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Analysis of the x-ray resonant scattering at the Mn K edge in half-doped mixed valence manganites

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Abstract

We reconsider the interpretation of x-ray resonant scattering experiments performed on the so-called charge-ordered manganites with $\text{Mn}^{3+}/\text{Mn}^{4+} = 1$. The comparison between these experiments and our x-ray absorption data shows that no real $\text{Mn}^{3+}/\text{Mn}^{4+}$ charge ordering occurs in these compounds. However, these experiments demonstrate the presence of two different types of manganese atom with a different local geometrical structure. We propose a structural model which accounts for these resonant scattering experiments. Within this model, the charge-ordering phase transition can be explained as a structural phase transition driven by the softening of a phonon mode. This produces a periodic arrangement of local distortions, which is responsible for the observed resonances. Furthermore, electronic localization in these materials would occur on a length scale larger than the atomic one.

1. Introduction

The knowledge of the electronic state of the manganese atom in mixed valence manganites is a point of fundamental interest in order to understand their different and unusual macroscopic properties [1]. The class of $\text{RE}_{1-x}\text{A}_x\text{MnO}_3$ and $\text{RE}_{1-x}\text{A}_{1+x}\text{MnO}_4$ perovskite systems is 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 $\text{RE}_{1-x}\text{A}_x\text{Mn}_{1-x}^{3+}\text{Mn}_x^{4+}\text{O}_3$, where a mixture of Mn^{3+} and Mn^{4+} ions is present for these intermediate compositions. Mn^{3+} is believed to have an electron configuration $t_{2g}^3 e_g^1$ with t_{2g} electrons unpaired (d_{xy} , d_{xz} and d_{yz}) and spin polarized according to the Hund rule.

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Apart from the potential interest of perovskites showing colossal magnetoresistance, a basic interest has emerged in manganites with $\text{Mn}^{3+}/\text{Mn}^{4+} = 1$ ratio. Perovskites approaching this composition develop the so-called charge-ordering transitions [2]. An order–disorder transition related to the charge localization has been proposed (it is noteworthy that this description is similar to the classical model for the Verwey transition in magnetite [3]). This phase transition has been observed in these manganites by x-ray [4], neutron [5] and transmission electron diffraction [2]. The phase transition is characterized by a discontinuity in the electrical conductivity together with an anomalous behaviour of the magnetic properties. Sometimes this transition is coupled with an antiferromagnetic order, but other times the long-range magnetic order occurs at temperatures different from the charge ordering transition temperature. The charge-ordering transition is a structural phase transition, so a change in the symmetry of the lattice occurs at the transition temperature. High-resolution neutron diffraction [5] and x-ray powder [4] diffraction have shown the presence of two different Mn atoms which differ in local geometry: one of them can easily be ascribed to the Jahn–Teller distorted Mn^{3+} atom. The appearance of structural satellites in electron diffraction experiments has also been considered as a proof of the occurrence of charge ordering [2] between Mn^{3+} and Mn^{4+} . 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.

X-ray absorption spectroscopy experiments cast doubts on the occurrence of real charge localization. X-ray absorption near edge structure (XANES) spectra at the Mn K-edge of $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ compound cannot be reproduced from the weighted sum of the reference compound spectra (LaMnO_3 and CaMnO_3) [6–8]. Similar contradictory results have been obtained from EPR [9] and Mn $\text{K}\beta$ emission experiments [10].

A direct way to demonstrate a periodic long-range charge arrangement is the observation of superstructure reflections by x-ray resonant scattering experiments [11]. The appearance of resonances at the metal K-edge energy is related to the different energy of s–p excitations (dipolar transitions) for atoms with different valence state [12]. Resonant reflections can also appear 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 [12]. Therefore, a periodic ordering of the anisotropic axis at each atom in the crystal allows these reflections to appear. This feature has been observed in the study of charge ordering in magnetite. The study of (002) and (006) forbidden reflections in magnetite has shown the absence of both charge fluctuation between octahedral Fe^{3+} and Fe^{2+} at room temperature and charge ordering below the Verwey transition [13, 14].

Recently, this technique has also been applied to different manganese perovskites with a formal $\text{Mn}^{3+}/\text{Mn}^{4+} = 1$ ratio [15–17]. The authors observed two resonant reflections in the so-called charge-ordered phase that are assigned to a Mn^{3+} – Mn^{4+} charge ordering and to an orbital ordering respectively. The two reflections are coupled, i.e. they appear at the same temperature, and the resonance occurs at the same photon energy. Although the ordering model proposed for the three studied compounds ($\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4$, $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ and $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$) is exactly the same, the experimental data show several differences that should be explained. Zimmerman *et al* [17] claim a $\sin^2 \phi$ azimuthal dependence of the resonance ascribed to the charge ordering in $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$. However, a nearly $\sin^2 \phi + \sin^4 \phi$ dependence has been reported for $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ [16]. Furthermore, no azimuthal dependence has been assumed for the assigned charge ordering reflection in $\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4$ [15]. It is noteworthy that the physical process involved is the same for both techniques, resonant scattering and x-ray absorption spectroscopy. Accordingly, a controversy exists between the interpretation of the XANES experiments taken at high resolution (they do not support the occurrence of charge localization, either temporal or spatial [6, 8]) and the results of the resonant scattering studies.

The aim of this work is twofold. First, we compare the experimental results obtained from x-ray absorption and resonant scattering diffraction. Second, we want to deduce the expected behaviour for the resonant reflections in a charge-ordering model clarifying the differences found in previous works [15–17]. It is worth remembering that the assignment of ATS reflections to a demonstration of a real d-orbital ordering [18] is a matter of discussion, and several authors claim for a structural origin of the anisotropy of the anomalous scattering factor [19, 20].

