES.

1. Introduction

$RE_{1-x}A_xMnO_3$ and $RE_{2-x}A_xMnO_4$ perovskite systems are usually assumed to be mixed valence. When divalent cations A substitute the trivalent cations RE, the average valence of Mn varies continuously from Mn^{3+} (x=0) to Mn^{4+} (x=1) corresponding to a change in the electronic configuration from d^4 to d^3. This assumption implies that the mixed valence perovskites can be described formally as $RE_{1-x}A_xMn^{3+}_{1-x}Mn^{4+}_xO_3$, where a mixture of Mn^{3+} and Mn^{4+} ions is present for these intermediate compositions.

Perovskites near the $Mn^{3+}/Mn^{4+}=1$ composition ratio develops the so-called charge ordering transitions (Chen *et al.*, 1997) where an order-disorder transition related to the charge localization has been proposed. The charge-ordering transition is a structural phase transition, so a change in the lattice symmetry occurs at the transition temperature. High-resolution neutron diffraction (Radaelli *et al.*, 1995; Radaelli *et al.*, 1997) and X-ray powder diffraction (Blasco *et al.*, 1997) have shown the presence of two different Mn atoms which differs in local geometry, one of which could be ascribed to the Jahn-Teller distorted Mn^{3+} atom. Nevertheless, the aforementioned diffraction techniques do not provide any direct evidence and the real charge ordering between Mn^{3+} and Mn^{4+} is still a hypothesis. Moreover, X-ray absorption spectroscopy experiments cast doubts on the occurrence of real charge localization (Subías *et al.*, 1997; García *et al.*, 2000).

A direct way to demonstrate the onset of a long-range periodic charge arrangement of the charge is the observation of superstructure reflections by X-ray resonant scattering experiments (Coppens *et al.*, 1992). The appearance of resonances at the metal K-edge energy is related (Materlik *et al.*, 1994) to the different energy of s-p excitations (dipolar transitions) for atoms with different valence state. Resonant reflections can also appear (Materlik *et al.*, 1994) due to the anisotropy of the anomalous scattering factor (Anisotropic Tensor Scattering reflections, ATS) mainly due to the directional splitting of the p-unoccupied states (also dipolar transitions).

Recently, this technique has also been applied to different manganese perovskites with a formal $Mn^{3+}/Mn^{4+} = 1$ ratio (Murakami *et al.*, 1998; Nakamura *et al.*, 1999; Zimmerman *et al.*, 1999). Two resonant reflections in the so-called charge-ordered phase were observed and assigned to a Mn^{3+} - Mn^{4+} charge ordering (CO) and to an orbital ordering (OO), respectively. The two reflections are coupled, i.e. they appear at the same temperature and the resonance occurs at the same photon energy. It is noteworthy that the physical process involved in the resonant scattering experiment is the same as in X-ray absorption spectroscopy. Accordingly, a controversy exists between the interpretation of the XANES experiments (they do not support the occurrence of charge localization neither temporally nor spatially) and resonant scattering experiments.

In this paper, we make use of X-ray absorption data to calculate the resonant scattering diffraction. This comparison shows that although two different kind of manganese atoms are present in the so-called charge ordering phase, no real atomic charge ordering occurs in these compounds. We also show that a local geometrical order can explain the observed resonant reflections and their azimuthal behaviour.
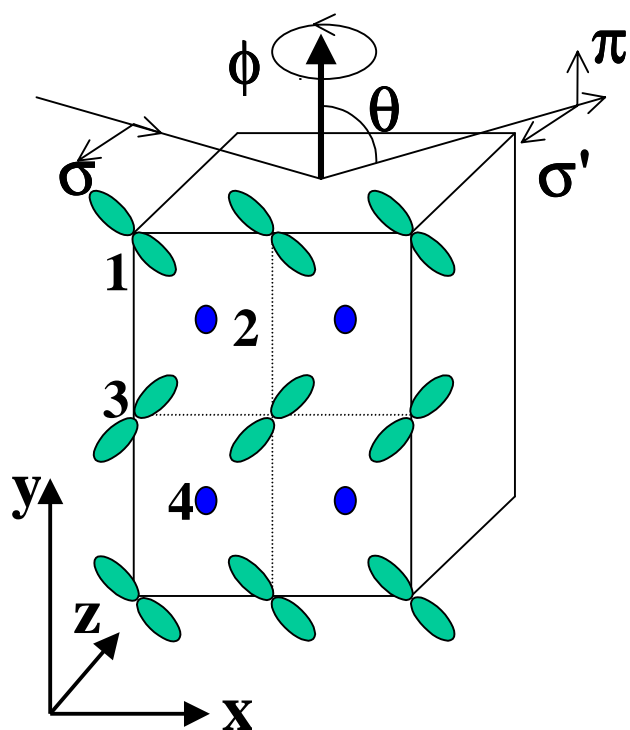
Figure 1
Model for charge and orbital orderings of $Mn^{4+}/Mn^{3+}=1$ manganites. The anisotropy direction for atoms 1 and 3 is indicated by lobules (Mn^{3+}). Atoms 2 and 4 are associated to Mn^{4+}. The reference frame and the scattering geometry are also shown.

