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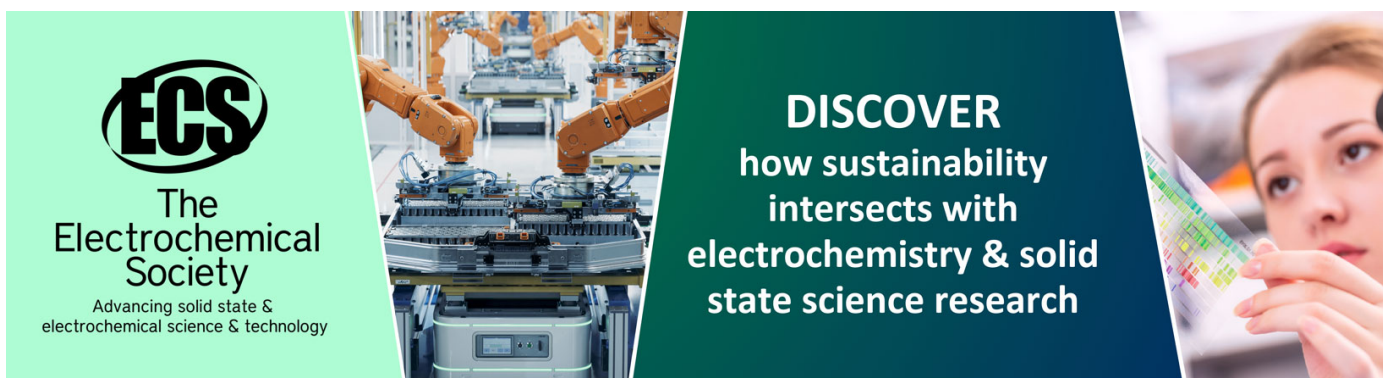
Which orbital and charge ordering in transition metal oxides can resonant X-ray diffraction detect?

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Which orbital and charge ordering in transition metal oxides can resonant X-ray diffraction detect ?

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Abstract. The present article is a brief critical review about the possibility of detecting charge and/or orbital order in transition-metal oxides by means of resonant x-ray diffraction. Many recent models of transition-metal oxides are based on charge and/or orbitally ordered ground-states and it has been claimed in the past that resonant x-ray diffraction is able to confirm or reject them. However, in spite of the many merits of this technique, such claims are ambiguous, because the interpretative frameworks used to analyze such results in transition-metal oxides, where structural distortions are always associated to the claimed charged/orbitally ordered transition, strongly influence (not to say suggest) the answer. In order to clarify this point, I discuss the two different definitions of orbital and charge orderings which are often used in the literature without a clear distinction. My conclusion is that the answer to the question of the title depends on which definition is adopted.

1. Introduction

The variety of phases characterizing transition-metal oxides (TMO) and, in particular, the ubiquitous presence of the metal-insulator transition are usually considered as a proof that their modelization requires going beyond Fermi-liquid models and that electron correlations play a major role [1]. Such correlations usually induce strong electronic localization and, in order to describe the physical behaviour of these localized electrons, several models (Hubbard single- and multi-band, t-J, p-d, Anderson, see again [1] and Refs. therein) have been derived. The solutions of these effective models at zero temperature are often characterized by the coherent onset (ordering) of charge and/or orbital degrees of freedom (the latter usually coupled to spin degrees of freedom [2]). Such orderings are the results of several kinds of electronic interactions, as we shall sketch in Section III for MgTi_2O_4 and in Section IV for Fe_3O_4 .

As in the derivation of any of the previous models one necessarily introduces several uncontrolled approximations, usually performed with physical intuition as the only guide, a question that arises naturally is whether the predicted ordering of such charge and orbital degrees of freedom can be detected experimentally. In this way one could have an *aposteriori* confirmation of the correctness of the approximations performed in the derivation of the effective models and, therefore, of their validity.

A positive answer to this question was given in the recent past and resonant x-ray diffraction (RXD) was identified as a leading technique in this domain. However, I believe that present-day results have not really answered the previous question, mainly because of a fundamental dichotomy in the understanding of the concepts of "charge" and "orbital-order" in the various research communities. Consider the case of OO, first. One possible definition of OO would be as follows: *i*) orbitals at equivalent sites related by some symmetry elements (eg, glide-planes, screw-axes) are oriented in different directions determined by the symmetry element. By such a definition one would basically embrace all classical cases of manganites and KCuF_3 , but also whatever case, like metallic V_2O_3 or α -haematite (see below), where the space-group is sufficiently low that glide-plane or screw-axes are present. Indeed, such a definition is more dependent on the crystallographic symmetry than on the electronic properties of a system, a kind of information in principle available even from non-resonant x-ray diffraction. Originally, the big appeal of OO in manganites was related to its fundamental role to explain colossal magnetoresistance, through the interplay with spin degrees of freedom. The main ingredient of these explanation was the breakdown of the original orbital degeneracy leading to the spin-orbital interaction [2]. In this sense, OO could have been defined as follows: *ii*) an original orbital degeneracy is lifted by a symmetry-breaking transition of electronic origin leading to a coherent orbital pattern. Unfortunately, as we shall see, RXS does not allow to measure OO in the sense of definition *ii*). We can adopt analogous definitions for the CO, at inequivalent sites as follows: *i*) the charge of the same chemical species at inequivalent sites differs by some integer (purely ionic case) or fractional amount; or *ii*) an original charge degeneracy (ie, all sites are characterized by the same charge) is lifted by a symmetry-breaking transition of electronic origin leading to a coherent charge pattern. Again, we shall see that we cannot understand the origin of the transition by RXS, with presently available theoretical analysis. In this sense, RXD is a valid tool to reject a model of CO, as done, eg, in Ref. [3], but not to accept it. I just notice in passing the usefulness of an empirical definition of CO related to the shift in the energy position of the absorption edge, which is a monotonous function of the formal valence state, nearly linear [4], and allows defining CO in the sense *i*) without ambiguity.