The first part of the paper will be devoted to developing the charge-orbital ordering model (similar to that reported by Nakamura *et al* [16]) and to obtaining the correspondent energy and azimuthal dependence of the diffracted intensity. The polarization rules will show that neither the absence of azimuthal dependence nor the lack of a σ – π channel guarantee the occurrence of charge ordering. In the second part, we will discuss these results by comparing the data already presented in the literature with our own XANES data: we will show that no charge ordering occurs although two different Mn atoms are needed to obtain the observed reflections. Finally, we propose a geometrical model based on the crystallographic data, which is coherent with the experimental findings.

2. Charge-orbital ordering model

A detail of the charge-orbital ordering model proposed for $\text{Mn}^{3+}/\text{Mn}^{4+} = 1$ manganites is given in figure 1 following the settings of the $Pbnm$ space group. This scheme is the same as that previously published [15–17]. It is worth noticing that the study of $(0, k, 0)$ and $(0, k/2, 0)$ reflections of perovskite compounds is equivalent to the study of $(1/2, 1/2, 0)$ and $(1/4, 1/4, 0)$ reflections of $\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4$. 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 figure 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 $f_{\perp} = f_{\gamma} = f_{\alpha}$ and $f_{\parallel} = f_{\beta}$, f_{\perp} and f_{\parallel} being the components perpendicular and parallel to the orbital anisotropy axis, respectively. Transforming to the crystallographic reference frame, the atomic scattering tensors for atoms 1 and 3 are given by

$$f_1 = \begin{pmatrix} \frac{f_{\alpha}+f_{\beta}}{2} & \frac{f_{\alpha}-f_{\beta}}{2} & 0 \\ \frac{f_{\alpha}-f_{\beta}}{2} & \frac{f_{\alpha}+f_{\beta}}{2} & 0 \\ 0 & 0 & f_{\gamma} \end{pmatrix} \quad \text{and} \quad f_3 = \begin{pmatrix} \frac{f_{\alpha}+f_{\beta}}{2} & \frac{f_{\beta}-f_{\alpha}}{2} & 0 \\ \frac{f_{\beta}-f_{\alpha}}{2} & \frac{f_{\alpha}+f_{\beta}}{2} & 0 \\ 0 & 0 & f_{\gamma} \end{pmatrix}.$$

We assume that the atomic scattering factors for atoms 2 and 4 are diagonal in the reference frame of the crystal, with different components f_{xx} , f_{yy} and f_{zz} . In the case that the atom is not anisotropic, $f_{xx} = f_{yy} = f_{zz}$.

$$f_2 = f_4 = \begin{pmatrix} f_{xx} & 0 & 0 \\ 0 & f_{yy} & 0 \\ 0 & 0 & f_{zz} \end{pmatrix}.$$

According to the dipolar approximation, the structure factor for the $(0, k, 0)$ charge ordering reflection is given by

$$F(0, k, 0) = f_1 - f_2 + f_3 - f_4 = \begin{pmatrix} f_{\alpha} + f_{\beta} - 2f_{xx} & 0 & 0 \\ 0 & f_{\alpha} + f_{\beta} - 2f_{yy} & 0 \\ 0 & 0 & 2(f_{\gamma} - f_{zz}) \end{pmatrix} \quad (1)$$

and for the $(0, k/2, 0)$ orbital ordering reflection by

$$F(0, k/2, 0) = f_1 + f_2 - f_3 - f_4 = \begin{pmatrix} 0 & f_{\alpha} - f_{\beta} & 0 \\ f_{\alpha} - f_{\beta} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}. \quad (2)$$

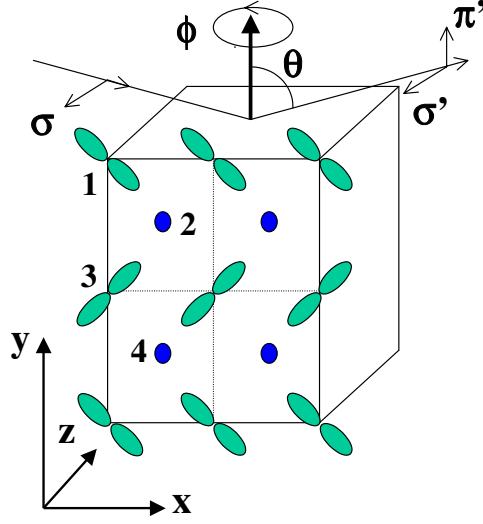


Figure 1. Model for charge and orbital orderings of $\text{Mn}^{4+}/\text{Mn}^{3+} = 1$ manganites. The anisotropy direction for atoms 1 and 3 is indicated by lobules (Mn^{3+}). Atoms 2 and 4 are associated with Mn^{4+} . The reference frame and the scattering geometry are also shown. Only Mn atoms are shown.

The intensity of the charge-ordering reflection, as a function of the polarization of the x-ray beam is

$$I_{\sigma\sigma}(0, k, 0) = \left| (\sin\phi \cos\phi) \begin{pmatrix} f_{\alpha} + f_{\beta} - 2f_{xx} & 0 & 0 \\ 0 & f_{\alpha} + f_{\beta} - 2f_{yy} & 0 \\ 0 & 0 & 2f_{\gamma} - 2f_{zz} \end{pmatrix} \begin{pmatrix} \sin\phi \\ 0 \\ \cos\phi \end{pmatrix} \right|^2$$

$$= [2(f_{\gamma} - f_{zz}) \cos^2\phi + (f_{\alpha} + f_{\beta} - 2f_{xx}) \sin^2\phi]^2 \quad (3)$$

and

$$I_{\sigma\pi}(0, k, 0) = [2(f_{xx} - 2f_{zz} + 2f_{\gamma} - f_{\alpha} - f_{\beta}) \cos\phi \sin\phi \sin\theta]^2. \quad (4)$$

For the orbital ordering reflection, the intensity will be given by $I_{\sigma\sigma}(0, k/2, 0) = 0$ and $I_{\sigma\pi}(0, k/2, 0) = [(f_{\alpha} - f_{\beta}) \cos\theta \sin\phi]^2$.

