Resonant X-Ray Diffraction Studies on the Charge Ordering in Magnetite

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Here we show that the low temperature phase of magnetite is associated with an effective, although fractional, ordering of the charge. Evidence and a quantitative evaluation of the atomic charges are achieved by using resonant x-ray diffraction (RXD) experiments whose results are further analyzed with the help of *ab initio* calculations of the scattering factors involved. By confirming the results obtained from x-ray crystallography we have shown that RXD is able to probe quantitatively the electronic structure in very complex oxides, whose importance covers a wide domain of applications.

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Known in ancient times as lodestone and used to magnetize the mariner's compass [1], magnetite (Fe_3O_4) is still today the archetype compound of a number of physical properties and applications. For instance, it is a promising candidate for the development of highly sensitive magnetoresistive devices in spin electronics. A sufficient comprehension of magnetite is mandatory in view of its applications and as a reference for similar effects in related materials. Particularly, the magnetic and magnetoelectric properties of magnetite exhibit a conspicuous anomaly at $T_V = 121$ K that still defies understanding [2]. First suggested by Verwey [3] and expected in many oxides [4,5], the low temperature phase transition in magnetite has been associated with a charge disproportion on the metal atoms sites, although a direct confirmation has never been evidenced in magnetite up to now. Theoretical predictions [6,7] have recently supported Verwey's scheme of the localization of the charge (but on a more complex pattern), and nuclear magnetic resonance [8] and Mössbauer [9] experiments are compatible with different oxidation states of the octahedral iron sites. However, direct confirmation of charge disproportionation is still lacking.

From the structural point of view, the determination of the atomic positions issued from the metal-insulator transition has challenged the scientific community ever since Verwey's seminal work [2,3]. Progress in the solution of the problem runs parallel to the development of new and sophisticated experimental techniques as well as to the implementation of refined computing codes and appropriate data analysis strategies. Despite all these technical advances, magnetite still remains a rather difficult case for conventional crystallography: the symmetry lowering ($Fd\bar{3}m \rightarrow Cc$, and $a_c \times a_c \times a_c \rightarrow \approx \sqrt{2}a_c \times \sqrt{2}a_c \times 2a_c$, with $a_c = 8.394$ Å) generates 8 and 16 nonequivalent iron sites at tetrahedral and octahedral positions, respectively, each one with its own atomic charge. However, the final structure is not yet perfectly known. Actually best refinement has been recently performed by Wright and collaborators [10] (in space group *Pmca*, with lattice parameters $\approx a_c/\sqrt{2} \times a_c/\sqrt{2}a_c \times 2a_c$). Complexity is greatly reduced in this structure model (Fig. 1), where there are 6 nonequivalent iron atoms, two in tetrahedral

