Reexamination of the Temperature Dependences of Resonant Reflections in Highly Stoichiometric Magnetite

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We have studied the temperature dependences of the so-called charge and orbital ordering reflections in the neighborhood of the Verwey transition by means of resonant x-ray scattering at the Fe K and L edges on a high purity single crystal of magnetite. Contrary to recently published results [J. E. Lorenzo *et al.*, Phys. Rev. Lett. **101**, 226401 (2008)], we show that all the reflections studied disappear simultaneously at the Verwey transition for both edges, on and off resonance. This means that there is no correlation between the Verwey (123.5 K) and the spin-reorientation (130 K) transitions and that the resonant reflections are driven by the lattice distortions.

The Verwey transition in magnetite (Fe_3O_4) is one of the most studied examples of a metal-to-insulator phase transition in mixed valence oxides. Verwey originally interpreted it as a charge ordering (CO) transition [1]. In his model, above the Verwey temperature, $T_V \approx 123$ K, the hopping of valence electrons on the spinel octahedral-site iron sublattice is responsible for the metallic conductivity. In the insulating phase, spatial localization of these valence electrons on the octahedral sites gives rise to an ordered pattern of Fe^{3+} and Fe^{2+} ions in successive (001) planes (cubic notation). Neutron diffraction demonstrated that the symmetry lowering predicted by Verwey's CO model cannot be correct [2]. After 60 years of intensive study, Verwey's hypothesis has survived despite the specific site ordering remains in doubt [3].

Experimental evidences against the Verwey model were found recently. ^{57}Fe NMR measurements [4,5] have identified 16 different octahedral site signals expected from the low-temperature Cc phase, in disagreement with the Verwey CO model of only two ionic species. Resonant x-ray scattering (RXS) studies at the Fe K edge found that the charge disproportion between the formal valences in the low-temperature phase of magnetite should be at maximum 25% for any kind of ordering [6] and 10% for (001) periodicity [7]. The existence of CO and orbital ordering (OO) in magnetite is a matter of debate in recent literature [8–18]. From the theoretical side, LDA + U (local density approximation plus the multiorbital mean-field Hubbard model) band structure calculations predict both charge ordering and an associated t_{2g} orbital ordering on the octahedral Fe^{2+} sublattice [8,9]. The experimental situation is much more confusing. This is in part due to the fact that the original concept of CO has been distorted to account for very small charge disproportionation [3,10]. Moreover, magnetite is a very difficult system, either regarding the chemical purity (oxygen stoichiometry) or due to the complexity of the low-temperature structure—a still

unsolved structure with 224 atoms/unit cell. A structural approximation from synchrotron powder diffraction data given by Wright *et al.* [11] consists of a $P2/c$ cell, where the octahedral Fe_O atoms are split into four nonequivalent sites with valences $Fe_{O1} = 2.39$, $Fe_{O2} = 2.61$, $Fe_{O3} = 2.59$, and $Fe_{O4} = 2.41$. The RXS study at the Fe K edge by Nazarenko *et al.* [12] concluded that there is a charge disproportion of ± 0.12 electrons between the Fe_{O1} and Fe_{O2} sites and ± 0.1 electrons between the Fe_{O3} and Fe_{O4} sites in agreement with Wright *et al.* [11]. However, the same authors have just corrected this CO pattern as no ordering between the Fe_{O3} and Fe_{O4} sites is found [13]. On the other hand, Goff *et al.* [14] claimed a significant charge disproportionation ($\sim 46\%$) in octahedral sites after refining anomalous powder x-ray diffraction patterns. Regarding the OO, RXS measurements of the forbidden $(0\ 0\ \frac{1}{2})$ reflection [15] at the O K edge that probes the O $2p$ states were interpreted as a proof for CO and OO on the basis of the p-d hybridization [15]. Using RXS at the Fe $L_{2,3}$ edges, Schlappa *et al.* [16] also concluded a CO of the octahedral Fe ions due to the appearance of the (001) reflection, and a t_{2g} OO on the octahedral Fe^{2+} ions owing to the existence of the $(0\ 0\ \frac{1}{2})$ reflection. This result seems to give experimental support for the LDA + U calculations, but the proposed orbital arrangement does not give contribution for $(0\ 0\ \frac{1}{2})$ reflection [8,9].