In the case of isotropic atoms, $f_{xx} = f_{yy} = f_{zz}$ and $f_{\gamma} = f_{\alpha} = f_{\beta}$, the intensity of the $(0, k, 0)$ resonance does not show an azimuthal dependence and no σ - π channel will be observed.

In the case that only atoms 2 and 4 (Mn^{4+}) are isotropic we can rewrite $f_{xx} = f_{yy} = f_{zz} = f$ and $f_{\alpha} = f_{\gamma} = f_{\perp}$, and $f_{\beta} = f_{\parallel}$. So the intensities will be given by

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

$$= 4(f_{\perp} - f)^2 + 4(f_{\perp} - f)(f_{\parallel} - f_{\perp}) \sin^2\phi + (f_{\parallel} - f_{\perp})^2 \sin^4\phi. \quad (5)$$

This expression is similar to the one obtained by Nakamura *et al* [16].

$$I_{\sigma\pi}(0, k, 0) = [(f_{\perp} - f_{\parallel}) \cos\phi \sin\phi \sin\theta]^2. \quad (6)$$

We obtain that the amplitude of the periodic contribution over the non-azimuthal dependent part of the structure factor for the $(0, k, 0)$ σ - σ channel would be equal to the factor of the σ - π channel. So a modulation superimposed on the non-azimuthal part in the intensity of the σ - σ channel and a σ - π channel contribution to the intensity would be observed in the so-called charge ordering reflection. We can say that the

apparent absence of a σ - π channel or azimuthal dependence, are not proofs of charge ordering when the atoms involved in the structure factor are anisotropic. We can conclude that the presence of anisotropy in atoms 1 and 3 is enough to produce the $(0, k, 0)$ reflection and its oscillatory behaviour. Moreover, the intensity factor for the σ - π channel would be the same for the $(0, k, 0)$ and $(0, k/2, 0)$ reflections, except for the $\sin^2 \theta$ dependence for the $(0, k, 0)$ reflection and $\cos^2 \theta$ dependence for the $(0, k/2, 0)$ reflection. In contrast, the periodicity is π for the $(0, k, 0)$ reflection and $\pi/2$ for the $(0, k/2, 0)$ one.

Finally, we must include a Thompson scattering factor, C , which accounts for the small displacements of the oxygen atoms and/or the manganese atoms. If we include this term in our formulation, the σ - σ channel for the so-called charge-ordering reflection will be modified as

$$I\sigma\sigma(0, k, 0) = [C + 2(f_{\perp} - f) + (f_{\parallel} - f_{\perp}) \sin^2 \phi]^2. \quad (7)$$

It is noteworthy that the presence of a Thompson term due to the oxygen displacements does not change the main conclusions of our discussion. In fact, this term can be added to the isotropic term and the main effect is a renormalization of the non-azimuthal scattering term.

In the following, we will essentially focus on the intensity of the σ - σ channel of the $(0, k, 0)$ reflection. The exact azimuthal behaviour depends on the relative importance between the independent term, $C + 2(f_{\perp} - f)$, and the oscillatory term, $(f_{\parallel} - f_{\perp})$, of the structure factor. Different azimuthal behaviours must be expected for $(f_{\parallel} - f_{\perp})$ higher, equal or larger than $C + 2(f_{\perp} - f)$. The periodic part will follow a $\sin^4 \phi$ dependence for the first case, a $\sin^4 \phi + \sin^2 \phi$ dependence for the second one and a very small contribution with $\sin^2 \phi$ behaviour for the third case. Furthermore, the anomalous scattering factor depends on the photon energy, and the relative intensity factor of the independent term with respect to the oscillatory term, must therefore vary with the energy.

3. XANES versus resonant scattering diffraction

The same physical processes are involved in both x-ray absorption spectroscopy and x-ray anomalous diffraction. The incoming photon promotes an electron from a core state to an empty bound state or an empty continuum state. The anomalous scattering factor can be expressed as $f = f' + if''$, where the real and imaginary parts are intimately related by means of the Kramers–Kronig relationship. For pure dipole scattering, the energy dependence of the imaginary component of the scattering amplitude is proportional to that of the absorption [12]. Accordingly, the information obtained from x-ray absorption spectroscopy is the same as the information obtained from anomalous x-ray diffraction experiments.

We reported [6, 8] x-ray absorption experiments at the Mn K edge of $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ which do not support an atomic charge localization. The XANES spectra of manganites with formal $\text{Mn}^{3+}/\text{Mn}^{4+} = 1$ cannot be explained as a bimodal distribution of Mn^{3+} and Mn^{4+} ions. The simulation obtained by the weighted sum of XANES spectra of parent compounds shows two resonances at the edge which are not present in the experimental spectrum. For instance, figure 2 shows the normalized XANES spectrum of $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ compared to the averaged addition of LaMnO_3 and CaMnO_3 spectra. Moreover, the XANES spectra of $\text{RE}_{1/2}\text{A}_{1/2}\text{MnO}_3$ (RE = La, Pr, Nd, Tb; A = Ca, Sr) and $\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4$ are similar showing a main edge resonance at the same energy [8].

