Charge and Orbital Correlations at and above the Verwey Phase Transition in Magnetite

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The subtle interplay among electronic degrees of freedom (charge and orbital orderings), spin and lattice distortion that conspire at the Verwey transition in magnetite (Fe_3O_4) is still a matter of controversy. Here, we provide compelling evidence that these electronic orderings are manifested as a continuous phase transition at the temperature where a spin reorientation takes place at around 130 K, i.e., well above $T_V \approx 121$ K. The Verwey transition seems to leave the orbital ordering unaffected whereas the charge ordering development appears to be quenched at this temperature and the temperature dependence below T_V is controlled by the lattice distortions. Finally, we show that the orbital ordering does not reach true long range (disorder), and the correlation length along the c-direction is limited to 100 Å.

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Introduction.—Magnetite (Fe_3O_4) has traversed history as a trustworthy room temperature ferrimagnet of interest in applied magnetism, mineralogy, biology, geophysics, and, in particular, the study of paleomagnetism. In addition, magnetite is the canonical prototype of a whole class of compounds, vaguely assembled under the banner of *Mott insulators* [1], whose puzzling collective interplay among charge, orbital, lattice, and magnetic electronic orderings has intrigued the scientific community over the last 60 years. Indeed, it exhibits a charge ordering (CO), metal-insulator transition known as the Verwey transition [2] in which the conductivity decreases by 2 orders of magnitude when the temperature is decreased below $T_V \approx 121$ K.

Magnetite crystallizes in the inverse cubic spinel structure AB_2O_4, space group $Fd\bar{3}m$ and lattice parameter $a_c = 8.394$ Å, with two types of Fe atoms: the tetrahedrally coordinated A-sites (Wyckoff site 8a, point group $\bar{4}3m$) and the octahedral coordinated B-sites (Wyckoff site 16d, point group $\bar{3}m$) with the magnetic moment *ferrimagnetically* aligned between both sites. Fe_3O_4 is in a mixed-valence state described as $Fe^{3+}(Fe^{2+}Fe^{3+})O_4{}^{2-}$ or as $Fe^{3+}(Fe^{(2.5+\delta)+}Fe^{(2.5-\delta)+})O_4{}^{2-}$ in terms of a fractional charge occupation. $\delta = 0.5$ describes the ionic, full integer charge order firstly hypothesized [2] whereas $\delta = 0$ represents either a charge disorder state or fully covalent bond ordering. The crystal structure below T_V is monoclinic Cc with a $\sqrt{2}a_c \times \sqrt{2}a_c \times 2a_c$ supercell and 16 different Fe-atoms at octahedral sites. First refined by Iizumi *et al.* [3], the structure has been further revisited in a combined x-ray and neutron powder diffraction experiment [4]. The powder diffraction spectra refinement was constrained within the $Pmca$ group although the cell was refined in $P2/c$, both with a $1/\sqrt{2}a_c \times 1/\sqrt{2}a_c \times 2a_c$ supercell and $\gamma = 90.2°$. The valence charge assigned to a given atom was estimated by the bond valence sum (BVS) method which is based on tabulated metal-oxygen average distances as a function of the valence of the metal ion. The occurrence of charge ordering and the validity of this refinement has been lately confirmed by a resonant x-ray diffraction (RXD) work where the energy dependence of the intensity of selected reflections has been refined yielding charge disproportionation value of $\delta_{12} = 0.12 \pm 0.025$ for one kind of Fe-atoms and $\delta_{34} = 0.1 \pm 0.06$, for another [5].