The recent RXS experiment of Lorenzo *et al.* [18] at the Fe K edge, claiming the observation of purely electronic orderings in magnetite decoupled from lattice distortions, reinforces the long-standing controversy of whether or not the Verwey transition results from charge and orbital ordering. They showed different temperature dependencies of charge, orbital, and lattice orderings, concluding that CO and OO transition does not occur at T_V but at the temperature of spin reorientation, $T_K = 130$ K, about 9 K above the Verwey transition they observe. This interpretation relies on the assumption that the $(0\ 0\ \frac{1}{2})$ forbidden reflec-

tion is due to 3d orbital ordering and that the (0 0 odd) reflections reflect a nearly pure CO effect on resonance while they would reflect the lattice distortion order out of resonance. This is highly surprising by the implications on both the Verwey transition and RXS theory. First, the Verwey transition has been characterized in the past by a unique phase transition in highly pure magnetite (as demonstrated by the temperature dependence of the heat capacity, electrical conductivity, and magnetic measurements) [3]. The results of that work suggest that charges localize at T_k but magnetite remains metallic down to T_V; i.e., the electronic localization has no effect in the electrical conductivity. Moreover, the heat capacity does not show any anomaly at T_k, where the electronic ordering would take place, indicating the same entropy for both phases, ordered and disordered. Concerning the consequences on RXS, the resonant reflections would be allowed between T_V and T_K in the Fd-$3m$ cell when the RXS theory for the cubic symmetry does not predict them [19]. Finally, these results are in contradiction to those found in the soft RXS studies [15,16].

In this work, we reexamine the so-called OO and CO reflections of magnetite in the neighborhood of T_V performing a detailed RXS experiment on a highly stoichiometric single crystal. Our results show that these reflections disappear simultaneously at the Verwey temperature ($T_V = 123.5$ K), thereby indicating that the previously reported phenomenology [18] cannot be generally ascribed to the Verwey transition. Moreover, the study of the magnetization shows that the magnetic anisotropy indeed disappears at about 130 K, indicating that there is no correlation between the spin reorientation and the proposed pure electronic CO and OO.

Magnetite was prepared by using high purity Fe_2O_3 (99.999%). The oxide was fired at 1200 °C for 24 h in a CO_2/CO (96/4) atmosphere. The powders were ground pressed into rods and sintered at 1400 °C for 24 h. Single crystals were grown from the rods in the same atmosphere by using the floating zone [20]. X-ray powder diffraction of the crushed crystals guaranteed the phase purity. The saturation magnetization at 5 K is 4.11μ_B and T_V is 123.5 K with a narrow transition width, a good indication that our sample is homogeneous and nearly ideal oxygen stoichiometry [3]. A large crystal was cut with the [001] cubic direction as the surface normal and polished to a flat, shiny surface. A small sphere of the same ingot (diam = 4.3 mm) was used for magnetic measurements. RXS experiments were carried out at the ESRF, Grenoble, France. Hard x rays (Fe K edge) were monochromatized by a Si(111) double crystal (energy resolution of 0.8 eV), and a MgO (222) analyzer crystal was used for polarization analysis on the ID20 beam line. Resonant soft-x-ray diffraction experiments were conducted on the ID08 beam line. The energy resolution is ~800 meV at 710 eV. Magnetic measurements were successively performed on the Fe_3O_4 spherical sample oriented along the [001] and

[111] directions, respectively, by means of a commercial SQUID magnetometer.

Figure 1 shows the temperature dependence of the ac initial magnetic susceptibility of the Fe_3O_4 sphere oriented in the [001] direction (upper panel) and the comparison of the magnetization curves between [001] and [111] directions in the neighborhood of T_V (lower panel). The ac susceptibility shows a sharp discontinuity at T_V (123.5 K) with a very narrow width and a small kink at about 129 K. Magnetization curves exhibit the continuous exchange of the easy magnetization axis from [111] to the [001] direction on cooling across T_V. At 129 K, the two magnetization curves superimpose, indicating that the K_1 anisotropic constant becomes zero. Below 129 K, the easy magnetization axis is slightly changing to the [001] direction, but the two curves are nearly undistinguishable. At the onset of the Verwey transition, the easy magnetization axis is clearly along the [001] direction [21].

Figure 2 shows the energy dependence of some characteristic resonant reflections as measured, i.e., without self-absorption correction.

