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Charge order as seen by resonant (elastic) X-ray scattering

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Abstract. We review the main features of charge order observation by means of Resonant (Elastic) X-ray Scattering. Different cases have been studied during the past 12 years (NaV_2O_5, $NdNiO_3$, Fe_3O_4, $BaVS_3$, manganites, ...) that have allowed us to develop a systematic approach for data collection, correction and data analysis.

1 Introduction

1.1 History

Resonant (Elastic) X-ray scattering (REXS) has been used since the appearance of the first tunable energy beamlines at dedicated synchrotron facilities. One of the very first explored issues was the study of the charge distribution among cations of the same chemical species located at different crystallographic sites by powder diffraction [1]. These first results were encouraging and showed that thorough studies of the resonance in diffraction conditions could be performed, beyond these demonstration experiments.

Following these initial accomplishments, the advent of third generation synchrotron light sources (ESRF, APS and Spring-8, and more recently national synchrotron facilities) dedicated REXS beamlines were constructed allowing for the first time diffraction experiments of the near edge (DANES), and the extended part (DAFS), with data quality approaching that of their equivalent absorption/fluorescence counterparts. These founding experiments have established REXS as an unmatched technique to study charge, orbital and spin degrees of freedom as relevant order parameters in a large variety of compounds.

1.2 Motivation

Charge order (CO), is also known in the literature as charge disproportionation, along with orbital order (OO), magnetic order and lattice distortions, are the main ingredients that enter the description of the intricate physics of strongly correlated electron systems (See [2] for a general overview). Undoubtedly the colossal magnetoresistance

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manganites is the family of compounds where extensive REXS have been carried out, following the seminal studies by Murakami et al. [17]. REXS experiments in manganites have been partly reviewed in the J. Herrero-Martin et al.'s contribution we will concentrate here on other *canonical* compounds whose study have largely contributed to the development of this technique, as well. Given a certain material or class of compounds ideally one would like to answer the questions *which order is doing what ?*, *how ?* and *why ?* REXS is the only experimental technique that allows to measure and quantify the effect of the charge independently of the others order parameters and thereby answer the questions of *which ?* and *what ?*.

Before describing REXS any further we stress the issues that we would like to answer with this technique. We are not exhaustive and have left aside cases where REXS has greatly contributed to the understanding of the physics of the compound.

- Quantify the charge ordering related to a metal insulator phase transition. Linus Pauling was the first to hypothesis the rules that stabilize ionic crystal structures [3] where the charges assume an integer value. This method was later extended and generalized to all kinds of crystals. This is the Bond Valence Sum (BVS) method. Metal-anion distances serve to quantify the charge (or valence state) at a given atom position, according to *tabulated values* [4], provided that the crystalline structure is well known. The validity of this semi-empirical technique in accounting for tiny values of the charge disproportionation is arguable. Despite its fundamental interest, often the crystal structure is not known. Or the charge order parameter is entangled with other distortions that induce uncertainties in the refinement of the charge disproportionation. For instance, this method, applied to the metal-insulator transition in $BaVS_3$, has yielded a rather large charge disproportionation [5] whereas REXS experiments showed no indication of this charge ordering [6]. REXS allows to quantify the charge projected onto the resonant atom and, in favourable cases like the example in Fig. 1 [1], independently of the underlying crystal structure. As we will see below, REXS is, in principle, sensitive to the difference in the charge state between two inequivalent atoms of the same chemical specie. And *ab initio* codes like FDMNES [7] have proven to be of great importance to quantify the charge.
- It is very important to quantify the dynamics of the electronic orders as a function of temperature, pressure, magnetic field or several of them combined [8]. Often this is the way in which the role of these electronic parameters can be best seen which turns out to propose answers to questions related to *how ?* and *why ?*. Present state-of-the-art computer codes can identify and account for the features revealed at the resonance in a given diffraction peak but they can not evaluate its importance at constituting the ground state. This statement applies to orbital order problems, as well, where there have been heated debates until it was admitted that REXS can account for electronic effects and for lattice distortions that may be associated with the orbitals, depending on experimental conditions. The important feature is to assess the relevance of this order parameter (either orbitals or lattice distortions or both) by any means and stay away of chicken and the egg problems.
- In some cases, like for instance NaV_2O_5, the low temperature structure (and thus the correct charge order pattern) was unknown and there has been a long debate as to which is the underlying ground state in the low temperature phase. As it turned out REXS experiments have revealed the occurrence of charge disproportionation at the V-atoms and from that inferred that the magnetic ground state was a quantum $s = 1/2$ spin chains [9]. Recently another breakthrough was achieved in the

[1] We can not assert this statement with all generality. However this has been the case in all the compounds that we have studied.