The aim of the present article is to critically review some of the past interpretations of RXD in TMO that led to the claims that orbital and/or charge orderings are or are not present in the light of the previous two definitions. In order to do this, I shall first briefly review what resonant x-ray diffraction can and what it cannot detect without further assumptions. This is done in Section II. Then, in Section III and IV, I shall sketch some of the characteristics of orbitally- and charge-ordered models of transition metal oxides, with the specific examples of, respectively, MgTi_2O_4 and Fe_3O_4 and with the idea to show what it should be demanded to an experiment to prove or disprove such models. The choice of these two sections was guided by the peculiar properties of these two spinel materials. The first is MgTi_2O_4 , one of the few systems, if not the only one, for which an exact solution in the whole crystal is known to the spin-orbital Hamiltonian derived from the multi-orbital Hubbard model [5, 6] (though in the $J/U \ll 1$ limit - here J is Hund's coupling and U the on-site Coulomb repulsion - and when $dd\pi$ and $dd\delta$ molecular-bond energies can be neglected compared to $dd\sigma$, which is the case for MgTi_2O_4). The second material of choice is Fe_3O_4 , magnetite, and it has been chosen mainly because of its historical importance and because of the contradictory results of RXD experiments that appeared in the recent literature [7, 8, 9, 10, 11, 12, 13]. In spite of this limitation, in Section V I try to generalize the conclusions to other transition-metal oxides (eg, cuprates, manganites, V_2O_3) and I shall finally conclude on the general interpretation of resonant x-ray diffraction experiments within the introduced theoretical framework.

2. Resonant x-ray diffraction.

Resonant x-ray diffraction (or resonant x-ray scattering as it is often termed) is a technique that takes advantage of the sensitivity of usual x-ray diffraction to ordered structure and of the sensitivity of electron resonances to local density of states. It is a core resonant spectroscopy that depends on the virtual processes that allow promoting a core electron to some empty energy levels. All these processes can be described by the transition matrix elements of matter-radiation interaction:

$$M_{ng}^{i(o)}(j) = \langle \psi_n | \hat{O}^{i(o)} | \psi_g(j) \rangle \quad (1)$$

where, in the x-ray regime, the operator \hat{O} is written through the multipolar expansion of the photon field up to electric dipole (E1) and quadrupole (E2) terms [14]:

$$\hat{O}^{i(o)} = \vec{\epsilon}^{i(o)} \cdot \vec{r} \left(1 - \frac{1}{2} i \vec{k}^{i(o)} \cdot \vec{r} \right) \quad (2)$$

In Eq. (1), $\psi_g(j)$ is the core ground state centered around the j^{th} atom and ψ_n the probed photo-excited state, whereas in Eq. (2), \vec{r} is the electron position measured from the absorbing ion, $\vec{\epsilon}^{i(o)}$ is the polarization of the incoming (outgoing) photon and $\vec{k}^{i(o)}$ its corresponding wave vector. In RXS the global process of photon absorption, virtual photoelectron excitation and photon re-emission, is coherent throughout the crystal, thus giving rise to the usual Bragg diffraction amplitude:

$$F = \sum_j e^{i\vec{Q} \cdot \vec{R}_j} (f_{0j} + f'_j + i f''_j) \quad (3)$$

Here \vec{R}_j stands for the position of the scattering ion j , \vec{Q} is the diffraction vector and f_0 is the usual Thomson factor. The resonant part, $f'_j + i f''_j \equiv f_j$, is the anomalous atomic scattering factor, given by the expression [15]:

$$f_j(\omega) = \frac{m_e}{\hbar^2} \frac{1}{\hbar\omega} \sum_n \frac{(E_n - E_g)^3 M_{ng}^{o*}(j) M_{ng}^i(j)}{\hbar\omega - (E_n - E_g) - i \frac{\Gamma_n}{2}} \quad (4)$$

where $\hbar\omega$ is the photon energy, m_e the electron mass, E_g the ground state energy, and E_n and Γ_n are the energy and inverse lifetime of the excited states. The sum is extended over all the excited states of the system.

The matrix element in Eq. (1) depends only on the electronic part of the operator \hat{O} , so that the radiation parameters $\vec{\epsilon}$ and \vec{k} can be factorized out. What one gets is therefore:

$$\begin{aligned} f_j(\omega) = & \sum_{\alpha\beta} \epsilon_{\alpha}^{o*} \epsilon_{\beta}^i F_{\alpha\beta}^{DD}(j; \omega) \\ & - \frac{i}{2} \sum_{\alpha\beta\gamma} \epsilon_{\alpha}^{o*} \epsilon_{\beta}^i \left(k_{\gamma}^i F_{j\alpha\beta\gamma}^{DQ}(\omega) - k_{\gamma}^o F_{\alpha\beta\gamma}^{QD}(j; \omega) \right) \\ & + \frac{1}{4} \sum_{\alpha\beta\gamma\delta} \epsilon_{\alpha}^{o*} \epsilon_{\beta}^i k_{\gamma} k_{\delta} F_{\alpha\beta\gamma\delta}^{QQ}(j; \omega) \end{aligned} \quad (5)$$

where we have explicitly separated the tensor dependence of the scattering amplitude. The terms F^{DD} , $F^{DQ(QD)}$ and F^{QQ} represent all what is left of Eq. (4) once the polarization and wave vector components are extracted from the transition matrix elements in the dipole-dipole,

dipole-quadrupole and quadrupole-quadrupole channels, respectively. $\alpha\beta\gamma\delta$ represent cartesian components (x, y, z). The interest for such a separation can be easily explained as follows: today polarization detectors in the x-ray range allow a reliable polarization analysis of the diffracted signal. At the same time, the incoming x-rays can also be completely polarized. This allows analysing different cartesian components of the signal by varying polarization and wave-vector directions of incoming and outgoing beams, thereby exploring the intrinsic anisotropies of the charge distribution, what in the earlier literature on the subject [16, 17] was called anisotropic tensor of susceptibilities.