(i) The (001) reflection was measured at both the Fe K [Fig. 2(a)] and the Fe L_1 [Fig. 2(c)] edges. At the Fe K edge, the (001) reflection is only detectable in the σ-σ' channel. The spectrum shows a strong maximum at the Fe K threshold ($E = 7.119$ keV) and a second resonance at
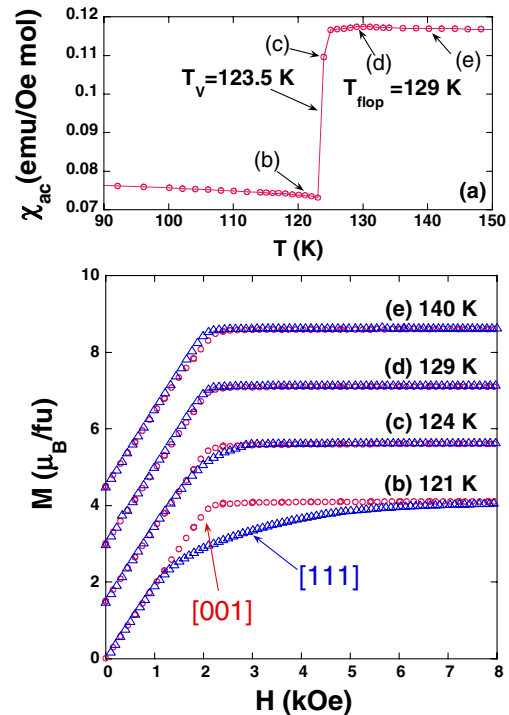

FIG. 1 (color online).   Upper panel: Temperature dependence of the initial ac magnetic susceptibility of magnetite, showing the sharp discontinuity at $T_V = 123.5$ K, $\Delta T = 1$ K. Lower panel: Magnetization versus magnetic field at fixed temperatures in the neighborhood of the Verwey transition, showing the change of easy magnetization axis from the [111] (above T_V) to the [001] (below T_V) crystallographic directions.
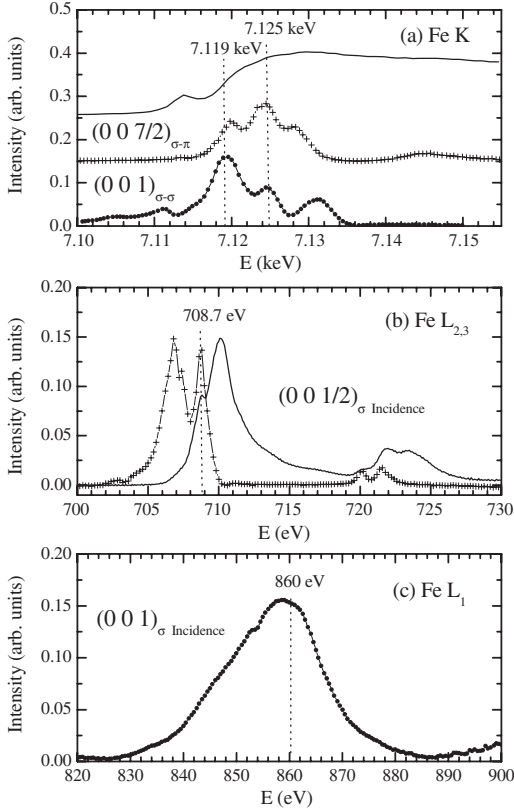
FIG. 2.   (a) The energy dependence of the intensities for the (001) and $(0\,0\,\frac{7}{2})$ reflections compared with the fluorescence spectrum around the Fe K edge and at $T = 60$ K. (b) The energy dependence of the $(0\,0\,\frac{1}{2})$ reflection recorded over the Fe $L_{2,3}$ edges at 30 K (crosses). For comparison, the total electron yield absorption spectrum (solid line) is shown in the same energy scale. (c) The energy dependence of the (001) reflection recorded over the Fe L_1 edge at 30 K.

7.125 keV, corresponding to the white line in the fluorescence spectrum. Compared to the K edge, the resonance over the L_1 edge shows much less structure due to the shorter L_1 core-hole lifetime. The (001) reflection is permitted by symmetry in the low-temperature $P2/c$ cell. The strong enhancement of the intensity at the Fe absorption edges is a consequence of electronic and structural differences among the Fe sites along this direction, due to the structural change at T_V. In the model by Wright *et al.* [11], it originates from the different anomalous atomic scattering factors of the Fe_{O1} and Fe_{O2} octahedral sites. However, the previous study [18] interpreted this resonance as a nearly pure CO effect.