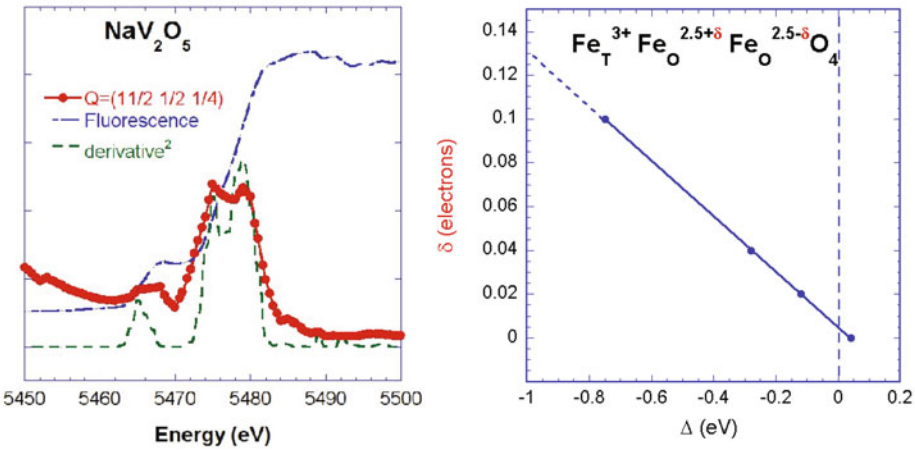

Fig. 1. (Left) the *derivative effect* in NaV_2O_5. The points are the diffraction data around the Vanadium K-edge of the reflection $Q = (11/2, 1/2, 1/4)$ resulting from a charge order transition taking place at 35 K. The fluorescence spectra is shown as a dot-dash line (in blue) and the dash line (green) is the derivative of the fluorescence spectra, squared. The exact amount of charge order was refined to be 0.04 electrons [13]. (Right) FDMNES calculations of the linear dependence between the charge disproportionation parameter, δ, and the shift of the absorption edge of a given iron atom at octahedral position (Fe_O), Δ, in the low temperature phase of Fe_3O_4. The zero abscissas and ordinate corresponds to the high temperature structure. Note that the low temperature structure is already distorted and thus the absorption edge is slightly distorted ($\Delta_{struct} = +0.04\,\text{eV}$) with respect to the position at room temperature. However this shift is (i) opposite in sign with respect to that expected for the charge order and (ii) is 25 times smaller than that corresponding to the actual charge order.

REXS crystallography. Joly and coworkers refined a set of 24 reflections allowing for Fe atomic distortions as well. The result [10] is the first proposal for the long sought low temperature structure of Fe_3O_4. This technique has also been used to contradict an unconventional model of charge ordering in half-doped manganites, confirming the checker board pattern at half doping by Grenier et al. [11], and to suggest pattern in large unit cells resulting from a large charge ordering propagation vector [12] (see Herrero-Martin et al. review). REXS is capable of distinguishing space groups and indicating neighbour atoms' displacements around the resonant atoms, providing a great help in cases where conventional crystallographic techniques are hard pressed to determine even symmetry elements in the charge-ordered unit cell.

