

Critical Reexamination of the Experimental Evidence of Orbital Ordering in LaMnO_3 and $\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4$

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The experimental evidence for orbital ordering in LaMnO_3 and $\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4$ is critically reexamined in the light of realistic calculations based on multiple scattering theory and finite difference method for the resonant x-ray scattered intensity at a forbidden reflection. It is found that the dipole resonant x-ray diffraction at the Mn K -edge is not a suitable technique for the *direct* observation of the orbital ordering in the considered compounds.

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It has long been recognized that charge, spin, and orbital degrees of freedom play an important role in the electric and magnetic properties of the transition metal oxides [1,2]. Recently there has been a resurgence of interest for the related physical phenomena, both because of the discovery of new phenomena of fundamental and technological importance (e.g., colossal magnetoresistance in perovskite-type manganites) and the availability of second and third generation synchrotron radiation sources allowing experiments which were impossible in the past.

In particular, while the charge and spin ordering could be investigated by the traditional neutron and electron diffraction techniques, the *direct* experimental observation of the orbital ordering (OO), predicted on the basis of various theoretical considerations, has until very recently proved quite difficult. In the last few months, however, two experimental works, using the resonant x-ray scattering technique at the Mn K -edge around a forbidden reflection of the crystal under investigation [3,4], respectively, in $\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4$ and LaMnO_3 perovskite(-type) compounds, have reported observation of scattered intensity with flipping of the polarization plane of the incident radiation, which has been presented as providing *direct* experimental evidence of the theoretically predicted orbital ordering in these materials.

In the second of these papers [4] a simple theory of the resonant scattering mechanism was also provided, which explains the peculiar $\sin^2\psi$ dependence of the diffracted intensity as a function of the azimuthal rotation angle ψ around the forbidden (3, 0, 0) reflection. In the following we shall refer for brevity of space mainly to this paper (and therefore to the LaMnO_3 compound), but we shall also comment briefly on the other compound.

The mechanism whereby x rays are resonantly scattered is well known. The incoming photon is virtually absorbed to promote a core electron to an empty intermediate excited state, which subsequently decays to the same core hole emitting a second photon with the same energy than the incoming one. Since the excited electron is sensitive to *any* anisotropy of the environ-

ment (be it of structural origin or due to the anisotropic charge distribution in the ground state of the system) it gives rise to a tensor component in the atomic scattering factor (ASF) with sharp photon energy dependence in the anomalous dispersion region. This anisotropy of the x-ray susceptibility tensor leads to a number of well known phenomena, like pleochroism, existence of "structurally forbidden" reflections [5,6], birefringence, orientational dependence of x-ray absorption near edge structure (XANES), and reflectivity, etc.

In the particular case under consideration [4] the excitation of the Mn $1s$ electron to empty $4p$ states (split in their y and x, z components by an energy Δ due to some interaction with the surrounding, to be specified in the following) gives rise to nonzero resonant scattered intensity proportional to Δ^2 at the forbidden reflections (3, 0, 0), which is sensitive to the difference between the ASF of the two "orbitally ordered" sublattices. The origin of the splitting Δ is not specified in the model proposed in Ref. [4], but the authors clearly state that one possible source is the Coulomb interaction between the $4p$ conduction band states and the ordered $3d$ orbitals. An alternative mechanism, they suggest, comes from the coherent Jahn-Teller distortion (JTD) of the oxygen octahedra surrounding the Mn atoms that accompanies the orbital ordering, with the long axis always along the occupied $3d_{e_g}$ orbital.

Now this same model (which we believe to be substantially correct) leads to the conclusion that the resonant diffracted intensity due to the two effects is at least 2 orders of magnitude greater in the case of the JTD. In fact, a simple XANES calculation of the x , y , and z absorption components of the $1s$ to $4p$ dipole transition of a Mn atom surrounded by six oxygens at their crystallographic positions ($\text{Mn-O}_y = 2.14 \text{ \AA}$, $\text{Mn-O}_x = 1.98 \text{ \AA}$, and $\text{Mn-O}_z = 1.91 \text{ \AA}$) (see Fig. 1) shows a splitting of the x and y components of 2.0 eV, whereas the Coulomb splitting of the $4p_{x(z)}$ and $4p_y$ Mn orbitals turns out to be $\frac{6}{35}F^2 = 0.4 \text{ eV}$, taking for F^2 , the Coulomb Slater integral for the $3d$ and $4p$ atomic Mn orbitals, the value of