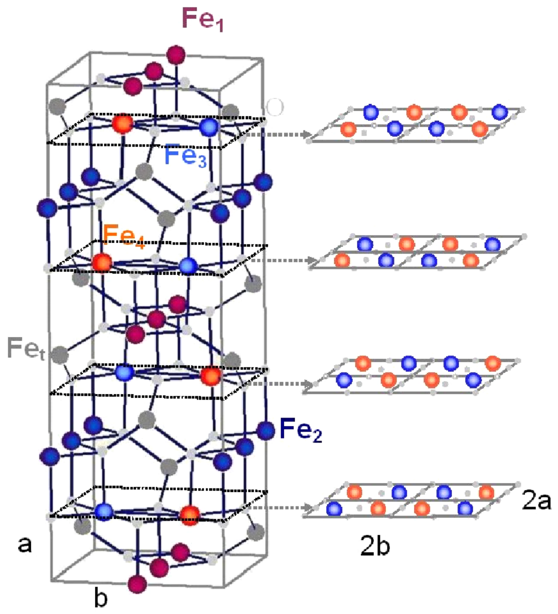

FIG. 1 (color online). (Left) A sketch of the low temperature Fe_3O_4 structure in the orthorhombic space group *Pmca*. There are six nonequivalent iron atoms, two in the tetrahedral sites (Fe_t) and four in the octahedral sites (Fe_1, Fe_2, Fe_3, Fe_4), and it is understood that charge ordering occurs at the octahedral sites. The actual structure is known to be *Cc* in a approximately $\sqrt{2}a_c \times \sqrt{2}a_c \times 2a_c$ unit cell, with 16 unequivalent Fe-sites at octahedral positions. However, no structural refinement in this space group has been successful yet. (Right) Cell doubling along the a $[\frac{1}{2}(a_c + b_c)]$ and the b $[\frac{1}{2}(a_c - b_c)]$ axis of the *Pmca* structure. The color code tags represent Fe_3 and Fe_4 positions in the settings of the *Cc* space group. This CO model has been tested and greatly improves the quality of the refinement.

sites (Fe_t) and four in octahedral sites (Fe_1, Fe_2, Fe_3 and Fe_4). Only the octahedral irons are supposed to undergo a charge ordering (CO). Whereas Fe_1 and Fe_2 are at the centers of their respective octahedra, Fe_3 and Fe_4, posses more distorted local environments, the iron atoms are slightly off center. It can also be noticed that these position shifts are responsible for the doubling of the cell along the c axis, whereas the Fe_1 and Fe_2 ordering has no effect on the cell doubled.

Resonant x-ray diffraction (RXD) is a technique where both the power of site selective diffraction and the power of local absorption spectroscopy regarding atomic species are combined to the best [11]. Reflections are recorded over some tens of electron volts around the absorption edge of the element(s) present in the material, where they show strong energy and angular dependencies. This phenomenon is due to the virtual photon absorption-emission associated with the resonant transition of an electron from a core level to some intermediate state above the Fermi level. By virtue of the dependence on the core level state energy and the three-dimensional electronic structure of the intermediate state, this technique is specially suited to study charge [12,13], orbital [14,15], or spin orderings [16], and associated geometrical distortions [17,18]. In the case of charge ordering, we exploit the fact that atoms with closely related site symmetries but with barely different charges exhibit resonances at slightly different energies. Here we show that the sensitivity of this effect allows for quantitative estimations of the charge disproportion. Opposite to fluorescence or absorption measurements, the power of diffraction relies on the capability of detecting differences that are even smaller than the inverse lifetime of the core hole level. Clearly, not all Bragg reflections are sensitive to charge ordering, and the failure in detecting CO signatures in previous RXD work on magnetite is partly related to an incomplete choice of them [19,20].

Our RXD experiments were carried out at the U.K. CRG beam line (XmaS) in the European Synchrotron Radiation Facility (Grenoble) operating at photon energies between 7060 and 7220 eV. The x-ray beam wavelength was selected by a Si(111) double crystal monochromator with an energy resolution of 0.8 eV at the photon energies of the experiment. After scattering, an analyzer crystal was used to filter out background coming from the sample (mostly fluorescence). The two samples used have been prepared using the vertical floating zone technique, with the help of an optical furnace (Crystal System, Inc. FZ-T-10000-H-VI-P-G). The Fe_3O_4 feed rods were prepared from high purity powder (Alfa Aesar 99.997%), compacted into cylindrical shape under isostatic press (up to 1200 bar). The Verwey transition was characterized by SQUID measurements and results have been given in Ref. [21]. The as-grown crystals exhibit a sharp bulk Verwey transition with $T_V = 121$ K. The scattering experiment was carried out in reflexion mode, off a $\{110\}$ surface for both samples and at 50 K.