The XANES high-resolution spectra of CaMnO_3 and LaMnO_3 together with their derivatives are shown in figure 3. We observe a chemical shift of 4.5 eV between LaMnO_3 and CaMnO_3 . Different groups reporting similar or equivalent spectra have confirmed this value [7, 22, 23]. The derivative of the XANES spectrum for LaMnO_3 suggests the presence of two

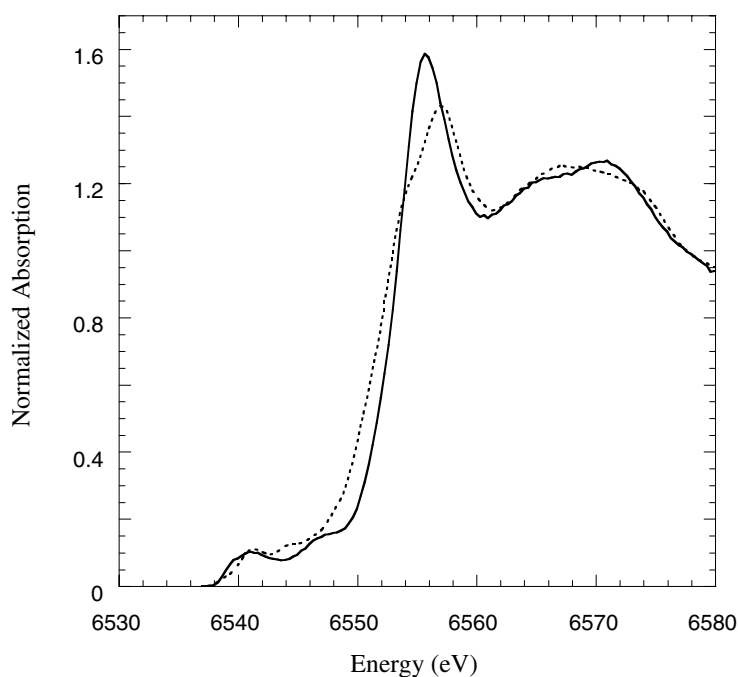


Figure 2. Comparison between the XANES spectrum of $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ (continuous curve) and the weighted addition of the end members LaMnO_3 and CaMnO_3 (dashed curve). The spectrum was taken by recording the intensity of the Mn $K\beta$ emission.

components, split by 1.5 eV. This splitting arises from the anisotropic absorption coefficient, i.e. it can be ascribed to its parallel and perpendicular components, with respect to the local tetragonal axis in the MnO_6 distorted octahedron [20].

For a charge-ordering reflection, the resonance would come from the difference between anomalous scattering factors at the edge due to the chemical shift between Mn^{3+} and Mn^{4+} . Instead, for the so-called orbital ordering, the appearance of a resonant reflection comes from the anisotropy of the anomalous scattering factor on each Mn atom (ATS reflection), i.e. the directional splitting. 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 artificially splitted the XANES spectrum of LaMnO_3 by 1.5 eV, in order to obtain the two components f_{\parallel} and f_{\perp} for the Mn^{3+} ion. The intensity terms $(f_{\text{Mn}^{4+}} - f_{\text{Mn}^{3+}})^2$ and $(f_{\parallel} - f_{\perp})^2$ are shown in figure 4. The first one corresponds to the charge ordering reflection and the second one to the ATS reflection. The charge ordering term shows an intensity larger than that of the anisotropic term. Furthermore, the energy position of both resonances is different, so they should appear shifted by about 2 eV. This shift was observed indeed, by Nakamura *et al* [16], who detected a discrepancy of 2 eV between the simulated and the experimental position of the charge ordering resonance.

We have also calculated the σ – σ channel intensity reflection ($I_{\sigma\sigma}$) considering isotropic Mn^{4+} (see figure 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. We used the formula (5) without a Thompson contribution. The results are given in figure 5. The azimuthal angular dependence for the intensity of a real charge ordering reflection would show an oscillatory contribution superimposed on a constant term whose relative intensity strongly depends on

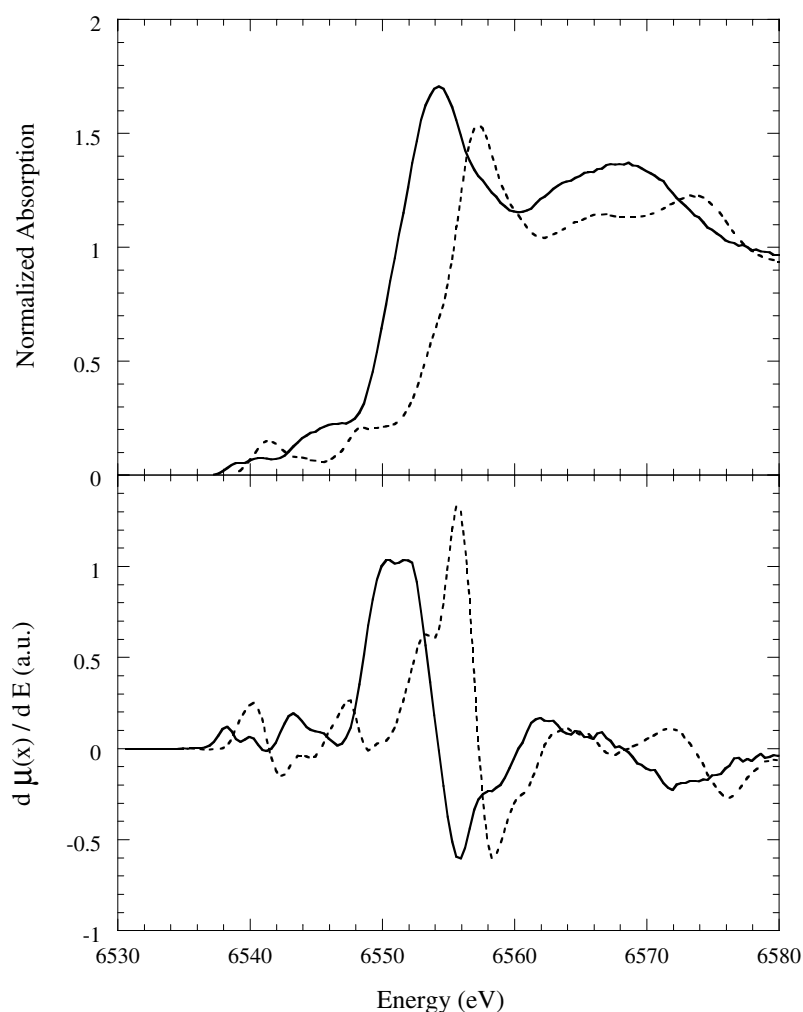


Figure 3. Normalized XANES spectra (upper panel) and the derivatives (lower panel) of LaMnO₃ (continuous curve) and CaMnO₃ (dashed curve).

the energy of the incoming photons. At the resonance, the amplitude of the oscillatory part represents only 25% of the total signal. This result does not agree with the reported data showing an oscillatory contribution higher than 75% of the total signal [16]. The energy dependence of the diffraction intensity recorded at different azimuthal angles also changes: the resonance at $\phi = 0^\circ$ is broader than at $\phi = 90^\circ$ and the energy position of the resonance depends on the azimuthal angle.