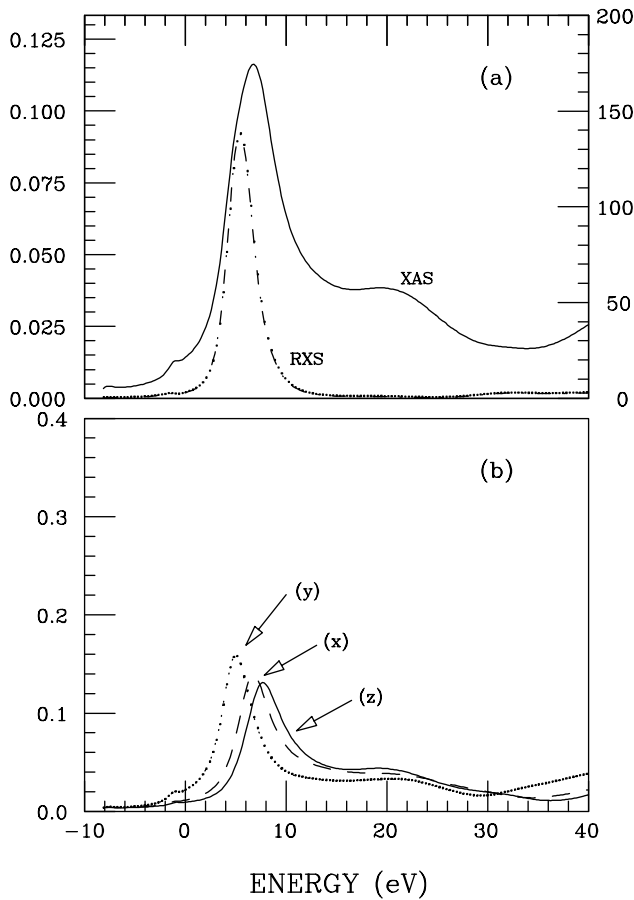


FIG. 1. (a) Mn K -edge unpolarized absorption cross section (XAS) (Mbarn, left scale) in LaMnO_3 and anomalous resonant diffraction signal (RXS) due solely to JTD, calculated in the muffin-tin approximation (adimensional units, right scale). (b) Polarized cross sections along the principal axis in Mbarn.

2.5 eV as calculated in the atomic approximation using the Cowan program [7]. This already implies a factor of 25 in favor of the JTD mechanism and certainly represents a lower bound, since screening and band effects in the solid tend to drastically lower the value of F^2 . A not unreasonable further reduction of this latter by a factor of 2 provides the 2 orders of magnitude difference in the diffracted intensities. Notice, by the way, that Ishihara *et al.* [8] in their model calculations on the anomalous x-ray scattering in manganites had to assume for F^2 a value of 13 eV to get a Coulomb splitting of 1.8 eV between the $4p_z$ and $4p_{x(y)}$ orbitals (they use a rotated frame), leading to a 1.3 eV splitting of the corresponding peaks of the imaginary part of the scattering factor. However such a high value for F^2 is clearly unreasonable.

Yet another mechanism concurs to depress the resonant signal due to orbital ordering. This effect originates from the electronic relaxation of the photoabsorbing Mn atom

following the creation of the $1s$ core hole. It is known, in fact, that, except in particular cases (fluctuating valence, etc.) which is not the present one, however, the final state “well screened” configuration $t_{2g}^3 e_g^2 \underline{L}$, where \underline{L} indicates a hole in the oxygen $2p$ band, carries almost 90% of the weight and therefore, being of cubic symmetry, does not contribute to the signal. Only the far away Mn atoms can, but their signal is depressed by the limited mean free path of the photoelectron in the final state.

In order to substantiate these considerations and assess the relative intensity originating from the two competing mechanisms we performed realistic model calculations for the ASF on the basis of the one particle approach moving in an effective optical potential. We used a non-muffin-tin scheme based on the finite difference method (FDM) as described in Refs. [9,10] to solve the Schrödinger equation (SE). However, we performed also muffin-tin calculations in the frame of multiple scattering theory (MST) [11] in order to assess the effect of the *sole* JTD, since this approach is physically more transparent and helpful in our “theoretical experiments.”