(ii) The $(0\,0\,\frac{7}{2})$ reflection was measured at the Fe K edge [Fig. 2(a)]. RXS intensity is observed only in the σ-π' channel at resonance, confirming that this is a forbidden reflection in the low temperature phase. The spectrum shows a three-peak structured resonance nearly at the same energies as the (001) reflection. The energy dependence of the scattered intensity of the counterpart $(0\,0\,\frac{1}{2})$ reflection was also measured at the Fe $L_{2,3}$ edges

[Fig. 2(b)], which probe directly the Fe empty states with d symmetry. The spectrum has a double-peak structure at energies corresponding to the L_3 and L_2 absorption edges. The shape of this spectrum is similar to that reported by Schlappa *et al.* in a thin layer [16], which shows a sharp resonance at 708.4 eV with a shoulder at the L_3 threshold and two maxima at 720 and 721.4 eV at the L_2 one. The main difference in the L_3 part between both spectra is due to the self-absorption effect in the bulk single crystal that strongly reduces the intensity of the peak at 708.7 eV. Some authors proposed that these $(0\,0\,\frac{2n+1}{2})$ reflections are caused by the t_{2g} OO of the octahedral Fe^{2+} ions [16,18]. However, the electronic anisotropy arising from local distortions around the different Fe ions, including the tetrahedral ones, accounts for the observed anisotropy tensor susceptibility (ATS) reflections [17,19].

(iii) The structural modulation was studied by measuring the (001) reflection off resonance (at $E = 7.1$ keV for the Fe K and at $E = 900$ eV for the Fe L_1). We have also used the superlattice $(4\,0\,\frac{1}{2})$ reflection at $E = 7.1$ keV, whose intensity is directly related to the lattice distortion below T_V [11] and it corresponds to the same periodicity along c as the so-called OO reflections. Longitudinal scans at 60 K of the Bragg $(4\,0\,\frac{1}{2})$ and (001) (assigned to CO) reflections at the Fe K edge show similar widths, corresponding to a FWHM of 0.0019 Å^{-1}, whereas for the $(0\,0\,\frac{7}{2})$ reflection (assigned to OO), the FWHM is 0.0037 Å^{-1}. This implies that the correlation lengths of the structure and of the CO are at least 1000 Å but that of the OO is ~700 Å. It follows from these correlation lengths that the present sample exhibits long-range structural CO and OO although the orbital domain size is smaller.

We have measured the temperature dependence of the intensity of the Bragg and the so-called CO and OO reflections in the neighborhood of T_V, characterizing the three different orderings. The temperature runs were performed either by waiting for thermal stabilization after each temperature step or by a slow continuous heating ramp of 0.3 K/min. The two procedures gave the same results. We report here the data taken with a heating ramp. Figure 3(a) shows the temperature dependence of the integrated intensity for the (001) reflection both at resonance and off resonance. The temperature dependences of the integrated intensities at the $(4\,0\,\frac{1}{2})$ reflection and at resonance at the $(0\,0\,\frac{7}{2})$ reflection are also compared in the same figure. The resonant and nonresonant scattering intensities simultaneously disappear at T_V (± 0.5 K) for the three studied reflections. The temperature dependence is essentially the same in the soft-x-ray regime. The evolution of the intensities of the $(0\,0\,\frac{1}{2})$ reflection at resonance and of the (001) reflection both at resonance and off resonance as a function of temperature is shown in Fig. 3(b). The resonant and nonresonant signals also disappear at T_V. We emphasize that the intensity of all the studied reflections is zero at temperatures above 125 K, contrary to what has been found in Ref. [18]. Our result points to a common
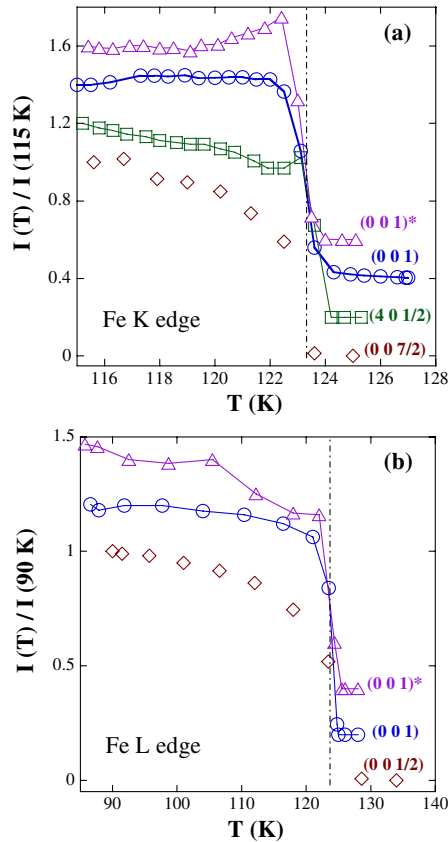
FIG. 3 (color online). The temperature dependence of the integrated intensities of the low-temperature reflections. The intensities have been normalized to the low-temperature value and they have been artificially shifted for clarity reasons. (a) (001) reflection at resonance ($E = 7.125$ keV) and off resonance ($E = 7.1$ keV, marked by asterisk), $(0\,0\,\frac{7}{2})$ reflection at resonance ($E = 7.125$ keV) and $(4\,0\,\frac{1}{2})$ off resonance ($E = 7.1$ keV). (b) (001) reflection at the Fe L_1 resonance ($E = 860$ eV) and off resonance ($E = 900$ eV, marked by asterisk) and $(0\,0\,\frac{1}{2})$ reflection at the Fe L_3 resonance ($E = 708.7$ eV).

