Critical reexamination of resonant soft x-ray Bragg forbidden reflections in magnetite


Department of Condensed Matter Physics and Materials Science, Brookhaven National Laboratory, Upton, New York 11973-5000, USA

Équipe de Physique des Surfaces et Interfaces, Institut de Physique de Rennes UMR UR1-CNRS 6251, Université de Rennes 1, F-35042 Rennes Cedex, France

Department of Physics, University of Durham, South Road, Durham DH1 3LE, United Kingdom

Institut Néel, CNRS and Université Joseph Fourier, BP 166, F-38042 Grenoble Cedex 09, France

European Synchrotron Radiation Facility, BP 220, F-38043 Grenoble Cedex 9, France

Department of Physics, Eindhoven University of Technology, NL-5600 MB Eindhoven, The Netherlands

Received 19 November 2008; revised manuscript received 10 April 2009; published 6 May 2009

Magnetite, Fe$_3$O$_4$, displays a highly complex low-temperature crystal structure that may be charge and orbitally ordered. Many of the recent experimental claims of such ordering rely on resonant soft x-ray diffraction at the oxygen K and iron L edges. We have reexamined this system and undertaken soft x-ray diffraction experiments on a high-quality single crystal. Contrary to previous claims in the literature, we show that the intensity observed at the Bragg forbidden (001)$^-$ reflection can be explained purely in terms of the low-temperature structural displacements around the resonant atoms. This does not necessarily mean that magnetite is not charge or orbitally ordered but rather that the present sensitivity of resonant soft x-ray experiments does not allow conclusive demonstration of such ordering.

DOI: 10.1103/PhysRevB.79.201102

PACS number(s): 71.27.+a

In many transition-metal oxides, the spatial localization of electrons on certain sites, the so-called charge ordering (CO), has been used to explain some of their more intriguing ground-state properties. For example, charge ordering has been invoked to describe phase transitions in some manganites,

Critical reexamination of resonant soft x-ray Bragg forbidden reflections in magnetite


Department of Condensed Matter Physics and Materials Science, Brookhaven National Laboratory, Upton, New York 11973-5000, USA

Équipe de Physique des Surfaces et Interfaces, Institut de Physique de Rennes UMR UR1-CNRS 6251, Université de Rennes 1, F-35042 Rennes Cedex, France

Department of Physics, University of Durham, South Road, Durham DH1 3LE, United Kingdom

Institut Néel, CNRS and Université Joseph Fourier, BP 166, F-38042 Grenoble Cedex 09, France

European Synchrotron Radiation Facility, BP 220, F-38043 Grenoble Cedex 9, France

Department of Physics, Eindhoven University of Technology, NL-5600 MB Eindhoven, The Netherlands

Received 19 November 2008; revised manuscript received 10 April 2009; published 6 May 2009

Magnetite, Fe$_3$O$_4$, displays a highly complex low-temperature crystal structure that may be charge and orbitally ordered. Many of the recent experimental claims of such ordering rely on resonant soft x-ray diffraction at the oxygen K and iron L edges. We have reexamined this system and undertaken soft x-ray diffraction experiments on a high-quality single crystal. Contrary to previous claims in the literature, we show that the intensity observed at the Bragg forbidden (001)$^-$ reflection can be explained purely in terms of the low-temperature structural displacements around the resonant atoms. This does not necessarily mean that magnetite is not charge or orbitally ordered but rather that the present sensitivity of resonant soft x-ray experiments does not allow conclusive demonstration of such ordering.

DOI: 10.1103/PhysRevB.79.201102

PACS number(s): 71.27.+a

In many transition-metal oxides, the spatial localization of electrons on certain sites, the so-called charge ordering (CO), has been used to explain some of their more intriguing ground-state properties. For example, charge ordering has been invoked to describe phase transitions in some manganites,

Critical reexamination of resonant soft x-ray Bragg forbidden reflections in magnetite


Department of Condensed Matter Physics and Materials Science, Brookhaven National Laboratory, Upton, New York 11973-5000, USA

Équipe de Physique des Surfaces et Interfaces, Institut de Physique de Rennes UMR UR1-CNRS 6251, Université de Rennes 1, F-35042 Rennes Cedex, France

Department of Physics, University of Durham, South Road, Durham DH1 3LE, United Kingdom

Institut Néel, CNRS and Université Joseph Fourier, BP 166, F-38042 Grenoble Cedex 09, France

European Synchrotron Radiation Facility, BP 220, F-38043 Grenoble Cedex 9, France

Department of Physics, Eindhoven University of Technology, NL-5600 MB Eindhoven, The Netherlands

Received 19 November 2008; revised manuscript received 10 April 2009; published 6 May 2009

Magnetite, Fe$_3$O$_4$, displays a highly complex low-temperature crystal structure that may be charge and orbitally ordered. Many of the recent experimental claims of such ordering rely on resonant soft x-ray diffraction at the oxygen K and iron L edges. We have reexamined this system and undertaken soft x-ray diffraction experiments on a high-quality single crystal. Contrary to previous claims in the literature, we show that the intensity observed at the Bragg forbidden (001)$^-$ reflection can be explained purely in terms of the low-temperature structural displacements around the resonant atoms. This does not necessarily mean that magnetite is not charge or orbitally ordered but rather that the present sensitivity of resonant soft x-ray experiments does not allow conclusive demonstration of such ordering.