2 Charge order observed by REXS

2.1 Fundamentals

The idea behind the observation and analysis of charge order experiments by REXS is very simple, although the actual mechanism of the resonance is rather complex (see Y. Joly et al. in these Proceedings). With all generality, the position and form of the absorption edge subtly depends on the number of electrons of the absorbing atom (including its ionic state) and on its environment (octahedral, tetrahedral, pyramid, plane, etc.). In particular, adding/removing one electron shifts the position of the

edge by some eV within the same local environment. Most generally the electron remains localized among the manifold of orbitals and the projection of this charge onto a given atom is bound to be a fraction of electron. To think that a metal insulator transition in a compact structure, occurring below room temperature, can give rise to an integer charge order effect is nothing else but an *overstatement*, to be taken as an initial model. FDMNES simulations show that the dependence between edge position and the number of electrons can be considered as linear (see Fig. 1 right). This is true when the core-hole does not induce exciton effects and has an influence on the transition process roughly similar among the different absorbing atoms. This is the case at the K-edges and at the $L_{2,3}$-edges of the heavy elements. Note also that the edge shift is usually stronger at the K-edge than at the $L_{2,3}$-edges of the same chemical element. The $M_{4,5}$-edges are usually too low in energy to be used in REXS experiments as the Bragg law can not be fulfilled by the larger wavelength (actinides compounds are the exception). Moreover, at these edges, the photoelectron probes highly localized states. Consequently the strong core-hole effect greatly depends on the configuration states of the different absorbing atoms, making a simple explanation in term of energy shift inappropriate.

Therefore if we consider an ion with two different charge states, 1 and 2, then the anomalous scattering factor ($f_j(\omega) \equiv f'_j(\omega) + if''_j(\omega)$) can be expressed as $f_1(\omega)$ and $f_2(\omega) \equiv f_1(\omega + \Delta)$, with Δ a shift of the absorption edge that linearly depends on the charge difference between ions 1 and 2. As we have seen in Sect. 1.1 it is possible to extract information of $f_1(\omega)$ and $f_2(\omega)$ in powder diffraction experiments, if Δ is not too small. Note that absorption/fluorescence techniques are proportional to the imaginary part of $f_1(\omega) + f_2(\omega)$ and therefore can hardly discriminate small values of Δ. The interesting feature of X-ray diffraction is that one can select Bragg peaks where the structure factor is proportional to $|f_1(\omega) - f_2(\omega)|^2$, or to $|\Delta\partial f_1(\omega)/\partial\omega)|^2$, and this makes this reflections extremely sensitive to minute differences of charge order between different sites. The scattering intensity as a function of energy

$$I(\mathbf{Q},\omega) \propto \left| \sum_j e^{i\mathbf{Q}\cdot\mathbf{R_j}} \left(f_j^0 + f'_j(\omega) + if''_j(\omega) \right) \right|^2 \tag{1}$$

can be rearranged in the following way

$$I(\mathbf{Q},\omega) \propto |A(\mathbf{Q})\,(f_1(\omega) + f_2(\omega)) + B(\mathbf{Q})\,(f_1(\omega) - f_2(\omega)) + F_0(\mathbf{Q})|^2 \tag{2}$$

if one considers a bimodal distribution of charges. Note that all the variables are complex numbers. Under this notation we see the clear signature of the charge order in $(f_1(\omega) - f_2(\omega)) \propto \Delta\partial f_1(\omega)/\partial\omega$. Figure 1 shows the application of this concept to NaV_2O_5 [13]. More terms are required ($C(\mathbf{Q})$, $D(\mathbf{Q})$, f_3, f_4, ...), if the number of inequivalent charges increases. $F_0(\mathbf{Q})$ includes the non-resonant contribution of all the atoms. Equation (2) is the *master equation* relevant to the study of charge order, as well as orbital and magnetic orders. In general the resonant scattering factors, f_j, are rank 2, 3, 4 tensors although for CO problems only rank 0 (scalar) or rank 2 (matrices) are used. The game is to find appropriate $\mathbf{Q}$-positions such that $A(\mathbf{Q})$ and $F_0(\mathbf{Q}) \rightarrow 0$. Note that orbital ordering studies can be performed in non-symmorphic materials at extinct Bragg reflections where, by definition, $A(\mathbf{Q}) = F_0(\mathbf{Q}) = 0$. In this case f_1 and f_2 do not refer to charge states but to non-scalar components of the local scattering factor and this scattering is referred to as anisotropic tensor scattering (ATS) in the literature [14,15]. Finally this equation can serve to study magnetic scattering in antiferromagnetic compounds. For the spin polarized part $f_1 \propto m_j$ and $f_2 \propto -m_j$ and hence the first term cancels and a new lattice periodicity results, at least along one of the axis of the crystal.