There is quite a lot of speculation on the nature of the orbital ordering (OO) in Fe_3O_4. Initially, it was believed that the degeneracy of the t_{2g} orbitals at the octahedral B-sites is raised by the trigonal field created by the next-nearest neighbors. The triplet state splits into a singlet (a_{1g}) and a doublet (e_g), with a gap estimated to be of the order of 0.15–0.25 eV. In a model where the magnitude of the electron bandwidth is neglected, the extra-electron in the Fe^{2+} state is going to fill the lowest state, the singlet, without any further lowering of the site symmetry [6]. However, recent theoretical studies [7] have disclosed the tremendous intricacy of orbital ground states, once the kinetic energy and the intersite Coulomb repulsion are taken into account with various possibilities for OO (real or complex), with and without charge disproportionation. Most of the available insight come from electronic structure calculations that find that the conduction electrons occupied spin-down d_{xy}, d_{xz}, and d_{yz} orbitals on different Fe^{2+} sublattices [8]. The orbital order is in agreement with the Kugel-Khomskii theory [9] and corresponds to the local distortions of oxygen octahedra surrounding the Fe-ions at B-sites [8,10].

However, in addition to the jump in the electronic conductivity, magnetic features remain largely unexplained within the charge-orbital models. These are the drop in the spontaneous magnetization well above T_V, a negative maximum of the magnetocaloric effect, anomalies in the magnetoresistance in the close vicinity of T_V, and the different dependence on magnetic field during low temperature cooling. A conspicuous change in the direction of the easy magnetization axis, from $\langle 111 \rangle$ at high temperature to $\langle 100 \rangle$ at low temperature, occurs at $T_K \approx 130$ K where the magnetocrystalline anisotropy is zero. After a long debate, it has been recognized that both T_V and T_K are distinct temperatures [11,12].

The Fe^{2+} cation contributes to the charge and orbital orders as well as to the anisotropy of the magnetization. One immediately recognizes that the temperature range between T_V and T_K is of special importance for the occurrence of charge and orbital orderings. In this Letter, we have carried out a detail study of the electronic orderings (charge and orbital) that develops within the temperature region between T_V and T_K by means of resonant x-ray diffraction (RXD). We show that they develop continuously right below T_K and that they are unequally affected by the lattice distortion occurring at T_V.

Experimental.—RXD experiments were carried out at the ID20 beam line in the European Synchrotron Radiation Facility (Grenoble) operating at photon energies between 7.05 and 7.14 keV, in the close neighborhood of the Fe K edge ($E = 7.119$ keV). The x-ray beam wavelength was selected by a Si(111) double crystal monochromator with an energy resolution of 0.8 eV. A MgO(222) analyzer crystal was used to filter out background coming from the sample (mostly fluorescence). Magnetite growth was described previously [5] and the samples were obtained from the rods by cutting perpendicular to a (001) direction and were gently polished. The scattering was performed off a [001] surface. At the Fe K edge, the photon penetration depth for the smallest angle reflections $(0, 0, \frac{1}{2})_c$ and $(0, 0, 1)_c$ is 1500 and 3500 Å, respectively. The temperature runs were performed always on increasing the temperature, from 50 to 150 K, and giving enough time for stabilization at every temperature change.

As we know from our previous studies on the charge ordering in $\mathrm{Fe_3O_4}$ [5,13], $k_\Delta = (0, 0, \frac{1}{2})$ and $k_X = (0, 0, 1)$ reciprocal-lattice points correspond to positions where purely electronics degrees of freedom may cleanly and independently manifest. This is a very important issue as the Fourier components of this electronic degrees of freedom are expected to be some orders of magnitude smaller than those of the concomitant lattice distortion occurring below T_V. We have succeeded in finding appropriate reflections where each one of the orderings can be studied independently. We show that orbital and charge ordering reflections have peculiar energy dependencies at the resonance (Fig. 1), as well as unequal correlation lengths along the c-direction (Fig. 2).