However, it is possible to provide a much deeper physical insight if we re-write Eq. (5) in terms of the scalar product of irreducible tensors [18, 19], instead of using cartesian tensors. Formally one can then re-write Eq. (5) as:

$$f_j(\omega) = \sum_{p,q} (-)^q T_q^{(p)} F_{-q}^{(p)}(j; \omega). \quad (6)$$

Here $T_q^{(p)}$ depends only on the incident and scattered polarization and wave vectors, ie, it is the spherical counterpart of the polarization and wave-vector terms in Eq. (5), while $F_q^{(p)}(j; \omega)$ represents the properties of the system under study, ie, it is the spherical counterpart of the F^{DD} , $F^{DQ(QD)}$ and F^{QQ} terms.

The advantage obtained with this reformulation is that the rank p of these irreducible tensors represents the order of the multipoles in the electromagnetic field expansion (see, e.g., Refs. [18, 20, 21]). For example, for each p , $F_q^{(p)}(j; \omega)$ is related to a specific term of the multipolar expansion of the system, as shown in Ref. [20]. The allowed p are, in the dipole-dipole channel $p = 0, 1, 2$, in the dipole-quadrupole channel $p = 1, 2, 3$ and in the quadrupole-quadrupole channel $p = 0, 1, 2, 3, 4$. For the physical meaning of each term, we refer to Ref. [20]. The explicit polarization and wave-vector dependence of dipole-quadrupole terms will be published elsewhere [22].

In what follows we shall be mainly concerned with $p = 0, 2$ in the dipole-dipole channel, as these two tensors (a scalar and an electric quadrupole) are directly related to the so-called charge- and orbital-ordering signals. However, we shall see in section V that also the $p = 4$ term in the quadrupole-quadrupole channel will be extremely useful to draw new comparison amongst the various results.

Before closing this section, we shall linger on an important aspect of what this experimental technique can and what it cannot say without a specific theoretical calculation of electron energy dispersion. Thanks to the polarization and the azimuth angle analysis, it becomes possible to perform an experimental separation of spherical tensors of different rank (and therefore different electromagnetic multipoles [20]). In particular, at the dipole-dipole level, this separation allows in principle identifying the scalar, $F_0^{(0)}(j; \omega)$ and the quadrupole $F_q^{(2)}(j; \omega)$ ($q = -2, \dots, 2$). The former term is necessarily related to a charge distribution (the only multipole transforming like a scalar), whereas the latter is related to an electric-quadrupole distribution (the only parity-even, time-reversal even multipole transforming like a second-rank spherical tensor). Therefore, terms of different symmetry can be separated experimentally in an efficient way by means of polarization and azimuth scan analysis.

However, what this technique cannot state, without further theoretical input, concerns the origin of these terms: do these terms really measure the charge and orbital degrees of freedom implied by the solution of Hubbard-related models? Is it therefore possible to find a confirmation of these models thanks to the analysis of such two contributions? The answer is not so easy as it may appear at first sight, because other effect, not taken into account into the Hubbard-based models, the first of which is the lattice deformation in the phase transition, could play an important role (and actually they do). In the next three sections we shall describe why the

consequences of these kinds of experiments on theoretical models are much more involved than usually thought.

In passing, I would like also to remind another important point in the interpretation of the data, which is usually undercited. RXD does not probe a ground state, but a highly excited state where a core-hole is formed. It is usually tacitly assumed that the core-hole does not disturb much the overall symmetry and, as in the case of absorption spectroscopy where sum-rules have been widely used, we are indeed probing ground-state properties.

3. Orbital ordering and MgTi_2O_4 .

The ground state of a transition-metal oxide can be insulating, metallic or superconducting, depending on temperature and stoichiometry, and its magnetic structure can vary from ferromagnetic (FM) to different antiferromagnetic (AFM) types [1]. The insulating behavior is generally attributed to a large Coulomb interaction that localizes the d electrons in Mott-Hubbard or charge-transfer regimes. We remind that, in the spirit of the Hubbard model, only the Coulomb on-site repulsion is considered and intersite energy is just kinetic and often limited to nearest neighbors. These ingredients allow explaining the onset of either orbital or charge ordering, as we shall sketch in this and in the next section.

In particular, if the transition-metal ion possesses an orbital degeneracy, low-energy excitations can often be described through an effective superexchange model which couples spin and orbital degrees of freedom. The result is a Heisenberg spin-Hamiltonian whose exchange constants are determined by the orbital degrees of freedom. The main prediction of this kind of approach, put forward for the first time by Kugel and Khomskii in 1973 for KCuF_3 [23], and independently for V_2O_3 in 1978 by C.R. Natoli [24], is that the onset of various kinds of orbital ordering allows switching towards as many magnetic phases, due to the different values assumed by the coupling constant and therefore explains the variety of magnetic phases. Interestingly, this mechanism is a purely electronic one and not determined by the electrostatic coupling with the ionic lattice (though the lattice enters the calculation because electrons are supposed to be localized at atomic sites). The reason why orbitals order is that, in the presence of an orbital degeneracy (a "condition sine qua non"), there is, at a sufficiently low temperature, a phase transition towards the symmetry-breaking ordered state because in this way the superexchange energy is lowered (whereas at high temperature the entropy term in the free energy allows selecting a disordered state).

Usually, however, the lattice is supposed to feel the electrostatic interaction due to the distorted valence electrons and should distort accordingly. This is for example well-known for e_g electrons in manganites [25]. In this case one cannot disentangle the two signals (the orbital ordering of e_g electrons and the Jahn-Teller distortion of the lattice) by RXD without a proper theoretical framework, as described quantitatively in Refs. [26, 27, 28, 29] and sketched in Section V. However, in the case of t_{2g} electrons, electron-lattice interactions are usually smaller in intensity than in the case of e_g electrons (as the latter point towards the anions, the former not). This might give rise to lattice distortions that do not have the same symmetry as the underlying orbital order, as it was indeed theoretically found for MgTi_2O_4 , that we shall describe below. The behaviour of the superexchange interaction in MgTi_2O_4 , moreover, can provide useful hints to deal with the much more complicated isostructural Fe_3O_4 , that we shall analyze in the next section.