2. Charge-ordering model

A detail of the charge-orbital ordering model proposed for $Mn^{3+}/Mn^{4+}=1$ manganites is given in fig 1 following the settings of the Pbnm space group. This scheme is the same to the previously published (Murakami *et al.*, 1998; Nakamura *et al.*, 1999; Zimmerman *et al.*, 1999). Within this model, atoms 1 and 3 are supposed to be Mn^{3+} while atoms 2 and 4 are assumed to be Mn^{4+} ions. The reference frame and the geometry of the scattering process are also given in Fig. 1. The atomic scattering factor for atoms 1 and 3 in its own reference frame is given by a diagonal tensor with two main components $f_\perp$ and $f_{||}$, i.e. the components perpendicular and parallel to the orbital anisotropy axis, respectively. Atoms 2 and 4 (Mn^{4+}) are isotropic, so we can write $f_{xx}=f_{yy}=f_{zz}=f$.

In this reference frame the following expressions for the intensity of the $(0,k,0)$ and $(0,k/2,0)$ reflections, due to CO and OO respectively, are found:

$$I_{\sigma\sigma}(0,k,0) = [2(f_\perp\text{-}f) + (f_\perp\text{-}f_{//})\,sin^2\phi]^2 \qquad (1)$$

$$I_{\sigma\pi}(0,k,0) = [\,(f_\perp\text{-}f_{//})cos\phi\,sin\phi\;sin\theta]^2 \qquad (2)$$

$$I\sigma\sigma(0,k/2,0) = 0 \quad \text{and,}$$

$$I\sigma\pi(0,k/2,0) = [(f\alpha - f\beta)cos\theta.sin\phi]^2 \qquad (3)$$

where $\sigma-\sigma$ and $\sigma-\pi$ indexes refer to the polarization channels (see Fig. 1).

Expressions (1) and (2) show that the CO reflection should also show a ϕ (azimuthal) dependence for both $\sigma-\sigma$ and $\sigma-\pi$ channels. Therefore the lack of either $\sigma-\pi$ channel or azimuthal modulation of the diffracted intensity, cannot be considered as a proof of a CO mechanism, when the atoms contributing to the Bragg reflection are anisotropic. Moreover, the anisotropy of atoms 1 and 3 is enough to produce the $(0,k,0)$ reflection and its oscillatory behavior.