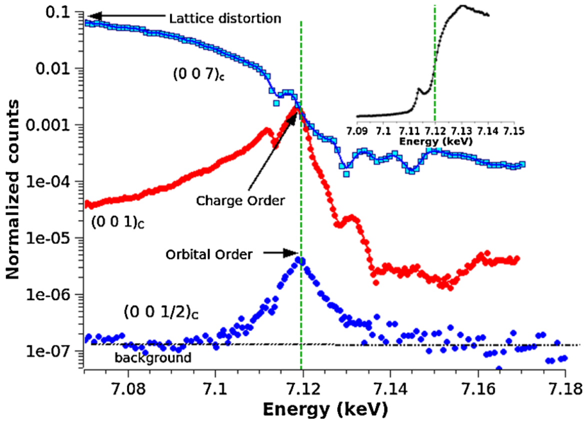

FIG. 1 (color online). Raw energy scans at three different Q-positions, $(0, 0, \frac{1}{2})_c$, $(0, 0, 1)_c$, and $(0, 0, 7)_c$, and at $T = 50$ K. Intensities have been corrected by the incident beam variations (monitor) and are shown in their actual scales. No absorption correction has been applied. The inset is a fluorescence spectra showing the absorption edge at 7.119 keV, right at the maximum of both energy scans. The different orderings have been measured at different Q-positions and energies, as shown in the graph.

Orbital ordering.—Orbital order (OO) in magnetite has recently been revealed through RXD experiments at the Fe $L_{2,3}$-edges on thin films [13]. These resonant experiments correspond to a virtual absorption-emission of a photon at the energy of the $2p \longrightarrow 3d$ dipole allowed transition. The reflection where this ordering has been disclosed is the $(0, 0, \frac{1}{2})_c$, in the cubic notation. In the low temperature phase of magnetite (space group Cc), this is a extinct (or forbidden) Bragg reflection. The presence of a c-glide plane warrants a null intensity of the $(0, 0, \frac{2n+1}{2})_c$ reflections except at the resonance. Associated to this *purely electronic* order parameter revealed at Fe $L_{2,3}$-edges there is a local lattice distortion that stabilizes it. As it has been shown in the case of OO in colossal magnetoresistance manganites [14,15], this is best observed at the K edge ($1s \longrightarrow 4p$ dipole allowed transition). Indeed, the $4p$ orbital is dense on the oxygen atom which makes this transition sensitive to any displacement of the oxygen atoms concomitant to the OO. The observation of OO in magnetite at the $(0, 0, \frac{1}{2})_c$ reflection also relies on the reasonable assumption that any new local anisotropy developing at and below the Verwey transition is going to be connected to local rearrangements of the orbitals.

The raw data shown in Fig. 1 shows that the intensity of the $(0, 0, \frac{1}{2})_c$ reflection above and below the edge is identical and only due to background, thus confirming that this reflection is a forbidden reflection. Figure 2 shows that the orbital reflections are very broad in q-space (correlation length of 112 Å), an order of magnitude broader than those corresponding to the charge ordering and lattice distortions, and very weak. We interpret this as a signature of a disorder in the orbital occupancy.

Charge ordering and lattice distortions.—Contrary to the OO signatures at the K edges that are mostly due to local lattice distortions, the CO signatures in RXD at this edge are *purely* electronic [5,16–18]. Experimentally, we have shown that the $(1, 1, 0)_c$ and the $(4, 4, 1)_c$ are the