In the MST context, following Vedrinskii *et al.* [12] one can write the adimensional anomalous part of the ASF anisotropic tensor at the photon energy $\hbar\omega$, using atomic units, as

$$f_{\alpha\beta}(\omega) = (\hbar\omega)^2 \langle 1s | \tilde{r}_\alpha G(\vec{r}, \vec{r}'; E_c) \tilde{r}_\beta | 1s \rangle. \quad (1)$$

Here $E_c = \hbar\omega + E_{1s} + i\Gamma/2$ is the complex excitation energy and $G(\vec{r}, \vec{r}'; E_c)$ is the Green function of the system which, according to MST, for \vec{r} and by \vec{r}' around the origin o where the initial $1s$ state is localized, is given by

$$G(\vec{r}, \vec{r}'; E_c) = k \sum_{LL'} R_L^o(\vec{r}) \tau_{LL'}^{oo} R_{L'}^o(\vec{r}') - k \sum_L R_L^o(\vec{r}_<) S_L^o(\vec{r}_>),$$

where $\tau_{LL'}^{oo}$ is the scattering path operator of MST, $k = \sqrt{E_c}$ and we refer to Ref. [11] for the conventional meaning of the other symbols. In Eq. (1) we have neglected the smooth background contribution coming from the integration over the occupied states [12].

Since in LaMnO_3 space group $Pnma$ and in the reference frame indicated in Fig. 1 of Ref. [4] the Mn site at the corner of the rhombohedral unit cell in the a - b plane Mn_1 is equivalent to the site at the center of the cell Mn_2 , after reflection in the vertical plane containing the z and the \vec{a} axes and translation by the vector $(1/2\vec{a}, 1/2\vec{b})$, even when orbital ordering is considered, one has $f_{xx}^{\text{Mn}_1} = f_{yy}^{\text{Mn}_2}$ and $f_{zz}^{\text{Mn}_1} = f_{zz}^{\text{Mn}_2}$. Consequently, the anomalous scattering amplitude at the (300) “forbidden” reflection can be written as

$$\sum_{\alpha\beta} \epsilon_\alpha^i [f_{\alpha\beta}^{\text{Mn}_1}(\omega) - f_{\alpha\beta}^{\text{Mn}_2}(\omega)] \epsilon_\beta^s = (\hbar\omega)^2 \frac{k}{3} R^2 (\epsilon_x^i \epsilon_x^s - \epsilon_y^i \epsilon_y^s) (\tau_{xx}^{oo} - \tau_{yy}^{oo}), \quad (2)$$

since in the D_{2h} point symmetry $\tau_{\alpha\beta}^{oo}$ is diagonal. Here the Cartesian indices of τ refer to the $l = 1$ components of the final allowed states in real spherical harmonics representation, $R = \int r^3 R_{1s}(r) R_{4p}(r) dr$ is the radial dipole matrix element of the virtual transition, and $\epsilon_{\alpha}^{i(s)}$ are the Cartesian components of the incident (scattered) photon polarization. We have also assumed that atom Mn_1 lies at site o .

In the conditions of the experiment of Ref. [4] and indicating by ψ the azimuthal angle around the scattering vector, we have for the $\sigma \rightarrow \pi$ channel $\vec{\epsilon}^i = (\sin\psi/\sqrt{2}, -\sin\psi/\sqrt{2}, \cos\psi)$ and $\vec{\epsilon}^s = (\sin\theta - \cos\theta \cos\psi)/\sqrt{2}, (\sin\theta + \cos\theta \cos\psi)/\sqrt{2}, \cos\theta \sin\psi)$, where $\theta = 30^\circ$ is the Bragg's angle; it is immediately seen from Eq. (2) that the scattering amplitude is proportional to $\sin\theta \sin\psi$, providing therefore the observed intensity dependence on the azimuthal angle ψ . Clearly the intensity for the $\sigma \rightarrow \sigma$ channel is zero since then $\vec{\epsilon}^i \equiv \vec{\epsilon}^s$.

It remains to establish the relative weight of the two competing mechanisms. Since the point group symmetry at the Mn site is the same for JTD and orbital order, "theoretical" experiments are needed to disentangle the different contributions.