We have calculated the anomalous scattering factor for Mn^{3+} and Mn^{4+} atoms from the experimental XANES spectra by means of the Kramers-Kronig relationship. As a rough approximation of the directional splitting, we have shifted the XANES spectrum of $LaMnO_3$ by 1.5 eV (estimated from the XANES spectrum), in order to get the two components $f_{//}$ and $f_\perp$ for the Mn^{3+} ion. The energy position of the intensity terms $(f_{Mn4+}\text{-}f_{Mn3+})^2$ (CO reflection) and $(f_{//}\text{-}f_\perp)^2$ (OO reflection) appear shifted by about 2 eV. This shift was also observed by K. Nakamura et al. (1999) who detected a discrepancy of 2 eV between the simulated and the experimental position of the charge ordering resonance. Then, we have also calculated the $\sigma-\sigma$ channel intensity for the CO reflection, considering the formal Mn^{4+} atom isotropic (see Fig. 1), as a function of the azimuthal angle at different energies of the incoming photons and as a function of the energy at fixed azimuthal angles. The results are given in fig 2.
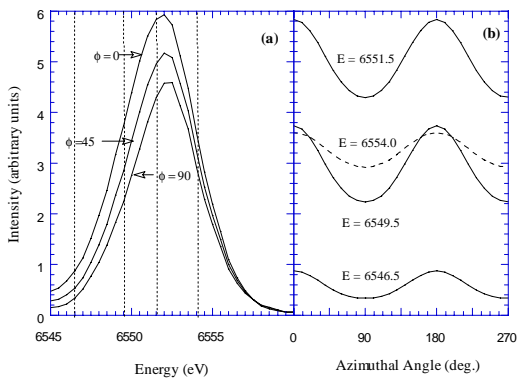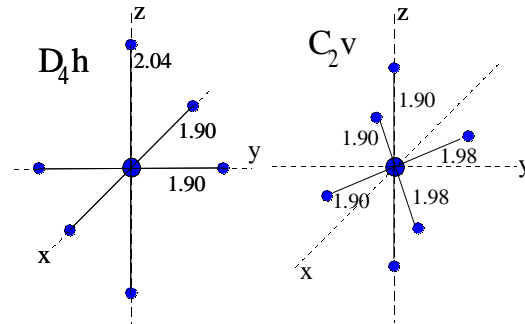

Figure 2
(a) Simulated intensity of the charge ordering reflection as a function of the photon energy at $\phi = 0$, $\phi = 45$ and $\phi = 90$ azimuthal angles. (b) Intensity versus azimuthal angle at the fixed photon energies indicated in Fig. 2(a) as dotted lines.

As we have pointed out, the azimuthal angular dependence of the intensity of a real charge ordering reflections would show an oscillatory component superimposed to a constant term, the relative intensities of them strongly depends on the energy of the incoming photons. At resonance, the amplitude of this ϕ dependent part represents only a 25% of the overall signal. This result does not agree with the reported data showing an oscillatory contribution higher than 75% of the total signal (Nakamura *et al.*, 1999). Moreover, the energy dependence of the diffraction intensity also

changes with the azimuthal angle: the resonance at $\phi=0$ is broader than at $\phi= 90$ and its energy position depends on the azimuthal angle (see fig 2(a)).

3. Geometrical model

We propose a simple structural model, which qualitatively explains the main experimental findings. We will take the simplest structure (figure 1) without considering tilting of MnO_6 octahedra. A tetragonal distortion for (odd) atoms 1 and 3 (as observed in $La_{0.5}Ca_{0.5}MnO_3$ and $Tb_{0.5}Ca_{0.5}MnO_3$) implies the loss of the octahedral symmetry for (even) atoms 2 and 4. We have calculated the absorption coefficient and the atomic anomalous scattering factor for the simplest case. The "odd" atoms (tetragonal distorted) and the "even" atoms with C^v_2 symmetry, as shown in Fig. 3. The theoretical calculations have been performed in the frame of the multiple scattering theory using the program CONTINUUM (Natoli *et al.*, 2000), and using the X_α approximation for the exchange correlation potential. A cluster including only the first oxygen coordination shell was considered.

Figure 3
Cluster models for (a) "odd" Mn atoms (1 and 3) and (b) "even" Mn atoms (2 and 4) used in the theoretical calculation.

The $(0,k,0)$ resonant reflection has been calculated using the real and the imaginary part of the atomic scattering factor obtained from the theoretical absorption coefficient. We have also included a term C to take into account the Thompson scattering originated by the motion of the other atoms in the cell. The presence of this term is justified by the observation of these reflections (with very low intensity) below the absorption edge.