DOI: 10.1103/PhysRevB.79.201102

PACS number(s): 71.27.+a

In many transition-metal oxides, the spatial localization of electrons on certain sites, the so-called charge ordering (CO), has been used to explain some of their more intriguing ground-state properties. For example, charge ordering has been invoked to describe phase transitions in some manganites,

Critical reexamination of resonant soft x-ray Bragg forbidden reflections in magnetite


Department of Condensed Matter Physics and Materials Science, Brookhaven National Laboratory, Upton, New York 11973-5000, USA

Équipe de Physique des Surfaces et Interfaces, Institut de Physique de Rennes UMR UR1-CNRS 6251, Université de Rennes 1, F-35042 Rennes Cedex, France

Department of Physics, University of Durham, South Road, Durham DH1 3LE, United Kingdom

Institut Néel, CNRS and Université Joseph Fourier, BP 166, F-38042 Grenoble Cedex 09, France

European Synchrotron Radiation Facility, BP 220, F-38043 Grenoble Cedex 9, France

Department of Physics, Eindhoven University of Technology, NL-5600 MB Eindhoven, The Netherlands

Received 19 November 2008; revised manuscript received 10 April 2009; published 6 May 2009

Magnetite, Fe$_3$O$_4$, displays a highly complex low-temperature crystal structure that may be charge and orbitally ordered. Many of the recent experimental claims of such ordering rely on resonant soft x-ray diffraction at the oxygen K and iron L edges. We have reexamined this system and undertaken soft x-ray diffraction experiments on a high-quality single crystal. Contrary to previous claims in the literature, we show that the intensity observed at the Bragg forbidden (001)$^-$ reflection can be explained purely in terms of the low-temperature structural displacements around the resonant atoms. This does not necessarily mean that magnetite is not charge or orbitally ordered but rather that the present sensitivity of resonant soft x-ray experiments does not allow conclusive demonstration of such ordering.

DOI: 10.1103/PhysRevB.79.201102

PACS number(s): 71.27.+a

In many transition-metal oxides, the spatial localization of electrons on certain sites, the so-called charge ordering (CO), has been used to explain some of their more intriguing ground-state properties. For example, charge ordering has been invoked to describe phase transitions in some manganites,
The sample of Fe$_3$O$_4$ was cut with a $a$-axis of 5.944 Å, $b$-axis of 16.775 Å, and $c$-axis of 90.2363°. This structure is close to the orthorhombic $Pmca$ structure as the $a$-axis is 5.925 Å. In this orthorhombic setting, the cubic (001)$_{\text{o}}$ reflection becomes the orthorhombic (001)$_{\text{n}}$. The sample of Fe$_3$O$_4$ was cut with a [001]$_{\text{n}}$ surface normal and polished with 0.1 μm diamond paste. It was then mounted on a SmCo magnet, providing a field of 0.3 T parallel to the surface normal. This field defines a unique $c$-axis so that no dislocations are present in the structure. The sample was then cooled to a base temperature of 30 K, with an energy of 706.5 eV. Such behavior arises from the very large self-absorption caused by the strong Fe $L_3$ resonance, leading to a total loss in the observed signal. The width of the diffraction peak as a function of energy as shown in the top panel of Fig. 2 confirms this. The peak width is broader than that found at the oxygen $K$ edge and tracks the calculated absorption (dashed line) indicating that the change in width arises from the increased absorption and consequently reduced penetration depth. Finally, Fig. 3 shows the temperature dependence of the integrated intensity of the (001)$_{\text{n}}$ reflection measured at both the iron $L_3$ and oxygen $K$ edges. The data were collected by performing rocking scans of the sample angle, $\theta$, at each temperature. The signal at both edges was found to be constant up to a temperature of $\approx$125 K above which no intensity is observed.

We now turn to our resonant scattering simulation. We have used the FDMNES program in the multiple-scattering mode. The results of these simulations are shown in Figs. 1 and 2 for the oxygen $K$ and iron $L$ edges respectively. In order to calibrate to the experimentally obtained data with the FDMNES simulations, the calculated absorption was com-

![Figure 1](image1.png)

**FIG. 1.** (Color online) The incident photon energy dependence of the (001)$_{\text{o}}$ reflection in Fe$_3$O$_4$ close to the oxygen $K$ edge (red circles). The solid black line represents ab initio calculations of the scattered intensity assuming structural distortions and no charge nor orbital order. The inset shows a scan along the [001]$_{\text{n}}$ direction through the (001)$_{\text{n}}$ reflection is shown (red circles); the solid line is a fit to a Lorentzian-squared line shape.