MgTi_2O_4 is a spinel whose Ti atoms, formally Ti^{3+} are situated at the corners of a pyrochlore lattice (see Fig. 3 and 4 of Ref. [6]). We remind here that, when employing Hubbard-related models, being principally interested in low-lying magnetic states, we deal with metal sites as if they were purely ionic. The reason is that a ionic model better describes the pairing of magnetic ions and therefore represents a more precise starting point for a magnetic model. This however

does not mean that the projected charge on Ti atoms is the one corresponding to just one $3d$ electron, because of the back-bonding effects of Ti atoms with surrounding oxygen atoms. It just means that the 3 electrons formally lost by the Ti^{3+} -ion, as they are magnetically paired with the electrons of surrounding oxygens to form "octets", do not contribute to the magnetic properties of metallic ions. However, they still contribute to its total valence charge.

As shown in Refs. [5, 6], if one considers just $dd\sigma$ molecular bonds between nearest-neighbors Ti^{3+} sites, it becomes possible to write down a superexchange hamiltonian for MgTi_2O_4 that can be solved exactly in the limit of $J/U \ll 1$. The main idea behind this model is to map the dynamical problem into a topological problem, which, due to the peculiar structure of the pyrochlore lattice, can be solved algebraically. The main ingredient of the problem is that each electron lowers its energy if it forms a spin-singlet with one of its nearest-neighbors. Because of the topology of pyrochlore structure, such a spin-singlet dimer-state is in principle highly degenerate with respect to dimer orientations (degeneracy can be estimated as bigger than $2^{N/4}$, where N is the number of atomic sites in the crystal [6]), but there is only one state that can also minimize the magnetoelastic energy giving rise to the chiral distortion, as experimentally observed [30]. Notice moreover that the spin-singlet is described by an entangled wave-function, entanglement which is fundamental to reduce the value of the global ground-state energy. This means that no kind of ab-initio calculations presently available can reproduce it without considering it since the very beginning.

Our final result [5] is that orbital degrees of freedom modulate the spin-exchange energies, drastically reduce the infinite spin degeneracy of pyrochlore structure, and drive the system towards a nonmagnetic spin-singlet manifold. The orientational degeneracy is then lifted by the magneto-elastic interaction that optimizes the previous energy gain by distorting the bonds in suitable directions and leading to the tetragonal phase. In this way a valence bond crystal state is formed, through the condensation of dimers along helical chains running around the tetragonal c axis, as actually observed in MgTi_2O_4 . The orbitally ordered pattern in the dimerized phase is predicted to be of ferro type along the helices and of antiferro type between them.

In a simpler language, this means that the symmetry around each ion is strongly anisotropic in the direction of the spin-singlet bond, where the valence charge of the unpaired d electron is concentrated. This suggests that ionic, site-centered charge ordering might not be the only possibility for spinel structures and also "bond-charge-ordering" might be considered. Moreover, the symmetry of the electronic wave-function projected on Ti-ions, as determined by superexchange interaction, is not the same as the one that would have been determined by the local electrostatic field due to the Jahn-Teller distortion, and therefore, contrary to manganites, it could be properly identified by RXD. One has to remind however that the other d charges, eliminated by the formal valence, still contribute in reality to the total charge, and in a more isotropic way (ie, determined by the electrostatic symmetry of surrounding oxygen atoms, ie, the point symmetry of Ti-ions). This makes again things more complex and actual calculations are in progress on this point.

4. Charge ordering and Fe_3O_4 .

Another interesting situation to consider is the situation when it is the charge density which is supposed to order on the *a priori* equivalent lattice sites (charge ordering). Such solutions may naturally come out from Hubbard-related models when one is allowed to break the lattice symmetry, making inequivalent two *a priori* equivalent sites because of two different charge occupancies that are considered to be frozen (ie, non-fluctuating). Such a kind of solution has been advanced even within different theoretical frameworks: for example, in the case of magnetite, a simple electrostatic (Madelung) energy computation [31], or a degeneracy argument within a purely ionic model for the computation of entropy in the free energy [32]. However,

whatever the ideal theoretical model is, the situation in real materials is often more complex, as the crystal structure usually distorts, too, in connection to this ordering (as we have seen also for orbital ordering), leading to a global charge distribution that is the combined effect of the electronic correlations (if they existed) and of the electrostatic configuration determined by the distorted lattice. As we shall see below, these are two coupled effects that is extremely difficult to identify and disentangle by RXD.

Magnetite was for long time considered to be the prototypical material for Mott-Hubbard insulating transitions driven by charge ordering. This compound has the same high-temperature structure than MgTi_2O_4 ($\text{Fd}\bar{3}\text{m}$ spacegroup), with Fe-ions at both tetrahedral and octahedral sites. The idea to explain the metal-insulator transition that led to the measured jump in conductivity around 120 K is the following: at octahedral sites Fe ions are formally either in the $2+$ or in the $3+$ ionic configurations, with an equal weight. In the high-temperature phase the extra valence electron (compared to the configuration with all Fe^{3+}) can move freely, in such a way that the system is conducting and the average occupancy at each site is $2.5+$. However, in the low-temperature phase, this extra-electron, for electrostatic reasons, freezes on well localized sites, forming a fixed pattern of Fe^{2+} and Fe^{3+} -ions: we have a transition from disorder (high-T) to order (low-T) and the system becomes insulating due to the localization of the extra electron responsible for the conduction in the high-temperature phase. This picture has the big advantage of being simple and easy to understand, but the drawback of being manifestly incorrect in its simplicity. It is interesting to note in this respect that Verwey himself was well aware of the drawbacks of his picture, as an oversimplified model. He stated [33]: "Since it is thus made plausible [through the analysis of x-ray experiments] that all Fe spinels, except Zn and Cd, have the inversed cation spinel arrangement, the explanation of this abnormal behaviour [ie, the fact that the minimization of electrostatic energy implied, oppositely, the normal cation spinel arrangement] must obviously be found in the circumstance that these structures cannot be completely understood from a purely ionic point of view. Comparatively important homopolar contribution to the bond must be considered". His statement was based on an electrostatic calculation he performed using the at-the-time available Evjen method [34], which showed that the minimal total energy was achieved in the normal spinel structure instead of the inverse spinel structure. Therefore already in 1947 a specific calculation showed that the ionic picture was untenable. Such a statement was then complemented by the other two in Ref. [35]: "[...] the ionic picture according to which the electrons are thought to be added entirely to one-half of the Fe^{3+} -ions is much too simple. A low transition temperature is very rare for a crystal lattice in which the atoms are held together by strong bonds [...]" and "The actual energy [calculated neglecting oxygen displacements and polarization effects] [...] is far too high [a few electronvolts] and suggest that the wave functions of the electrons extend over several atomic distances". Yet, a subsequent calculation [35], with the insertion of the empirical bond-distance, sufficed to justify the ionic model for the subsequent 50 years, up to the advent of more sophisticated calculations of total energy than Verwey's by means of density functional theory (DFT) [36, 37, 38, 39, 40], that again showed that the ionic picture is untenable for magnetite and all gave a different estimate of the (fractional) charge occupancy at each inequivalent Fe-site.