origin of the structural and the so-called CO and OO reflections in magnetite. This also indicates that the phenomenology found in Ref. [18] is not intrinsic to the Verwey transition but may be caused by the peculiar characteristics of their sample.

In summary, we show that the structural and the resonant reflections disappear exactly at the same temperature as the sharp discontinuity of the initial susceptibility, i.e., at T_V. Our result agrees with other RXS studies either in bulk [15,17] or in a thin layer [16] of magnetite and indicates that the spin reorientation and the proposed CO and OO ordering are not correlated. Moreover, a double transition was never found, except for either nonstoichiometric or contaminated samples, whose Verwey transition temperature is always below 120 K [3]. In this sense, the unusual

behavior shown in Ref. [18] might be originated by a strained or highly defective sample. This would explain the values of $T_V = 119$ K and $\Delta T_V = 6$ K (see Ref. [19] cited by Lorenzo *et al.*) and the short correlation length of their low-temperature reflections. As a final remark, we note that structural forbidden reflections also occur in systems where no long-range structural order exists [19], and in the case of magnetite, the local structure at the Fe atoms is already dynamically distorted above T_V [22]. In this sense, the different temperature dependence of the CO and OO reflections with respect to the structural ones cannot be considered as a final compelling evidence of purely electronic CO and OO ordering.

Since the lattice distortion, the Fe site distinction, and the ordered anisotropy of the Fe atoms [we note here that tetrahedral Fe atoms also contribute to ATS $(0\,0\,\frac{2n+1}{2})$ reflections] occur simultaneously in a highly stoichiometric sample, we conclude that RXS in magnetite comes from the ordered local distortions at the structural transition. This gives rise to an ordered charge disproportionation and electronic anisotropy at the Fe atoms.

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[1] E. J. W. Verwey, Nature (London) **144**, 327 (1939); E. J. W. Verwey *et al.*, J. Chem. Phys. **15**, 181 (1947).
[2] M. Izumi and G. Shirane, Solid State Commun. **17**, 433 (1975).
[3] J. Garcia and G. Subías, J. Phys. Condens. Matter **16**, R145 (2004); F. Walz, J. Phys. Condens. Matter **14**, R285 (2002).
[4] P. Novak *et al.*, Phys. Rev. B **61**, 1256 (2000).
[5] M. Mizoguchi, J. Phys. Soc. Jpn. **70**, 2333 (2001).
[6] J. García *et al.*, Phys. Rev. B **63**, 054110 (2001).
[7] G. Subías *et al.*, Phys. Rev. Lett. **93**, 156408 (2004).
[8] I. Leonov *et al.*, Phys. Rev. Lett. **93**, 146404 (2004).
[9] H-T. Jeng *et al.*, Phys. Rev. Lett. **93**, 156403 (2004).
[10] J. García and G. Subías, Phys. Rev. B **74**, 176401 (2006).
[11] J. P. Wright *et al.*, Phys. Rev. B **66**, 214422 (2002).
[12] E. Nazarenko *et al.*, Phys. Rev. Lett. **97**, 056403 (2006).
[13] Y. Joly *et al.*, Phys. Rev. B **78**, 134110 (2008).
[14] R. J. Goff *et al.*, J. Phys. Condens. Matter **17**, 7633 (2005).
[15] D. J. Huang *et al.*, Phys. Rev. Lett. **96**, 096401 (2006).
[16] J. Schlappa *et al.*, Phys. Rev. Lett. **100**, 026406 (2008).
[17] S. B. Wilkins *et al.*, arXiv:0811.3350v2.
[18] J. E. Lorenzo *et al.*, Phys. Rev. Lett. **101**, 226401 (2008).
[19] V. E. Dimitrienko *et al.*, Acta Crystallogr. Sect. A **61**, 481 (2005).
[20] J. Blasco *et al.*, J. Cryst. Growth **310**, 3247 (2008).
[21] R. Aragón, Phys. Rev. B **46**, 5334 (1992).
[22] G. Subías *et al.* Phys. Rev. B **71**, 155103 (2005).