In order to assess the effect of the *sole* JTD we performed a MS calculation in the muffin-tin approximation for a cluster of 21 atoms around a central Mn with a radius of 5 Å, containing seven Mn atoms with a distorted oxygen octahedron (six O) and eight La atoms, enough to reach cluster size convergence due to the finite mean free path of the excited electron. We used the atomic coordinates as derived from the crystal structure established by Norby *et al.* [13]. State-of-the-art prescriptions were used to construct the charge density and Coulomb potential of the cluster and to simulate the relaxation of the photoabsorber as illustrated, e.g., in Refs. [11,14]. In particular, the energy- and position-dependent complex Hedin-Lundqvist (HL) self-energy $\Sigma(\vec{r}, E)$ was taken for the exchange-correlation part of the potential. A constant $\Gamma_h/2$ equal to the core hole half-width at half-maximum (0.5 eV) was added to its imaginary part to account for the finite core hole lifetime.

The results of this calculation are shown in Fig. 1 where the upper panel (a) shows the first 40 eV of the unpolarized absorption cross section in Mbarn (left scale) together with the resonant diffraction signal [the square of Eq. (2) with $\sin\theta = 1/2$ and $\psi = \pi/2$, right scale, corresponding to a number of effective scattering electrons of the order of five]. The lower panel (b) in Fig. 1 displays instead the anisotropy of the polarized absorption along the principal axis which is responsible for the effect. The agreement with experiments is good. Clearly the intensity of the resonant signal is related to the linear dichroism of the crystal along the x and y directions. Notice that no charge order is present in the model, since the charge is spherically symmetric around each atom. Substantially the same result is obtained from

a 51 atom cluster calculation containing seven Mn atoms with their distorted oxygen octahedra (36 O) and eight La atom, with a radius of 7 Å, thus confirming cluster size convergence.

We then performed non-muffin-tin calculations using the FDM approach [10]. In the absence of a self-consistent charge density with orbital order we used an input charge density obtained from the superposition of neutral atomic charge densities with a Mn configuration given by $t_{2g}^3 e_g^1 4s^2$ with the last e_g electron oriented in the right way. From this charge density we constructed the Coulomb potential of the cluster and the HL self-energy.

In this scheme the ASF tensor $f_{\alpha\beta}(\omega)$ is given by the expression

$$f_{\alpha\beta}(\omega) = (\hbar\omega)^2 \int_{E_f}^{\infty} dE \times \sum_L \frac{\langle 1s | \vec{r}_\alpha | \Psi_L(E) \rangle \langle \Psi_L(E) | \vec{r}_\beta | 1s \rangle}{\hbar\omega + E_{1s} - (E + I_{1s}) + i\Gamma(E)/2},$$

where I_{1s} is the ionization energy of the 1s level up to the Fermi level (FL) E_f and $|\Psi_L(E)\rangle$ is the continuum scattering solution of the SE for the cluster of atoms at energy E above the FL in response to an exciting wave $J_L(\vec{r})$ calculated using the real part of the HL self-energy. $\Gamma(E)/2$ is then the sum of the imaginary part of this latter plus the half-width at half-maximum of the core hole state. The effective scattering amplitude for the (3, 0, 0) reflection is found to be $(\epsilon_x^i \epsilon_x^s - \epsilon_y^i \epsilon_y^s) (f_{xx}^{Mn_1} - f_{yy}^{Mn_1})$, since again the tensor $f_{\alpha\beta}(\omega)$ is diagonal in D_{2h} symmetry. Notice that the imaginary part of $f_{xx}^{Mn_1}$ is proportional to the absorption coefficient for x polarization convoluted with a Lorentzian function of width $\Gamma(E)$, so that the effect will be related to the linear dichroism of the crystal.

In order to assess directly the relative weight of the two competing mechanisms we preliminarily performed two seven atom calculations (a central Mn and six O, not shown), first in a distorted octahedral coordination without orbital ordering and then with a fictitious orbital ordering on the central Mn (no core hole relaxation) and no distortion. The calculated scattered intensities are in the ratio 1:100 in favor of the JTD, in keeping with the rule of thumb estimate given above. A further calculation in which both distortion and orbital ordering are present shows that there is a destructive interference between the two mechanisms, leading to a decrease of scattered intensity, compared to the case of pure distortion, by roughly 20%, therefore confirming the intensity ratio between the calculation with only JTD and that with only OO. This is understandable since the elongation of a bond (e.g., in the y direction) tends to diminish the energy of the rising edge in the same polarization, whereas the orbital occupancy along the same direction tends to increase it, due to the repulsive Coulomb interaction.