I believe that for a deeper understanding of this system and the role of electron correlations on the metal-insulator transition, a closer look at the results of these calculations could be enlightening. The ensemble of calculations performed in Refs. [36, 37, 38, 39, 40] is so complete that it is sufficient to use their results in order to extract an interesting global picture of the ground-state of magnetite. For example, LDA+U calculations [37] in the cubic, non-distorted state give a metallic ground-state, thereby signalling that the Coulomb correlation alone cannot give rise to the insulating state, but only when coupled to the lattice distortion (in which case the same LDA+U calculation give rise to an insulating state). This evidence is still more striking when combined with the DFT-BLYP3 results of Ref. [40], without Hubbard-U Coulomb

repulsion, but with an hybrid exchange functional, BLYP3, that takes $\sim 15\%$ of the exchange energy from an Hartree-Fock calculation, therefore leading to an increase in exchange compared to usual LDA or GGA calculations. These results show (Fig. 6 of Ref. [40]) that in this case monoclinic constraints alone, without Hubbard-U terms, give rise to an insulating ground-state. Still more important, in their Table IV, it is shown that the same amount of charge disproportionation on the four inequivalent Fe sites as the LDA+U calculations [36, 37, 38, 39] can be obtained. This clearly shows that the charge disproportionation, of the order ~ 0.2 electrons, is not necessarily a consequence of U and it can be enhanced/decreased by other interactions like the electrostatic lattice potential if only a different exchange-energy functional is provided. It is clear that the only conclusion that we can derive at this level of approximation is that the role of Hubbard-U repulsion as a source of charge-ordering is far from being proved by the available calculations. We notice in passing that Ref. [40] predicts a P1 triclinic space-group for a fully unconstrained total-energy minimization. Notice also that pure GGA calculation in the cubic phase give rise to a charge separation, but of minor amount (~ 0.03).

In this respect, what can RXD tell us about this compound? Let me briefly review the most recent achievements from Refs. [7, 8, 9, 10, 11, 12, 13]. In Ref. [11] a detailed analysis of oxygen and iron displacements is performed, when passing from the high-temperature cubic phase to the low-temperature phase, supposed monoclinic (P2/c) but with orthorhombic constraints as in Ref. [43]. Such an analysis was performed with the help of Y. Joly's program *fdmnes* [44], allowing the comparison of the scattering power of each ion in both crystal structures. There we showed that measuring a single peak at (0,0,1/2) reflections, as done at the O K-edge [8] or at Fe L-edges [9], does not allow stating anything about the orbital and/or charge-ordering origin of that signal. I believe that in the absence of any definite answer, a simple principle of economy would tell us that we do not need to invoke any charge or orbital ordering in the compound (in the sense of *ii*), clearly) from RXD data, as the lattice-distortion alone would suffice to explain our experimental results. Another argument leading to the same conclusion, concerning orbital ordering at L-edges will be given in Section V.

A much higher degree of sophistication and a greater objectivity can be in principle obtained, instead, with the suggestion from Joly and collaborators [7, 10] to measure a wider set of reflections (in this case, necessarily at the K-edge, where Bragg condition can be satisfied even at higher Miller indices). The idea is then to fit the different models (just structural distortion, several charge-ordering patterns, hybrid cases) and let a χ -square analysis to decide what is the best model. Whereas I believe that this idea provide us with a more objective criterion for future analysis, at present, it has been tested only with charge patterns modeled on the results of DFT-based calculations, which are all centered on the transition-metal ion. The same idea could be used, instead, with bond-centered charge patterns or eventually, for Fe_3O_4 , tetrahedrally-centered charge patterns, in such a way as to have a quantitative tool for accepting or rejecting models based on strongly correlated electrons.

Unfortunately, in the specific case of Fe_3O_4 there is still some uncertainty on the values of crystal parameters, whose variation, even small, may as well simulate the characteristics of a smaller or bigger charge disproportionation, leaving the uncertainty over this estimate rather undetermined. This is exemplified by comparing the results of Ref. [7] where the P2/c cell is used with those of Ref. [10], where the Cc cell is used with a minimized χ -square obtained with different values of the charge disproportionation on some Fe sites. I just notice in passing that a similar position on this point, though more focussed on the experimental analysis, is usually expressed by the group of J. Garcia [3, 41, 42].

Let me compare these interpretations with the rather well established theory that is available for the isostructural MgTi_2O_4 . If one advances, by simple analogy, the hypothesis that the correlations might localize the charge not only at specific sites, but, especially, along specific bonds, then this might explain on one side the intrinsic difficulty to all DFT-based approaches

to explain the origin of the metal-insulator transition (as the entangled solution presented in Ref. [5] for MgTi_2O_4 is not obtainable by the present functionals), and on the other might allow explaining why the low-temperature crystal symmetry of magnetite is so low: the combination of site and bond charge-ordering would remove several symmetry elements like the inversion-symmetry, thereby driving the system towards a magnetoelectric ground-state (as the time-reversal symmetry is lost already at an higher temperature, the system being ferrimagnetic). Interestingly, this could explain the magnetoelectricity of Fe_3O_4 recently found [45]. Clearly, if the charge is mainly localized at the bond sites rather than at atomic sites, all calculations trying to determine the degree of charge-ordering in this system [7, 8, 9, 10] should be revisited.