This term was also included by Nakamura et al., 1999. The formula (1) is then rewritten as:

$$I_{\sigma\sigma}(0,k,0) = [C+2(f_\perp\text{-}f) + (f_\perp\text{-}f_{//})\,sin^2\phi]^2 \qquad (4)$$

The calculated intensity at $\phi = 90$, as a function of the energy, is shown in fig 4(a) for different values of C. The intensity at the resonance strongly depends on the C value, changing about one order of magnitude. This behavior can explain the remarkable intensity differences between the $(0,k,0)$ and the $(0,k/2,0)$ reflections for the different samples. The intensity of the $(0,3,0)$ reflection is about ten times higher than that of the $(0,3/2,0)$ reflection for $Pr_{0.6}Ca_{0.4}MnO_3$ (Zimmermann *et al.*, 1999). However, this difference is only two times between $(0,3,0)$ and $(0,5/2,0)$ in $Nd_{0.5}Sr_{0.5}MnO_3$ (Nakamura *et al.*, 1999). We would like to note that both, the shape of the $(0,k,0)$ resonance and the ratio between non-resonant and the resonant intensities, are also in agreement with this dependence. The azimuthal behavior at the energy of the resonance for different

values of the C term is also shown in fig 4(b), which illustrates the relative importance of the C term with respect to the anomalous part. For C = 0, the interference of the different terms of the anomalous scattering factor gives rise to a periodic behavior similar to a $\sin^4\phi$ dependence. This dependence changes to $\sin^2\phi$ dependence by increasing the C value. We note that the azimuthal behavior for $Nd_{0.5}Sr_{0.5}MnO_3$ would correspond to low C values while the reported $\sin^2\phi$ dependence of $Pr_{0.5}Ca_{0.5}MnO_3$ would correspond to high C values.
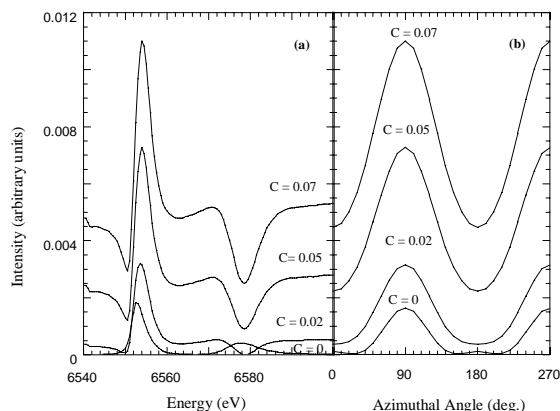
Figure 4
(a) Calculated intensity of the (0,k,0) reflection at ϕ = 90, as a function of the photon energy, for different values of the isotropic atomic scattering factor C; (b) Azimuthal dependence of the (0,k,0) reflection at the energy of the resonance (6554 eV).

4. Conclusions

The detailed analysis of the resonant reflections, which appear in the so-called charge-ordering phase in Mn^{3+}/Mn^{4+}=1 manganites, has shown that:

1. The simultaneous appearance of both, (0,k,0) "charge" and (0,k/2,0) "orbital" ordering reflections, is not fortuitous. As we have shown, the anisotropy of "odd" atoms is enough to observe simultaneously the two reflections. Therefore, "odd" and "even" atoms are different.

2. The use of atomic scattering factors obtained from the measured X-ray absorption spectra gives an energy and azimuthal dependence for a pure (0,k,0) charge ordering reflection incompatible with the published data. The simulation of charge and orbital ordering will produce resonant reflections, the resonance energy position of which would be shifted by about 2 eV. This result is at odd with the published data where the same resonant energy is obtained for both reflections. Moreover, the azimuthal behavior for the (0,k,0) reflections can be described as the sum of two terms: a constant term plus an oscillatory term. The oscillatory amplitude at the resonance is about 25% of the total intensity in the case of real charge ordering.

3. The proposed structural model can explain qualitatively several features: (i) the simultaneous appearance of the (0,k,0) and (0,k/2,0) resonant reflections; (ii) the main resonance appears at the same energy for both kind of reflections; (iii) the proposed azimuthal behavior agrees well with the reported ϕ dependence of the two reflections. Furthermore, the enhanced effect of the Thompson term on the intensity of the (0,k,0) reflection can explain the large intensity differences found for this reflection compared with the (0,k/2,0) for the different compounds.

In conclusion, the anisotropy of one kind of the Mn atoms ("odd" atoms) is enough to observe the so-called charge-ordering reflections. The comparison of X-ray absorption data with the resonant scattering experiments clearly shows that no real charge ordering occurs in these compounds. Moreover, our analysis demonstrates the presence of two kinds of Mn ions in the charge-ordered manganites in agreement with neutron and X-ray diffraction data. Within this model the charge-ordering phase transition can be described as a structural phase transition, where a phonon-mode condense producing a new periodicity on the oxygen atoms.

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