All these considerations are confirmed by a series of calculations in the 21 atom cluster mentioned above. To

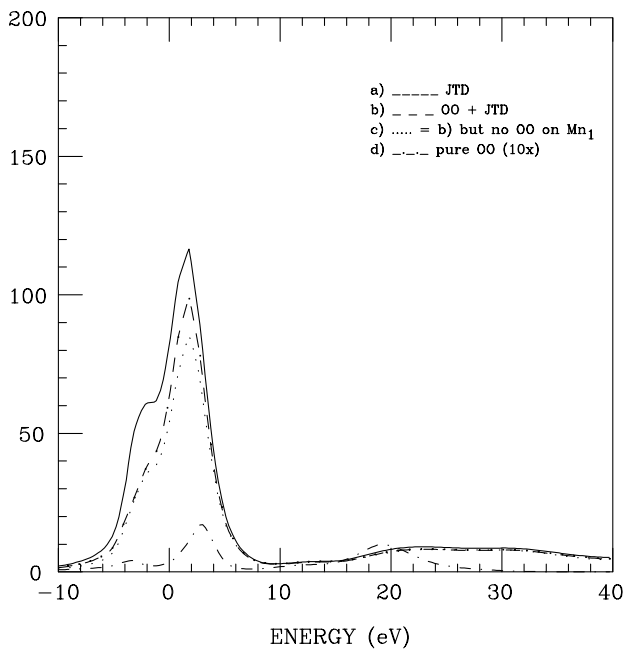


FIG. 2. Anomalous resonant diffraction intensity (adimensional units) at the (3,0,0) reflection by full potential calculations (FDM). (a) Full line: Pure JTD; (b) long-dashed line: JTD plus OO on all Mn atoms; (c) dotted line: same as (b) with no OO on central Mn_1 atom; (d) dot-dashed line: pure OO without JTD ($\times 10$).

serve as a reference we first performed two calculations, one with the atoms in their crystallographic positions and no OO, the other with OO on all Mn atoms and elimination of the coherent JTD of the oxygen octahedra. As shown in Fig. 2 (full and dot-dashed lines, this latter multiplied by 10) the intensity ratio is roughly 100, as expected. Notice also the rather good agreement in the intensity maximum of the first calculation (no OO) with the similar calculation in Fig. 1 (right scale) performed in the muffin-tin approximation, considering the different potential shape and the neglect of the correction due to the occupied states below the FL. The absorption coefficient is similar in both cases and not shown.

For comparison we also performed two more model calculations with the atoms in their crystallographic positions, one with OO on all Mn atoms and the second one with OO only on neighboring Mn atoms. They are presented in Fig. 2 as dashed and dotted lines, respectively, and show the already mentioned interference between JTD and OO with the expected order of magnitude.

It is clear from these calculations that in the absence of an absolute calibration of the intensity due to the pure JTD it is impossible to assess the effect due to OO. Therefore the claim made in Ref. [4] of a *direct* observation of OO in $LaMnO_3$ is not substantiated by our findings, in contrast

with the conclusions of Ref. [8]. On the other hand, the temperature dependence of the observed intensity at the forbidden (3,0,0) reflection, which disappears at $T_O = 780$ K in concomitance with a structural phase transition, is well in keeping with our analysis. X-ray resonant scattering for transitions to empty $3d$ states would be more suitable for such a *direct* observation, as pointed out in Refs. [15,16] in the case of V_2O_3 , since then the “well screened” configuration $3d^{n+1}\underline{L}$ would be much less effective due to the self-screening effect of the excited photoelectron, while it can be shown that the ligand distortion cannot affect the resonant signal at the measured (111) monoclinic reflection.

Considering now the case of $La_{0.5}Sr_{1.5}MnO_4$, the claim in Ref. [3] is that, since there does not seem to be significant distortion around Mn sites [8,17], the observed signal must come from the orbital ordering. However, it is difficult on physical grounds to imagine a Mn^{3+} ion without the accompanying distortion of the ligand configuration, and we actually believe that the absence of JTD has not been proven in this system. Moreover, according to our simulations, even a distortion of 2.5% (0.05 Å) would give rise to a signal still 20 times more intense than that due to OO. Therefore this question deserves at least further investigation.

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