5. Conclusions.

After devoting Sections III and IV on the properties of these two materials, we can briefly review some other results at the transition-metal K-edge, and, for particularly long unit cells, in such a way that the Bragg diffraction condition is met (as firstly suggested in Ref. [46]), even at the transition-metal L-edges or at the O K-edge.

At transition-metal K-edges, after the seminal papers by Murakami *et al.* [47], suggesting the possibility that orbital ordering could be "directly" detected at Mn K-edge in LaMnO_3 , several papers have been written to support [48] or reject [26, 27, 28] this thesis. It is nowadays well accepted that the Mn K-edge spectroscopy is not directly sensitive to $3d$ orbitals, but just the Jahn-Teller distortion of the lattice. This conclusions can be justified by the following considerations [27]: at the measured reflection (the (300) of LaMnO_3) the signal is determined by the energy splitting of p_y and p_z orbitals (in the basis of Ref. [27]). There are two possible sources of splitting: the first, determined by the coherent Jahn-Teller effect, was calculated to be about 2.0 eV. This splitting is necessarily present because of the (measured) structural distortion. The second source is the (eventual) underlying orbital order of $3d$ orbitals, that can influence, through the U_{3d-4p} Coulomb repulsion, the splitting of p_y and p_z orbitals. The latter, calculated as 0.4 eV by atomic multiplet calculations (and necessarily further reduced by band-effects), allows estimating an upper bound of $(2.0/0.4)^2 = 25$ in intensity in favor of the Jahn-Teller origin of the signal, which is directly proportional to the square of the splitting [27, 47]. Therefore, the orbital order, if it existed, could not be measured in such a way. We remind the further result of Ref. [49], showing that the measured increase of the signal at T_N , which was used in Ref. [48] to support the OO origin of the signal, was actually an artefact.

We notice in passing that the V K-edge Bragg-forbidden reflection $(111)_m$ in the antiferromagnetic insulating phase of V_2O_3 , at first interpreted as orbital ordering [50], was later on shown to be of magnetic nature [51].

At O K-edge one is sensitive indirectly to the transition-metal ion (through the oxygen $2p$ -TMO $3d$ hybridization). Here too, however, several papers claiming the detection of charge ordering (eg, in cuprates [52] or in manganites [53]) should be revisited after the analysis of Ref. [11], where it was demonstrated that, if not false, these statements are at least undecidable. In fact, in these works the authors of Refs. [52, 53] interpreted the resonant scattering signal in the pre-edge region *a priori* as a signature of the doped holes in these materials, due to the $p-d$ hybridization. However, as this pre-edge region is very sensitive also to structural distortions, as shown in Ref. [11], this would at a minimum suggests that it would be worthwhile to calculate quantitatively the relative contributions to this signal before concluding that the signal arises solely from doped holes. Again, however, all these structural calculations might share the same warnings as above.

The situation at $L_{2,3}$ -edges is apparently different: as it was argued in Ref. [46], the detection of a Bragg-forbidden reflection at these edges is necessarily related to a different occupancy of d orbitals at the two sites characterized by the out-of-phase atomic scattering factors. This

necessarily implies that the two sites have, coherently throughout the lattice, a different orbital occupancy. Consider for example the measurement of the Bragg-forbidden $(001/2)_c$ reflection at Fe L_3 edge in magnetite [9, 11]. The $2p$ core electrons are promoted to the empty d levels by a dipolar transition: this is a direct proof that d orbitals of the two Fe sites whose difference contributes to the scattering factor have different occupancies. Does it suffice to say that magnetite is characterized by orbital ordering, in the sense of our definition *ii*) ? Before answering, let us consider the following two other examples at the pre K-edge of Fe in α -haematite (Fe_2O_3) [54] and at the pre K-edge of V in the paramagnetic metallic (PM) phase of V_2O_3 (see Ref. [55], Fig. 2(a) and (c)). In both these cases [18, 19] we are probing only d states at the transition-metal site, due to a particular selection rule of the corundum structure that forbids dipole transitions at the $(00.3)_h$. We could ask the same question: are we probing orbital ordering, as before for magnetite, just because we are directly looking at a coherent difference in the occupancy of empty d states ? These examples show how much the question may appear semantic: if by orbital ordering we mean our definition *ii*), the answer is clear: no. It is not the case in α - Fe_2O_3 because this system is not orbitally degenerate (Fe^{3+} -ions are in a high-spin configuration, characterized by a filled magnetic shell), and therefore it cannot develop an orbital order in the sense of *ii*). It is again not the case for V_2O_3 , which is in its metallic phase and therefore should be characterized by delocalized wave-functions.

If instead by orbital ordering we mean whatever distribution corresponding to a coherent inequivalent filling of transition-metal ions, ie, our definition *i*), then the answer is yes. In this case, however, we should conclude that if we look at a wider set of experiments than just the usual ones on the systems which are supposed to be orbitally or charge-ordered, we find out that basically whatever system with a sufficiently low crystal-symmetry could be said to be orbitally ordered, which is clearly not the original idea of those who proposed the ordering as an effect of electron correlations. In this sense, then, one might say that even the claim of detection of orbital ordering by usual (ie, non-resonant) x-ray diffraction (by, eg, Ref. [56]) is self-evident, which is not the case, in the acceptance *ii*).