2.2 Experiments

The first question that arises before starting any REXS experiment is where to look for the desired signature of charge order, as shown in Eq. (2). To answer this question we emphasized that REXS is just a sophisticated form of crystallography. The charge order is induced by a symmetry breaking phase transition, violating either the symmetry of the parent structure or the translation symmetry or both. As a result new reflections should appear, in case of a new periodicity, or extinct Bragg reflections become active if the unit cell volume is preserved. We should not expect these charge order features at extinct Bragg reflection if the lattice periodicity is not preserved. The second feature that we have to consider is the minimization of $A(\mathbf{Q})$ and $F_0(\mathbf{Q})$. As a rule of thumb, we have to explore the weakest reflections of the new structure, off-resonance. Different strategies have been applied to different charge order cases depending on the knowledge of the low temperature structure. A careful definition of the problem followed by an extensive survey of different reflections (by means of energy scans) is certainly the best way to start.

Although charge order as seen by REXS is accounted for in Eq. (1) the proportionality between the measured intensity and the structure factor squared includes another energy dependent term that adds some complexity to the data analysis. We are referring here to the absorption correction, that enters the scattering equation (Eq. (1)) from *thick* samples. Absorption is not an issue in thin samples, the safe thickness for a given compound and edge can be easily calculated. The absorption correction in the reflection geometry goes as follows [16],

$$\frac{\sin(\theta_B)}{2\mu(\omega)} \exp\left(\frac{-2\mu(\omega)\cdot d_{deadlayer}}{\sin(\theta_B)}\right) \tag{3}$$

where $d_{deadlayer}$ is the thickness of the part of the sample at the surface that absorbs but does not diffract (or *dead layer*). θ_B is the Bragg angle[2] of the reflection and $\mu(\omega) \propto f''(\omega)/\omega$ is the absorption cross section. In the absence of a deadlayer the usual absorption equation of an infinitely absorbing sample is retrieved. The manifestation of a deadlayer is best seen in the jump of the diffracted intensity between energies well below and well above the edge, which is larger than expected from the number of electrons. In this case and as indicated in Eq. (3) the logarithm of the intensity contains a measure of $\mu(\omega)$. We illustrate the influence of a *dead layer* on *magnetite* in Figs. 2(a) and 2(b). Dramatic effects of this *dead layer* have been found in REXS experiments at the Fe L-edges [18].

There are several ways to extract $\mu(\omega)$ from experiments. (i) From fluorescence or absorption experiments [20,21]. This is the standard method, if the sample is well defined, homogeneous and there are no extra parasitic phases of the same resonant atom. For instance *magnetite*, Fe_3O_4, may contain *maghematite*, $\gamma - Fe_2O_3$ and *hematite*, Fe_2O_3, at the surface. (ii) From diffraction experiments. To that end we look for a Bragg peaks such that $F_0(\mathbf{Q}) \gg A(\mathbf{Q})$, $B(\mathbf{Q})$. The energy variation of the diffracted intensity at these peaks contains information on $\mu(\omega)$, alone. In Fig. 2(c) we display the energy dependence of actual measured Bragg peaks in the low temperature phase of *magnetite* [19]. Figure 2(d) displays the same reflections with the intensities divided by the intensity of the (4 4 4) reflection. Despite the large differences between intensities below and above the edge the correction works rather well in all the energy range.

[2] In case of a Bragg reflection that is not symmetric with respect to the surface of the sample the $2/\sin(\theta_B)$ term has to be replaced by $1/\sin(\alpha) + 1/\sin(\beta)$ with α and β the angle between the surface of the sample and the incident and scattering beam, respectively.