4. Theoretical structural model

We propose a simple structural model, which qualitatively explains the main experimental findings. We will take the simplest structure (figure 1) without considering tiltings of MnO₆ octahedra. A tetragonal distortion for (odd) atoms 1 and 3 (as observed [4, 5] in La_{0.5}Ca_{0.5}MnO₃ and Tb_{0.5}Ca_{0.5}MnO₃) implies the loss of the octahedral symmetry for (even)

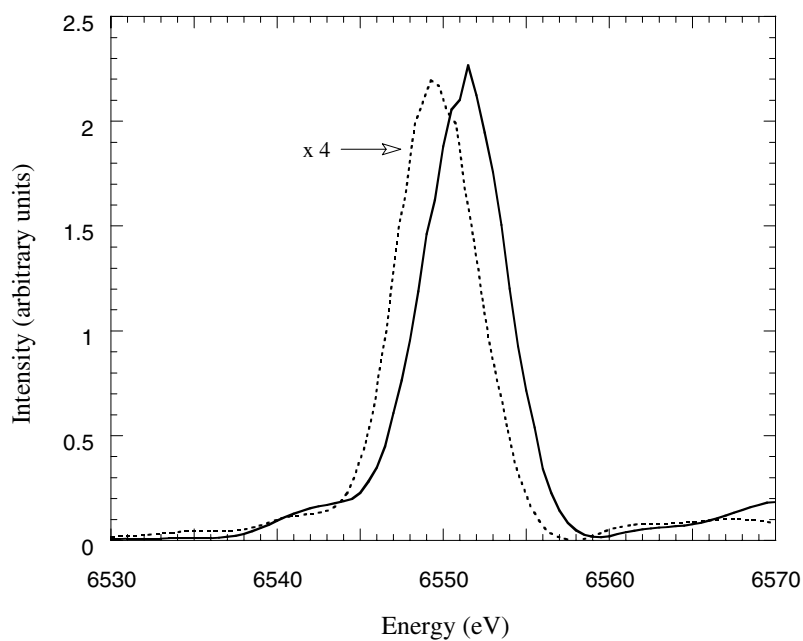


Figure 4. The intensity terms $[f_{\text{Mn}^{2+}} - f_{\text{Mn}^{3+}}]^2$ (continuous curve) and $[f_{\parallel} - f_{\perp}]^2$ (dashed curve) corresponding to the charge and the ATS (orbital) reflections, respectively.

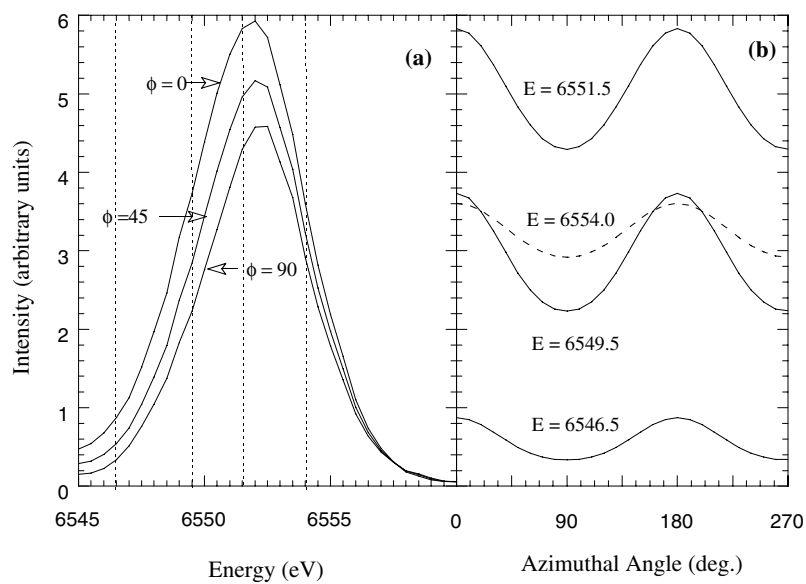


Figure 5. (a) Simulated intensity of the charge ordering reflection as a function of the photon energy at $\phi = 0^\circ$, $\phi = 45^\circ$ and $\phi = 90^\circ$ azimuthal angles. (b) Intensity versus azimuthal angle at the fixed photon energies indicated in (a) as dotted lines.

atoms 2 and 4. Two possibilities can be considered: first, the crystallographic position of 'even' atoms is maintained in the unit cell whereas the interatomic Mn–O distances modify,

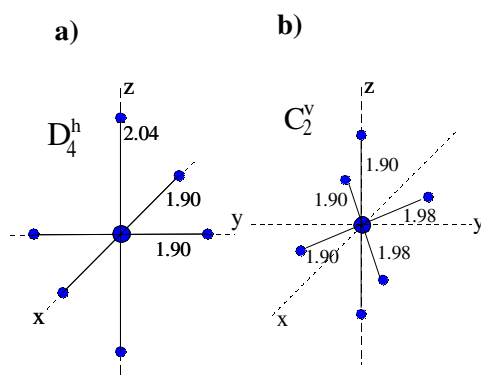


Figure 6. Cluster models for (a) ‘odd’ Mn atoms (1 and 3) and (b) ‘even’ Mn atoms (2 and 4) used in the theoretical calculation.

as shown by Jirak *et al* [24]; second, the movement of ‘even’ atoms along the x -axis to form ‘odd-even’ chains (note that atoms 2 and 4 move in opposite directions). In both cases, the local symmetry of the ‘even’ Mn atom would change from O_h to C_2^v , and the unit cell axes coincide with the anisotropic axis for the absorption coefficient (μ) and for the atomic anomalous scattering factor (f) tensors. 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_2^v symmetry are considered as shown in figure 6. The theoretical calculations have been performed in the frame of the multiple scattering theory using the program CONTINUUM [25], and using the X_α approximation for the exchange correlation potential. The approximation $Z + 1$ was used to simulate the excited state. The valence state has not been considered in the calculation. The calculation has been performed for a cluster including only the first oxygen coordination shell.