My conclusion is that detecting orbital and/or charge ordering may be meaningful only in connection to the confirmation or rejection of a specific model (as was the case for the rejection of Anderson's criterion in magnetite [3, 42]), or, independently of any model, if linked to the understanding of a specific physical properties. We might ask: do we understand better why magnetite has a metal-insulator transition through the analysis of the fractional charge distribution given by ab-initio calculations or by fitting RXD spectra ? I found no answer in the literature, and personally, I tend to believe this is not the case, in the absence of a specific theoretical framework. At present, we can possibly find some interesting element of analysis in Ref. [57], where the same reflection was detected at L-edges but not at K-edge, or in rare-earths and actinides [58]. The terminology usually adopted in these cases by the corresponding research community is rather "multipolar ordering" (it extends the concept of charge and orbital ordering to the $p \geq 2$ in Eq. 6). These systems, like NpO_2 are characterized by a huge local charge at the actinide site, which apparently can order without deforming the (usually cubic) crystal structure [58] and therefore the corresponding RXD signal can be interpreted unambiguously.

Concerning the question of the title, it is clear that RXD can detect both CO and OO in the sense *i*), which we showed rather useless for a proper theoretical comprehension of the system, whereas it is insensitive to OO and CO in the sense *ii*). However, a future quantitative analysis of RXS experimental data on specific systems for which the ground-state correlated solution is known, that takes into account of the correlated charge distribution, eg, for MgTi_2O_4 on bonds instead of atoms, might possibly allow a direct criterion for selecting or rejecting such a ground state and therefore provide a mean for detection of orderings also in the sense *ii*), much more interesting for the community working on theoretical models of strongly correlated electron systems.

References

- [1] Masatoshi Imada, Atsushi Fujimori, and Yoshinori Tokura, *Rev. Mod. Phys.* **70**, 1039 (1998)
- [2] M. Cuoco, N.B. Perkins, A.M. Oles, Magnetic and orbital ordering in cuprates and manganites, Proceedings of the Fourth Training Course in the Physics of Correlated Electron Systems and High-Tc Superconductors Vietri sul Mare, Salerno, Italy, AIP (2000) **4**, 226.
- [3] J. Garcia, G. Subias, M. Proietti, H. Renevier, Y. Joly, J. Hodeau, J. Blasco, M. Sanchez, and J. Berar, *Phys. Rev. Lett.* **85**, 578 (2000)
- [4] J. Garcia, private communication at the XAFS XIV Conference.
- [5] S. Di Matteo, G. Jackeli, N.B. Perkins, and C. Lacroix, *Phys. Rev. Lett.* **93**, 077208 (2005)
- [6] S. Di Matteo, G. Jackeli, and N.B. Perkins, *Phys. Rev. B* **72**, 024431 (2005)
- [7] E. Nazarenko, J. E. Lorenzo, Y. Joly, J. L. Hodeau, D. Mannix, and C. Marin, *Phys. Rev. Lett.* **97**, 056403 (2006)
- [8] D. J. Huang, H.-J. Lin, J. Okamoto, K. S. Chao, H.-T. Jeng, G. Y. Guo, C.-H. Hsu, C.-M. Huang, D. C. Ling, W. B. Wu, C. S. Yang, and C. T. Chen, *Phys. Rev. Lett.* **96**, 096401 (2006)
- [9] J. Schlappa, C. Schüssler-Langeheine, C. F. Chang, H. Ott, A. Tanaka, Z. Hu, M. W. Haverkort, E. Schierle, E. Weschke, G. Kaindl, and L. H. Tjeng *Phys. Rev. Lett.* **100**, 026406 (2008)
- [10] Y. Joly, J. E. Lorenzo, E. Nazarenko, J.-L. Hodeau, D. Mannix, and C. Marin, *Phys. Rev. B* **78**, 134110 (2008)
- [11] S. B. Wilkins, S. Di Matteo, T. A. W. Beale, Y. Joly, C. Mazzoli, P. D. Hatton, P. Bencok, F. Yakhov, and V. A. M. Brabers *Phys. Rev. B* **79**, (R)201102 (2009)
- [12] J. E. Lorenzo, C. Mazzoli, N. Jaouen, C. Detlefs, D. Mannix, S. Grenier, Y. Joly, and C. Marin, *Phys. Rev. Lett.* **101**, 226401 (2008)
- [13] J. Garcia, G. Subias, J. Herrero-Martin, J. Blasco, V. Cuartero, M. Concepcion Sanchez, C. Mazzoli, and F. Yakhov, *Phys. Rev. Lett.* **102**, 176405 (2009)
- [14] The magnetic dipole term can be safely neglected in the x-ray range.
- [15] M. Blume, in *Resonant Anomalous X-ray scattering*, edited by G. Materlik, J. Sparks and K. Fisher (Elsevier, Amsterdam, 1994), p. 495.
- [16] D.H. Templeton, L.K. Templeton, *Acta Cryst.* **A36**, 237 (1980); *ibid.* **A38**, 62 (1982)
- [17] V.E. Dmitrienko, *Acta Cryst.* **A39**, 29 (1983)
- [18] P. Carra, B.T. Thole, *Rev. Mod. Phys.* **66**, 1509 (1994)
- [19] S. Di Matteo, Y. Joly, A. Bombardi, L. Paolasini, F. de Bergevin, and C. R. Natoli, *Phys. Rev. Lett.* **91**, 257402 (2003)
- [20] S. Di Matteo, Y. Joly, C.R. Natoli, *Phys. Rev. B* **72**, 144406 (2005)
- [21] S. Di Matteo, and C.R. Natoli, *J. Synchrotron Radiat.* **9**, 9 (2002)
- [22] S. Di Matteo, *Journal of Physics Conference Series*, PNSXM - 2009, unpublished
- [23] K.I. Kugel, D.I. Khomskii, *Zh. Eksp. Teor. Fiz.* **64**, 1429 (1973).
- [24] C. Castellani, C. R. Natoli, and J. Ranninger, *Phys. Rev. B* **18**, 4945 (1978).
- [25] L. F. Feiner and A. M. Oles, *Phys. Rev. B* **59**, 3295 (1999)
- [26] I.S. Elfimov, V.I. Anisimov, and G.A. Sawatzky, *Phys. Rev. Lett.* **82**, 4264 (1999)
- [27] M. Benfatto, Y. Joly, C.R. Natoli, *Phys. Rev. Lett.* **83**, 636 (1999)
- [28] M. Takahashi, J. Igarashi, and P. Fulde, *J. Phys. Soc. Jpn.* **68**, 2530 (1999)
- [29] S. Di Matteo, T. Chatterjee, Y. Joly, A. Stunault, J.A. Paixao, R. Suryanaryanan, G. Dhahlenne, and A. Revcolevschi, *Phys. Rev. B* **68**, 024414 (2003), and references therein.
- [30] M. Schmidt, W. Ratcliff II, P. G. Radaelli, K. Refson, N. M. Harrison, and S. W. Cheong, *Phys. Rev. Lett.* **92**, 056402 (2004)
- [31] E.J. Verwey and J.H. de Boer, *Rec. Trav. Chim.* **55**, 531 (1936); E.J. Verwey and P.W. Haayman, *Physica* **9**, 979 (1941)
- [32] P.W. Anderson, *Phys. Rev.* **102**, 1008 (1956)
- [33] E.J. Verwey and E.L. Heilmann, *Jour. Chem. Phys.* **15**, 174 (1947)
- [34] H.M. Evjen, *Phys. Rev.* **39**, 675 (1932)
- [35] E.J. Verwey, P.W. Haayman and F.C. Romeijn, *Jour. Chem. Phys.* **15**, 181 (1947)
- [36] I. Leonov, A. N. Yaresko, V. N. Antonov, M. A. Korotin, and V. I. Anisimov, *Phys. Rev. Lett.* **93**, 146404 (2004)
- [37] Horng-Tay Jeng, G.Y. Guo, and D.J. Huang *Phys. Rev. Lett.* **93**, 156403 (2004)
- [38] G. K. H. Madsen and P. Novak, *Europhys. Lett.* **69**, 777 (2005)
- [39] I. Leonov, A. N. Yaresko, V. N. Antonov, and V. I. Anisimov, *Phys. Rev. B* **74**, 165117 (2006)
- [40] A.D. Rowen, C.H. Patterson, and L.V. Gasparov, *Phys. Rev. B* **79**, 205103 (2009)
- [41] G. Subias, J. Garcia, J. Blasco, M. Proietti, H. Renevier, and M. Sanchez, *Phys. Rev. Lett.* **93**, 156408 (2004)
- [42] J. Garcia and G. Subias, *J. Phys. Condens. Mat.* **16**, R145 (2004)