![Figure 2](image2.png)

**FIG. 2.** (Color online) Top panel: measured total electron yield (x-ray absorption spectrum) at 27 K (red dashed line) and calculated absorption spectrum (solid black line) through the Fe $L_{2,3}$ edges. The solid black line shows ab initio calculations of the resonant signal. The red line shows the incident photon energy scan at constant incident energy is included in the top panel for comparison with the experimental and calculated absorption (blue diamonds).
pared with the sample absorption measured by total electron yield at the oxygen K edge. Our simulation reproduces well the main experimental features, including the energy gap of about 10 eV between the RXS signal and the main oxygen absorption edge, as well as the energy width of the peak.

In this specific case, there are eight inequivalent oxygen sites of 4d Wyckoff symmetry in the Pmca space group. Considering only the oxygen atoms which dominate at this energy, the structure factor of the (001)$_o$ reflection is

$$S(001)_o = \sum_{j=1,\ldots,8} 2f_j(1 - \hat{m}_j \cos(2\pi w_j)),$$

where $f_j$ is the atomic scattering amplitude, $(j=1,\ldots,8)$ labels the inequivalent sites, $w_j$ is the fractional coordinate of the $j$th oxygen atom in the $c$ direction, and $\hat{m}_j$ is the mirror plane in the $b$ direction of the Pmca setting. Using the local mirror symmetry $\hat{m}_j$ of the 4d sites, we find that $f_j \approx Q_{xy}^{j\,\text{c}}$, the electric quadrupole matrix element. In the monoclinic $P2_1/c$ setting, the $\hat{m}_j$ symmetry is lost and a further contribution $f_j \approx Q_{yz}^{j\,\text{c}}$, appears. This can be shown to be negligible since it is proportional to the small angular distortion, $\beta \neq 90^\circ$, from the orthorhombic Pmca structure. Upon evaluating the structure factor $S$ we can conclude that almost all the scattered intensity comes from the sum of the quadrupoles $Q_{yz}$ at oxygen sites $O_1$ and $O_2$ only. That is $S(001)_o = Q_{yz}^{o_1} + Q_{yz}^{o_2}$ in the high-temperature phase $Q_{yz}^{o_1} = -Q_{yz}^{o_2}$ due to the $C_{2\hat{z}}$ screw axis of the high-temperature $Fd\bar{3}m$ space group, and therefore their sum is zero. Below the Verwey transition, the unequal atomic displacements of the $O_1$ and $O_2$ oxygen sites from their high-temperature positions give a finite signal even if $Q_{yz}^{o_1} = -Q_{yz}^{o_2}$. However, this signal is tiny because of the very small displacement, and has an expected amplitude of $\approx 10^{-4} \times |Q_{yz}^{o_2}|$. In contrast, a much bigger amplitude might be expected if the surrounding iron tetrahedra are distorted making $Q_{yz}^{o_1} \neq -Q_{yz}^{o_2}$.

To investigate which of these contributions to be the most significant we have performed several numerical calculations in which the tetrahedral or octahedrally coordinated iron atoms, and/or the oxygens were in turn placed in their high-temperature positions, with the rest of the cluster held in their low-temperature positions. By this method, we found that the main contribution to the signal comes from the $O_2$ position (70% of the total): in fact $Q_{yz}^{o_2}$ does not change much when the iron sites move from the high-temperature to the low-temperature positions while $Q_{yz}^{o_1}$ varies by about 100%. This dominant change is due in particular to the displacement of the octahedral iron atoms surrounding the $O_2$ site. The iron sites belong to the Fe B3 sites, in the notation of Ref. 20, and undergo the strongest distortion when passing from the high-temperature to the low-temperature phase: the Fe$_{\text{B3}}$–O$_2$ distance changes from 2.06 to 1.96 Å, about a 5% contraction. Therefore the O K edge signal is mainly determined by the hybridization of $2p$ oxygen orbitals at $O_2$ sites with 3d iron orbitals belonging to octahedral Fe B3 sites.

The fact that we can explain the signal through these atomic displacements contradicts the interpretation of the signal at (001)$_o$ in Ref. 13 that explicitly excluded a structural origin to the (001)$_o$ reflection at the oxygen K edge. In particular, the arguments made by the authors of Ref. 13, for the assignment of their signal to charge and orbital orders due to its polarization dependence, are reproduced in our calculations based solely on structural distortions. This makes clear that invoking charge or orbital ordering to explain the detection of this superlattice reflection is unnecessary and potentially misleading.