The calculated polarized XANES spectra for the two clusters are shown in figure 7. We observe that the largest anisotropy is obtained for the tetragonal distorted D_4^h configuration, the anisotropy for the C_2^v cluster being practically negligible. The energy shift between the polarized D_4^h (‘odd’ atom) XANES spectrum, parallel and perpendicular to the tetragonal axis, is about 1 eV. The non-polarized XANES spectrum obtained after averaging the different polarizations is compared with the experimental XANES spectrum of $La_{0.5}Ca_{0.5}MnO_3$ sample in the same figure. The non-polarized XANES spectra for the two geometrical different Mn atoms are nearly identical and a deconvolution of the experimental spectrum in these two components is practically impossible. The main resonance is located at the same photon energy for both Mn atoms and the agreement with the experimental data is fairly good in spite of the small size of the cluster used in the calculation.

The $(0, k, 0)$ resonant reflection has been calculated after obtaining the real and the imaginary part of the atomic scattering factor from the theoretical absorption coefficient (see formula (3)). 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 calculated $(0, k, 0)$ intensity as a function of the energy at $\phi = 90^\circ$ with different values of C is shown in figure 8. The intensity at the resonance strongly depends on the C value and it changes by about one order of magnitude in the C range considered. This behaviour 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 $Pr_{0.6}Ca_{0.4}MnO_3$. However, this difference is only two times for $(0, 3, 0)$ and $(0, 5/2, 0)$ in

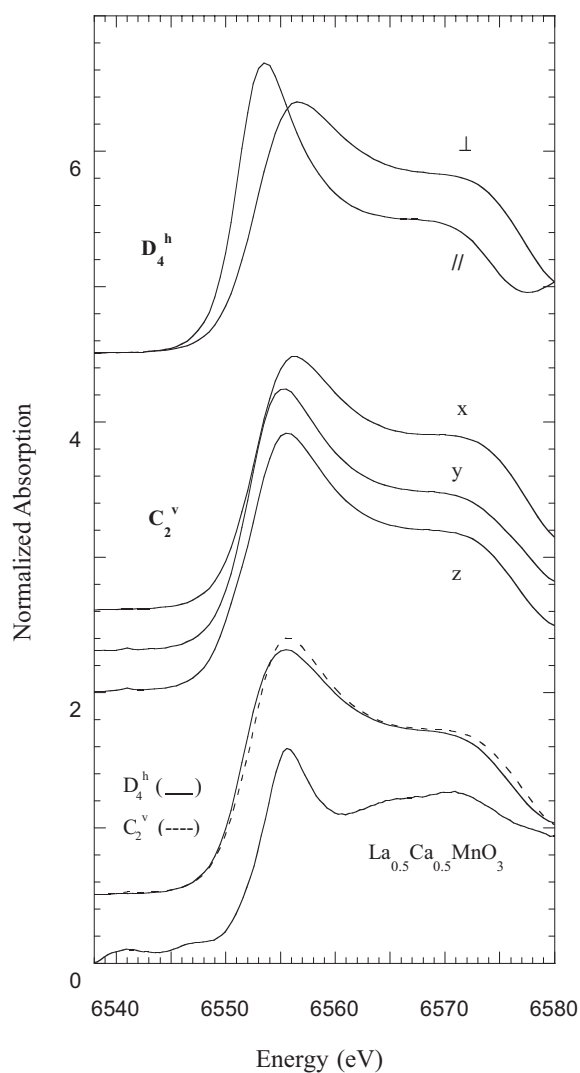


Figure 7. Theoretical polarized resolved XANES spectra for the D_4^h and C_2^v clusters (see figure 6). The non-polarized calculated XANES spectra for the two clusters are compared with the experimental XANES spectrum of the $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ compound in the lower part.

$\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$. We would like to note that the shape of the $(0, k, 0)$ resonance and the ratio between non-resonant and the resonant intensities is also in agreement with this dependence. The azimuthal behaviour at the energy of the resonance for different values of the C term is also shown in figure 8, 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 behaviour similar to a $\sin^4 \phi$ dependence. This dependence varies to a $\sin^2 \phi$ dependence by increasing the C value. We note that the azimuthal behaviour for $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ would correspond to low C values while the reported $\sin^2 \phi$ dependence of $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ would correspond to high C values.