- [43] J. P. Wright, J. P. Attfield, and P. G. Radaelli, *Phys. Rev. B* **66**, 214422 (2002)
- [44] Y. Joly, *Phys. Rev. B* **63**, 125120 (2001). The program can be downloaded at the web address <http://www-cristallo.grenoble.cnrs.fr/simulation>.
- [45] M. Matsubara, Y. Shimada, T. Arima, Y. Taguchi, and Y. Tokura *Phys. Rev. B* **72**, 220404 (2005)
- [46] C.W.M. Castleton and M. Altarelli, *Phys. Rev. B* **62**, 1033 (2000)
- [47] Y. Murakami, H. Kawada, H. Kawata, M. Tanaka, T. Arima, Y. Moritomo, and Y. Tokura, *Phys. Rev. Lett.* **80**, 1932 (1998); Y. Murakami, J.P. Hill, D. Gibbs, M. Blume, I. Koyama, M. Tanaka, H. Kawata, T. Arima, Y. Tokura, K. Hirota, and Y. Endoh, *Phys. Rev. Lett.* **81**, 582 (1998).
- [48] S. Ishihara and S. Maekawa, *Phys. Rev. Lett.* **80**, 3799 (1998)
- [49] G. Subias, J. Herrero-Martin, J. Garcia, J. Blasco, C. Mazzoli, K. Hatada, S. Di Matteo, C.R. Natoli, *Phys. Rev. B* **75**, 235101 (2007)
- [50] L. Paolasini, C. Vettier, F. de Bergevin, F. Yakhov, D. Mannix, A. Stunault, W. Neubeck, M. Altarelli, M. Fabrizio, P. A. Metcalf, and J. M. Honig, *Phys. Rev. Lett.* **82**, 4719 (1999)
- [51] Y. Joly, S. Di Matteo, and C.R. Natoli, *Phys. Rev. B* **69**, 224401 (2004)
- [52] P. Abbamonte, G. Blumberg, A. Rusydi, A. Gozar, P. Evans, T. Siegrist, L. Venema, H. Eisaki, E. Isaacs, and G. Sawatzky, *Nature* **431**, 1078 (2004)
- [53] S. Grenier, K. J. Thomas, J. P. Hill, U. Staub, Y. Bodenthin, M. Garcia-Fernandez, V. Scagnoli, V. Kiryukhin, S.-W. Cheong, B. G. Kim, and J.M. Tonnerre, *Phys. Rev. Lett.* **99**, 206403 (2007)
- [54] K. D. Finkelstein, Qun Shen, and S. Shastri, *Phys. Rev. Lett.* **69**, 1612 (1992)
- [55] L. Paolasini, S. Di Matteo, C. Vettier, F. de Bergevin, A. Sollier, W. Neubeck, F. Yakhov, P.A. Metcalf, and J.M. Honig, *Jour. Elec. Spectr. Rel. Phen.* **120**, 1 (2001)
- [56] I. Wakabayashi, M. H. Upton, S. Grenier, J. P. Hill, C. S. Nelson, J.-W. Kim, P. J. Ryan, A. I. Goldman, H. Zheng and J. F. Mitchell, *Nature Materials* **6**, 972 (2007).
- [57] J. Herrero-Martin, J. García, G. Subías, J. Blasco, M.C. Sánchez, and S. Stanesco, *Phys. Rev. B* **73**, 224407 (2004)
- [58] Paolo Santini, Stefano Carretta, Giuseppe Amoretti, Roberto Caciuffo, Nicola Magnani, and Gerard H. Lander, *Rev. Mod. Phys.* **81**, 807 (2009)