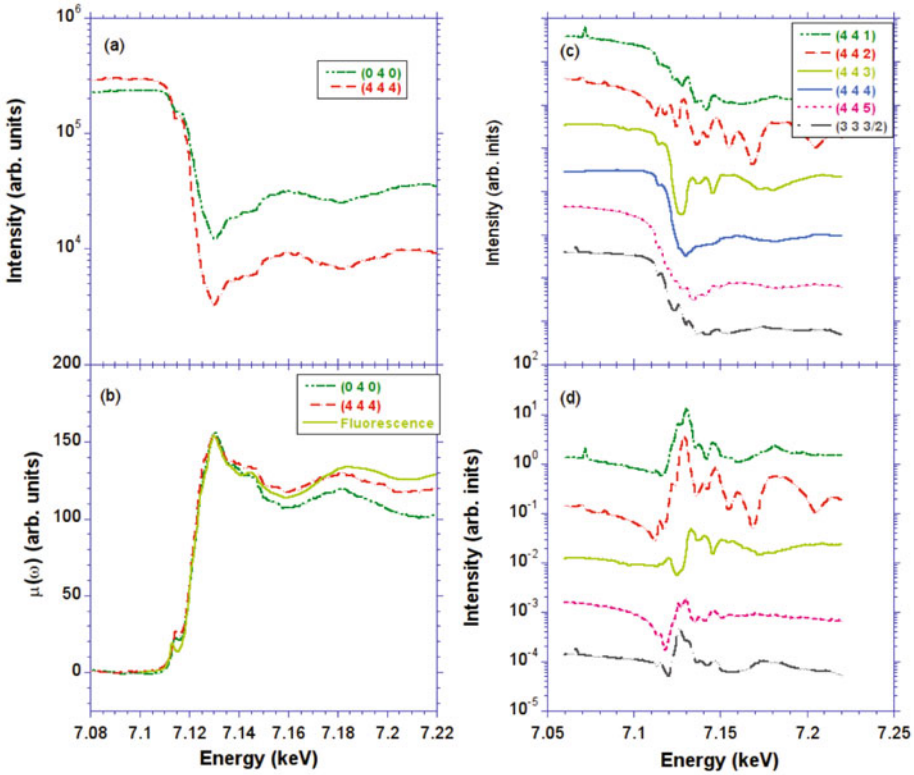

Fig. 2. (a) Intensity of two strong reflections ((4 4 4) and (0 4 0)) as a function of energy in *magnetite*. The jump at the absorption is larger than expected $(\mu_2(\omega \gg E_T)/\mu_1(\omega \ll E_T) = 7.2)$ which is explained if one considers the presence of a *dead layer* at the surface. Eq. (3) accounts well for this *dead layer*. The magnitude of the *dead layer* varies from 3 microns for the (4 4 4) reflection to 1 micron for the (0 4 0), which might indicate that it is not homogeneous throughout the sample. (b) Scans in (a) but represented as $-\log(I(\omega))$ along with the fluorescence spectra of the sample. The coincidence of these three spectra is remarkable. (c) Energy dependence of some other Bragg reflections and (d) the same reflections absorption corrected by the intensity of the (4 4 4) reflection. Despite of the rather large corrections imposed by the presence of a *dead layer* useful data can be retrieved and further compare with simulations as in Ref. [19]. In particular the (4 4 1) reflection contains the signature of the charge ordering and the (4 4 2) the signature of the ATS of the high temperature structure, after absorption correction.

REXS experiments on thin films allow to overcome this hurdle, provided that the physics of the thin film and of the bulk sample are alike. This is the case of $NdNiO_3$, where both thin film [22] and single crystals [23] (40 microns side) experiments on the same Bragg reflection reveal identical features although transition temperatures are very different [24].

3 Conclusions

Since the seminal Conference at Malente in 1992 we have mastered a number of issues related to REXS and one of them is the determination of charge order resulting from a metal-insulator phase transition. The process that gives rise to charge order is rather well established, instrumentation has been developed and tested (see C. Detlefs et al. in this Proceedings), data are reliable, correction are needed and should be carefully

evaluated in order to get reliable data. Very importantly, quite substantial advances in the understanding of the data are due to the availability of codes, like FDMNES, that allow to reproduce the energy spectra and to fit quantitatively the charge parameters.

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