RXD experiments must be performed on a single crystal, if a good signal-to-noise ratio is required. Traditionally one of the major difficulties of crystallographic work on magnetite has been to overcome a very strong self-absorption, twinning, extinction, and the presence of multiple scattering. These issues can be easier overcome in RXD studies than in conventional single crystal diffraction experiments. Indeed, parameter refinement in the former is carried through the analysis of the energy dependence of the photons scattered within each of the measured Bragg reflections, the absolute scale being a unrefined proportionality constant. In order to minimize the number of crystallographic domains, a magnetic field of 0.3 T has been applied parallel to one of the $[001]$ directions that uniquely defines the c direction. Multiple-scattering events are eliminated by the measurement of the energy spectra at different azimuths and crystal settings. Raw data have been plotted in Fig. 2, top panel. Finally, and more importantly, the absorption correction (Fig. 2, bottom panel) is carefully performed by using the energy dependence of the intensities of several very strong Bragg reflections as a measure of absorption. The anomalous contribution of these reflections is relatively small and can be easily computed.

To account for the uncertainty of the crystallographic structure and the fact that the charge ordering must be disentangled from the associated atomic displacements, a complete methodology was developed. It needs a very important set of experimental data, first principle simulations and the use of objective confidence factors for comparing experiment and theory [22,23]. Thus, no less than 50 reflections were recorded over an energy range of 120 eV around the Fe K edge and at $T = 50$ K. This collection of peaks is at the variance of the RXD data collected in Refs. [19,20] and use to dismiss CO in Fe_3O_4. Thirty-two reflections were kept for the optimization of the parameters, 12 were reflections indexed in the Cc cell (not used in this refinement), and 6 strong reflections were used for normalization purposes. The calculations are performed using the state-of-the-art code FDMNES [24,25]. It calculates the final states and the resulting structure factors with first principal theories. In the present study, the multiple-scattering theory was used. This code has already been efficient in the simulation of different spin, orbital, charge, or geometrical ordering phenomena [26,27].

Trial calculations were performed for the two low temperature phase structures proposed by Iizumi *et al.* [28]. As expected, calculations in the noncentrosymmetric space group ($Pmc2_1$) produced a modest agreement with the experimental data (not shown). Calculations in the $Pmca$ structure produces a far better agreement, and in the following we have used the recent results of Ref. [10] with the charge occupancies on the $3d$ iron sites as the only adjustable parameters. From the local structures we conjecture that charge ordering can be characterized by two different