The resonant energy for $(0, k, 0)$ and $(0, k/2, 0)$ reflections within this model is the same, as observed in these manganites [15–17]. In addition, the azimuthal behaviour for

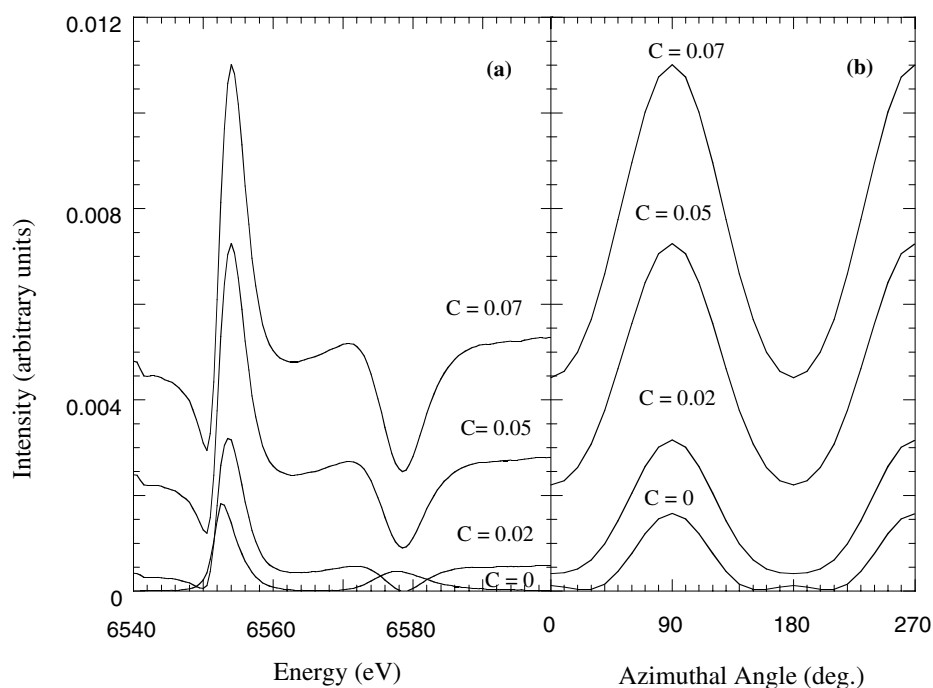


Figure 8. (a) Calculated intensity of the $(0, k, 0)$ reflections as a function of the photon energy at $\phi = 90^\circ$ for different values of the isotropic atomic scattering factor C ; (b) azimuthal dependence of the $(0, k, 0)$ reflections at the energy of the resonance (6554 eV).

$(0, k, 0)$ reflections would depend on the energy of the scattered photons but for the $(0, k/2, 0)$ reflections, it is independent of the energy, as indicated in section 3.

5. Discussion

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

- (i) The simultaneous appearance of the two reflections $(0, k, 0)$ ‘charge’ and $(0, k/2, 0)$ ‘orbital ordering’ 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. Moreover, we cannot use either the absence of σ – π channel or the non-azimuthal dependence as a proof of charge ordering when the atoms involved in the scattering process are anisotropic, i.e. to observe this channel only anisotropy in ‘odd’ atoms is necessary.
- (ii) XANES spectra of these manganites do not support a real charge ordering. The use of atomic scattering factors obtained from the measured x-ray absorption spectra, gives an energy and azimuthal dependence of the $(0, k, 0)$ reflection for a real charge-ordering reflection incompatible with the published data. In any case, our results establish that a non-negligible azimuthal behaviour would be observed for the $(0, k, 0)$ reflection. The simulation of charge and orbital ordering will produce resonant reflections whose resonance energy would be shifted by about 2 eV. This result is at odds with the published data where the same resonant energy is obtained for both reflections. Moreover, the

azimuthal behaviour for a real charge-ordering reflection must change with the photon energy and the energy dependence also depends on the azimuthal angle in our realistic simulations.

The azimuthal behaviour for $(0, k, 0)$ reflections can be described as the addition 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. The azimuthal behaviour for the charge ordering reflection has only been reported by Nakamura *et al* [16] for $\text{Nd}_{1/2}\text{Sr}_{1/2}\text{MnO}_3$. In this case, the reported anomalous constant term is negligible. As they pointed out in their paper, this implies the absence of a chemical shift between the Mn^{3+} and Mn^{4+} atoms, showing implicitly that no charge segregation occurs between ‘odd’ and ‘even’ Mn atoms. Finally, a $\sin^2 \phi$ dependence has been claimed for the charge ordering reflection of $\text{Pr}_{0.6}\text{Ca}_{0.4}\text{MnO}_3$ [17]. However, this work does not report on the azimuthal evolution for the charge ordering reflection as desirable to get unambiguous conclusions.

Although none of the three papers [15–17] provides data on the analysis of the polarization for the charge ordering reflections, we would like to comment on why the $\sigma-\pi$ channel would be difficult to observe for the so-called charge ordering reflections. Due to the $\sin^2 \theta$ dependence and the lack of the enhanced effect of the Thompson term for the $\sigma-\pi$ channel, the expected contribution of this channel is very small. Moreover, the $\pi/2$ periodicity obtained for the $\sigma-\pi$ channel implies that the intensity of the $(0, k/2, 0)$ reflection is zero when the intensity of the $(0, k, 0)$ reflection is maximum. These could be the reasons why the $\sigma-\pi$ channel has not been detected.

- (iii) Multiple scattering calculations for the proposed model explain qualitatively the experimental XANES spectra of the $\text{Mn}^{3+}/\text{Mn}^{4+} = 1$ manganites, in spite of the small cluster size used in the simulation. This calculation shows that XANES spectra of the mixed valence manganites cannot be deconvoluted into two components, i.e. the non-polarized spectra of the two clusters are nearly identical. Nevertheless, 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 kinds of reflection and (iii) the reported azimuthal dependence of the two reflections. Furthermore, the enhanced effect of the Thompson term on the intensity of the $(0, k, 0)$ reflections can explain the large intensity differences found between $(0, k, 0)$ and $(0, k/2, 0)$ reflections for different compounds. Within this model, the charge ordering state can be described as Mori *et al* [26] observed by electron microscopy: Chains of manganese atoms composed by a Mn tetragonal distorted and a Mn with C_2^v symmetry. It would be easy to assign the tetragonal distorted Mn ion as a Jahn–Teller Mn^{3+} ion and the other more symmetric to a Mn^{4+} ion. However, our analysis shows that the charge density on the two atoms is very similar, indicating that the e_g electron is not actually localized at the so-called Mn^{3+} atoms.