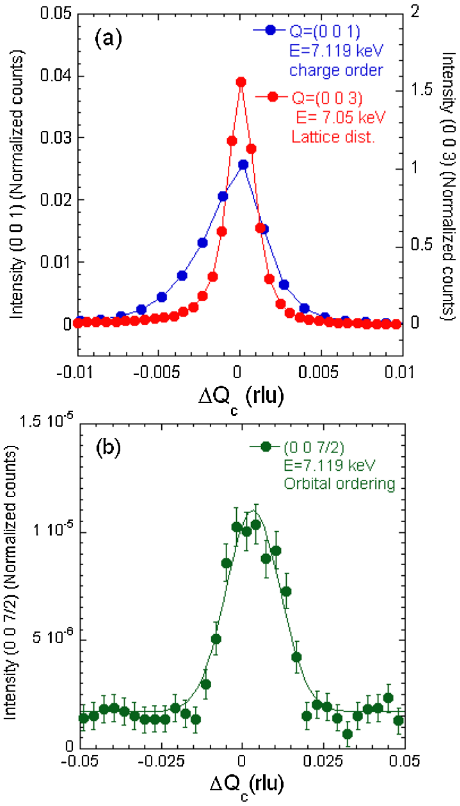

FIG. 2 (color online). Q_l scans along the three different Q-positions and photon energies displaying the different orderings. $T = 50$ K. Intensities are shown in real scales, once corrected by the incident flux variations. (a) The elastic lattice distortions and the charge order peaks have been measured at symmetry equivalent positions but different photon energies. (b) The orbital order peaks are considerably broader than the previous orderings. Integrated intensities (lattice:charge:orbital) are in the ratio 1:0.02:0.0003.

Bragg reflections where the occurrence of charge ordering at the B-sites can be best studied [5]. An important finding of this Letter is that the $(0, 0, 1)_c$ reflection displays a nearly *pure* CO effect for photon energies close to the resonance (Fig. 1). At this energy, the scattered intensity is directly proportional to the charge difference between two nonequivalent B-sites whereas off-resonance ($E = 7.06$ keV, for instance) the intensity of this reflection is related to the lattice distortion occurring below T_V. As it is shown in Fig. 1, the intensity of the former is 100 times larger than that of the latter, and therefore one can safely neglect the lattice distortion contribution to this reflection at the resonance. Conversely, we have used the $(0, 0, 3)_c$ position and photon energy $E = 7.05$ keV as a reference position for the measurement of the temperature dependence of the lattice distortion order parameter. At these low energies and reflection, the nonresonant scattering is at least 3 orders of magnitude larger than that at resonance, and therefore the contribution of the charge ordering order parameter can be safely neglected.

Temperature dependence and T_K.—We have followed the evolution of the intensity and FWHM as a function of temperature of the three reflections (and photon energies) characterizing the three different orderings. The results are shown in Figs. 3 and 4. Surprisingly, the three order parameters follow different temperature dependencies. A jump is observed at T_V in the temperature dependence of the lattice distortions, a manifestation of the 1st order nature of the Verwey phase transition (Fig. 3). Both CO and OO smoothly and continuously decrease down to a temperature close to 130 K, where in parallel, we observe a clear change in the width of the CO peak (Fig. 4). Below T_V, the CO order parameter is affected by the onset of the lattice distortions, as it is shown by both the kink at T_V and a temperature dependence of the intensity that runs parallel to that of the lattice distortion. We understand this *sudden* change in the slope as a freezing of the CO fluctuations at T_V. It may be noted that the OO remains unaffected by the onset of T_V. For $T > T_V$, charge and orbital fluctuations are coupled and drive the lattice fluctuations. The data displayed in Fig. 4 show the order parameter of the charge ordering has a longer correlation length than the lattice distortion fluctuations in the interval $T_K > T > T_V$. This means that in this fluctuating region, CO correlations are, very likely, not stabilized by a lattice distortion and thus hint at the possibility of another mechanism that either involves Coulomb repulsion between neighboring carriers (Wigner crystallization) or is mediated by OO. It is important to stress that magnetization experiments carried out in crystals cut from the same ingot as our sample, have yielded a spin-reorientation temperature of $T_K = 130$ K [19], very close to the temperature where CO and OO set in.