This same procedure was then used to evaluate the resonant signal of the (001)$_o$ reflection at Fe $L_{2,3}$-edges, as shown in Fig. 2. The calibration between our experimental data and the FDMNES simulation was set by comparison of the calculated absorption with the as measured by total electron yield.

We can repeat the same analysis as performed at the oxygen K edge for the data at the iron $L_{2,3}$ edges. The results of the FDMNES simulation are shown in Fig. 2. In the top panel a comparison between the measured and calculated absorptions is shown, while the bottom panel shows the comparison between the integrated intensity of the (001)$_o$ reflection as a function of incident photon energy and our simulation.

In the Pmca setting there are six inequivalent groups of iron atoms, with two groups of tetrahedral iron sites (A1 and A2, following the notation of Ref. 20), and four groups of octahedral iron sites (B1, B2, B3, and B4), each group containing four iron atoms. A1, A2, B3, and B4 sites have a local $\hat{m}_3$ symmetry (4d Wyckoff site) so that the same considerations discussed above for the structure factor at the oxygen K edge are still valid. The only signal that can be measured for these ions is due to the $\hat{Q}_{yz}^{j\,\text{c}}$, this time projected on the corresponding iron sites $j$. The B2 site has a $C_{2\hat{z}}$ local symmetry (4e Wyckoff site) and the two groups of two ions that contribute in antiphase at the (001)$_o$ are related by inversion symmetry, so their total contribution equal to zero. Finally the B1 sites, with local inversion symmetry (4b Wyckoff site), also contribute with the quadrupole component $\hat{Q}_{yz}^{j\,\text{c}}$. When we numerically compare the separate contributions of the A1, A2, B1, B3, and B4 sites, we find that the intensity from the B1 site is smaller by a factor of 500 relative to the contribution from the B4 site. We can conclude therefore that
the dominant contribution of the intense low-energy peak seen in the calculations at 708.5 eV is from the iron atoms sitting at the B4 sites. The tetrahedral A sites and the octahedral B3 site contribute mainly to the smaller shoulder at higher energy, and the fact that they have opposite amplitudes gives rise to the local minimum at 710 eV. Therefore all the experimentally detected signal comes from the B4 sites (nominally Fe2+). This is in keeping with some previous results obtained with rather different approaches which concluded that the low-energy part of $L_3$ spectrum (around 707 eV) is mainly determined by the $t_{2g}$ states of the nominally divalent iron ions.\textsuperscript{7,21} However there is an important difference between the work presented here and atomic-multiplet-based calculations such as those reported in Refs. 14 and 21. By focusing on the orbital occupancy in a ionic model, these latter authors have neglected the important structural differences that exist between sites such as B1 and B4 (that are otherwise equivalent where formal charge is concerned, both being formally Fe2+). The fact that we calculated their relative contribution to the total signal in the ratio 1:500 proves such a difference.

The similar temperature dependence shown in Fig. 3 can now be explained as a natural consequence of the signals at the oxygen $K$ edge and iron $L$ edges both measuring the same order parameter. As discussed above we argue that this order parameter is structural distortions associated with the structural phase transition from the $Fd\bar{3}m$ high-temperature structure to the low-temperature $P2_1/c$ structure.

In conclusion, we have shown that the (001)$_o$ reflection of Fe$_3$O$_4$ is sensitive to the local displacements around the resonant ion at both the oxygen $K$ and iron $L$ edges. The electronic anisotropy arising from the crystal distortions are sufficient to explain the origin of the scattered signals. It is clear that further work is required to ascertain the ratio in quantitative terms between any signal from charge or orbital ordering and the contribution from structural effects. It is clear that further studies will require more definitive structural information that is still unknown. At the oxygen $K$ edge, the signal is determined by the hybridization of O 2$p$ orbitals of the four $O_2\bar{8}$ atoms with the $B3$ Fe 3$d$ orbitals (nominally Fe$^{3+}$). At the iron $L_3$ edge, in contrast, the resonant x-ray scattering is mainly sensitive to the contribution of Fe 3$d$ orbitals from B4 sites (nominally Fe$^{2+}$).

We believe that our experiments and their analysis, while not contributing directly to the fashionable issue of charge ordering and orbital ordering, will help nonetheless understanding the structural transition of Fe$_3$O$_4$ below the Verwey temperature, at the same time indicating how a proper analysis of x-ray resonant scattering should, in our opinion, be conducted.

Work at Brookhaven was supported by the (U.S.) Department of Energy under Contract No. DE-AC02-98CH1-886. S.B.W would like to thank J. P. Hill for critical reading of the manuscript and S. R. Bland for helpful discussions. P.D.H. wishes to acknowledge EPSRC-GB for support.