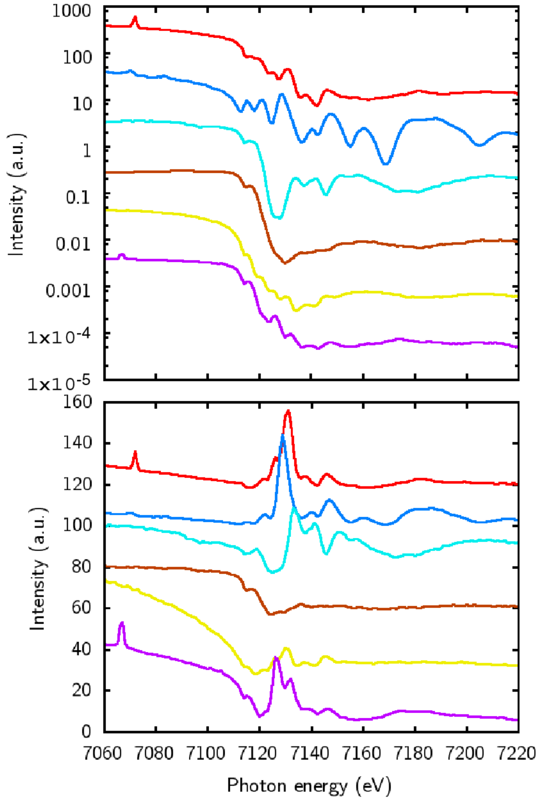

FIG. 2 (color online). (Top panel) Energy variation of the intensities at the peak for a number of Bragg reflections around the Fe K edge and at $T = 50$ K. From top to bottom, the reflections are $(\bar{4}\,4\,1)$, $(\bar{4}\,4\,2)$, $(\bar{4}\,4\,3)$, $(\bar{4}\,4\,4)$, $(\bar{4}\,4\,5)$, and $(\bar{3}\,3\,3/2)$. Reflections are indexed according to the Miller indices of the high temperature cubic phase. Data are completely reproducible between the two studied samples. The small peaks at around 7070 eV in the scans of the $(\bar{4}\,4\,1)$ and $(\bar{3}\,3\,1.5)$ reflections are multiple-scattering events that can be shifted in energy by a slight change in the azimuth angle. The log scale allows one to appreciate the quality of the data, mainly above the edge. (Bottom panel) The same reflections corrected from absorption. Actual intensities have been normalized so as to fit into the graph.

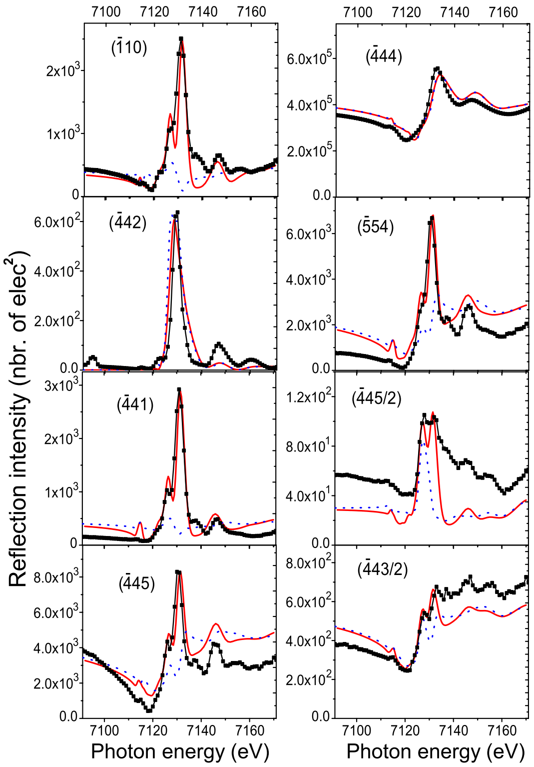

FIG. 3 (color online). Some of the experimental and calculated resonant x-ray diffraction peak spectra in Fe_3O_4 at $T = 50$ K. Experimental data have been corrected for absorption. Shown are the experimental data (black dots), the calculated spectra with (red line) and without (blue dots) charge ordering. Some reflections such as the $(\bar{1}\,1\,0)$ and the $(\bar{4}\,4\,1)$ clearly display the *derivative effect* (see text) and are therefore very sensitive to the CO. Some others, as the $(\bar{4}\,4\,2)$, exhibit a line shape that does not arise from the charge ordering. It is an extinct Bragg reflection of cubic phase that displays features related to the anisotropy of the Fe-form factors [17,18]. Strong reflections, such as the $(\bar{4}\,4\,4)$, were used for normalization purposes. Half-integer reflections, such as $(\bar{4}\,4\,5/2)$, are sensitive to the charge difference between Fe_3 and Fe_4. Reflections are indexed according to the high temperature cubic phase settings.

charge disproportions, δ_{12} and δ_{34}, between the centered Fe_1 (charge state represented as $Fe^{+(2.5-\delta_{12})}$) and Fe_2 ($Fe^{+(2.5-\delta_{12})}$) sites and the off-centered Fe_3 ($Fe^{+(2.5-\delta_{34})}$) and Fe_4 ($Fe^{+(2.5-\delta_{34})}$) sites, respectively. Tests on other orderings, including the tetrahedrally iron coordinated or other combinations of octahedral iron atoms, have systematically yielded rather poor confidence factors.