6. Conclusions

X-ray scattering resonances observed in $\text{Mn}^{3+}/\text{Mn}^{4+} = 1$ manganites have been compared with high-resolution XANES spectra and a structural model has been proposed to explain these resonances. The main result of this analysis is that the anisotropy of one kind of the Mn atoms (‘odd’ atoms) is sufficient to observe the so-called charge ordering reflection. 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 ion in the charge-ordered manganites in agreement with

neutron and x-ray diffraction data. Two different crystallographic sites were determined for these compounds and two different but similar magnetic moments [27], 3.0 and 2.8 μ_B , were observed for Mn(1) and Mn(2) respectively (figure 1). Nevertheless, they cannot be considered as pure ionic Mn^{3+} or Mn^{4+} states. The electronic localization in these systems would occur on a length scale larger than the atomic one. Moreover, the lack of a real charge-ordering state makes it very difficult to assign the tetragonal distortion of the odd ions to the Jahn–Teller effect or to a real orbital ordering of e_g states. Within this model the charge-ordering phase transition can be described as a structural phase transition, where a phonon mode condenses, producing a new periodicity on the oxygen atoms. The coupling of the electronic states with the phonons would be responsible for the change in the electrical transport properties of the system. Finally, more detailed resonant scattering experiments are necessary to show the different scattering factors of the two Mn atoms involved. The energy dependence of the intensity of $(0, k, 0)$ reflections at different azimuthal angles, the azimuthal behaviour at different energies for both reflections and the search of the $\sigma-\pi$ channel for the $(0, k, 0)$ reflections are necessary to give a complete description of these systems.

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References

- [1] Coey J M D, Viret M and Vonmolnar S 1999 *Adv. Phys.* **48** 167
- [2] Chen C H, Cheong S-W and Hwang H Y 1997 *J. Appl. Phys.* **81** 4326
- [3] Verwey E J W 1939 *Nature* **144** 327
- [4] Blasco J, García J, De Teresa J M, Ibarra M R, Perez J, Algarabel P A, Marquina C and Ritter C 1997 *J. Phys.: Condens. Matter* **9** 10 321
- [5] Radaelly P G, Marezio M, Hwang H Y, Cheong S-W and Batlogg B 1995 *Phys. Rev. Lett.* **75** 4488
Radaelli P G, Cox D E, Marezio M and Cheong S-W 1997 *Phys. Rev. B* **55** 3015
- [6] Subías G, García J, Proietti M G and Blasco J 1997 *Phys. Rev. B* **56** 8183
- [7] Booth C H, Bridges F, Kwei G H, Lawrence J M, Cornelius A L and Neumeier J J 1998 *Phys. Rev. B* **57** 10 440
- [8] García J, Sanchez M C, Subías G and Blasco J 2001 *J. Phys.: Condens. Matter* **13** submitted
- [9] Oseroff S B, Torikachvili M, Singley J, Ali S, Cheong S-W and Shultz S 1996 *Phys. Rev. B* **53** 6521
- [10] Tyson T A, Qian Q, Kao C C, Ruef J P, de Groot F M F, Croft M, Cheong S-W, Greenblat M and Subramanian M A 1999 *Phys. Rev. B* **60** 4665
- [11] Coppens Ph 1992 *Synchrotron Radiation Crystallography* (San Diego, CA: Academic)
- [12] Materlik G, Sparks C J and Fischer K (eds) 1994 *Resonant Anomalous X-Ray scattering, Theory and Applications* (Amsterdam: Elsevier)
- [13] García J, Subías G, Proietti M G, Renevier H, Joly Y, Hodeau J L, Blasco J, Sanchez M C and Berar J F 2000 *Phys. Rev. Lett.* **85** 578
- [14] García J, Subías G, Proietti M G, Blasco J, Renevier H, Hodeau J L and Joly Y 2001 *Phys. Rev. B* **63** 054 770
- [15] Murakami Y, Kawada H, Kawata H, Tanaka M, Arima T, Moritomo Y and Tokura Y 1998 *Phys. Rev. Lett.* **80** 1932
- [16] Nakamura K, Arima T, Nakazawa A, Wakabayashi Y and Murakami Y 1999 *Phys. Rev. B* **60** 2425
- [17] Zimmerman M V, Hill J P, Gibbs D, Blume M, Casa D, Keimer B, Murakami Y, Tomioka Y and Tokura Y 1999 *Phys. Rev. Lett.* **83** 4872
- [18] Ishihara S and Maekawa S 1998 *Phys. Rev. B* **58** 13 442
- [19] Elfimov I S, Anisimov V I and Sawatzky G A 1999 *Phys. Rev. Lett.* **82** 4264
- [20] Benfatto M, Joly Y and Natoli C R 1999 *Phys. Rev. Lett.* **82** 636
- [21] Templeton D H and Templenton L K 1994 *Phys. Rev. B* **49** 14 850
- [22] Tyson T A, Mustre de Leon J, Conradson S D, Bishop A R, Neumeier J J, Roder H and Zang J 1996 *Phys. Rev. B* **53** 13 985

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- [23] Croft M, Sills D, Greenblatt M, Lee C, Cheong S-W, Ramanujachary K V and Tran D 1997 *Phys. Rev. B* **55** 8726
- [24] Jirak Z, Damay F, Hervieu M, Martin C, Raveau B, André G and Boureé F 2000 *Phys. Rev. B* **61** 1181
- [25] Natoli C R, Benfatto M, Brouder C, Ruiz Lopez M F and Foulis D L 1990 *Phys. Rev. B* **46** 14 274
- [26] Mori S, Chen C H and Cheong S-W 1998 *Phys. Rev. Lett.* **81** 3972
- [27] Kawano H, Kajimoto R, Yoshizawa H, Tomioka Y, Kuwahara H and Tokura Y 1997 *Phys. Rev. Lett.* **78** 4253