The most important result is that a significant improvement of the data fitting is achieved when an explicit CO is introduced (Fig. 3). Reflections such as $(\bar{4}\,4\,1)$ are highly sensitive to the magnitude of δ_{12}. All of them exhibit a double structure around 7126–7131 eV, which can be taken as a signature of the charge ordering phenomenon as seen by RXD. They are a clear example of the *derivative line shape*, characteristic of CO as likewise observed in other compounds [13,14]. Indeed, for a specific charge pattern and the reflections under consideration, the partial structure factor associated with oppositely charged iron atoms almost cancel. The optimization of the parameters at the Fe_1-Fe_2 sites gives a $\delta_{12} = 0.12 \pm 0.025$ electrons which corresponds to a shift of the absorption edge by 0.9 eV. This result is particularly robust and remains unchanged whether a large or a small data basis is used in the refinement. The effect of δ_{34} is contained in half-integer reflections and even more in reflections indexed in the *Cc* cell. Interestingly, and despite of the lack of knowledge about the actual lattice distortion yielding a *Cc* unit cell, the charge can be refined in this space group (see Fig. 1, right, for the charge distribution compatible with the *Cc* symmetry) by using reflections indexed for the *Pmca* symmetry. The value of δ_{34} is associated with a large

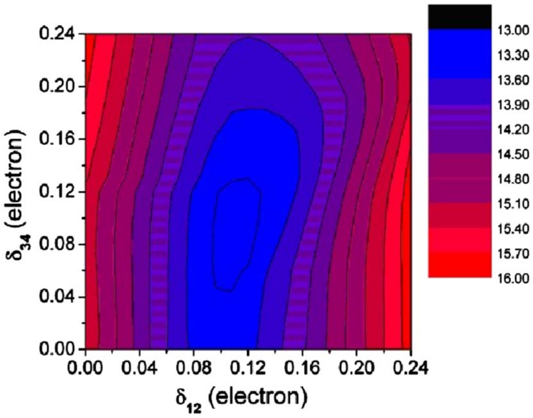

FIG. 4 (color online). Isovalue of the confidence factor, the metric D_1 of Philip and Rundgren [22]. The best agreement is obtained for $\delta_{12} = 0.12 \pm 0.025$ electrons and $\delta_{34} = 0.10 \pm 0.06$ electrons. It corresponds to the 5.38, 5.62 and 5.40, 5.60 charge occupancies of Fe_1 to Fe_4, respectively.

uncertainty: 0.10 ± 0.06 electrons, most probably reflecting the fact that each of the Fe_3 and Fe_4 positions gives rise to four nonequivalent sites, being not considered in this work. To obtain a precise estimate of δ_{34} would require a concomitant knowledge of the atomic displacements producing the *Cc* structure and the use of reflections indexed in the $\sqrt{2}a_c \times \sqrt{2}a_c \times 2a_c$ unit cell. Figure 4 represents the confidence factor plotted in the form of a contour plot. All the refined charges are in very good agreement with the theoretical predictions using local density approximation calculations [6,7]. The contours run nearly parallel to the δ_{34} axis meaning that there is little correlation between both charge orderings.

In this work we have solved the long standing controversy of whether actual charge ordering develops at the octahedral Fe sites of Fe_3O_4 as a result of the metal-to-insulator (Verwey) phase transition. Several conclusions can be drawn out. First, we have shown that significant, noninteger charge localization occurs at the metal sites in the low temperature phase of magnetite. This result is robust and independent of the uncertainties of the actual crystallographic structure. In view of the short interaction time of the photons, $\approx 10^{-16}$ s, we conclude that the ordering is purely static. Second, the results of our experiment and additional calculations considering the magnitudes of the charge are in good overall agreement with those resulting from the bond valence sum method. Third, CO at Fe_1 and Fe_2 sites gives rise to a $[001]c$ charge modulation whereas CO at Fe_3 and Fe_4 originate the $[00\frac{1}{2}]c$ ordering, and both are relatively uncoupled. Fourth, the magnitude of the charge is in agreement with the several band structure calculations [6,7], which implies that the phase transition, at least the ordered part, can be explained under electronic considerations alone.

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Note added.—Recently, we became aware of a RXD paper [29] where evidence for the CO has been found, thus supporting our results.

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