*Discussion and conclusions.*OO and CO set at the same temperature where the spin reorientation takes place, in what appears to be a continuous transition. Interestingly,

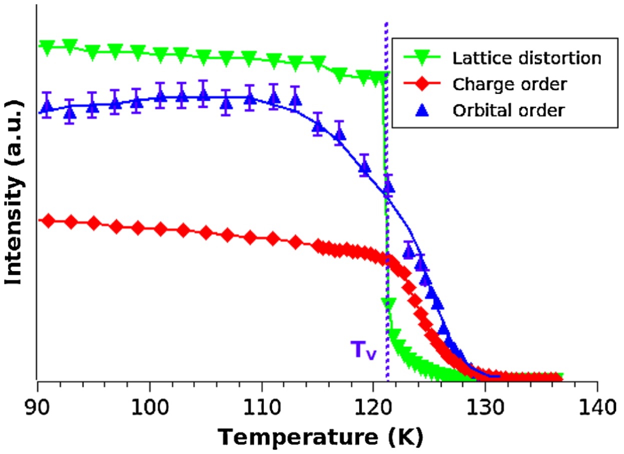

FIG. 3 (color online). Temperature dependence of the intensity of the three different orders: lattice distortion (down triangles), charge ordering (diamonds), and orbital ordering (up triangles). The intensities have been adjusted to fit into the same plot and the actual values are shown in Fig. 2. Lines are guides to the eye.

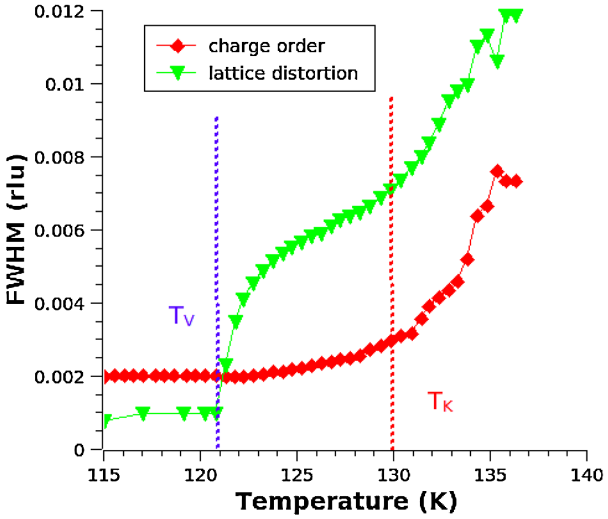

FIG. 4 (color online). Temperature dependence of the FWHM of the charge order (diamonds) and of the lattice distortion (down triangles) peaks. The correlation length of fluctuations is defined as $\xi = \frac{a_c}{\pi}\text{FWHM}^{-1}$. The FWHM of the $(0,0,\frac{1}{2})_c$ reflection associated with OO is 0.024 reciprocal-lattice units (≈112 Å) and is temperature independent in this range.

the spin reorientation transition $\langle 111\rangle \rightarrow \langle 100\rangle$ is predicted to be of second order in magnetite as the magnetic anisotropy constants of magnetite, K_1 and K_2, are both of the same sign [11,12]. It has been proposed [11,12] that the cancellation of K_1 at T_K and a further jump at T_V is related to the localization of the hopping electrons in the t_{2g} orbitals giving rise to a slight increase of the magnetic orbital moment and to a strengthening of the spin-orbit interaction. As a result, a single-ion anisotropy develops at this temperature that eventually favors the observed spin-reorientation. This model agrees with our findings in that both the CO and OO appear continuously below T_K.

We have found that the OO correlation length is of short range, very likely implying a disorder in the occupancy of the t_{2g} orbitals by the Fe^{2+} electron. A CO develops concomitantly to the OO and T_K marks the onset of rather long range CO correlations, as well. We believe that this may be a consequence of the extremely low mobility of the carriers [11].

Lattice fluctuations that are going to stabilize and give rise to the observed low temperature Cc monoclinic structure do not follow the same trend. Our data show that between T_K and T_V, CO correlation length of fluctuations is longer than the lattice fluctuations, pointing to the onset of an electron lattice and stressing the importance of Coulomb repulsion as a salient feature of the Verwey transition. At T_V, a first order phase transition occurs; the noticeable feature is the sharp increase in the intensity of the lattice distortion, as shown in Fig. 3. Interestingly, the CO order parameter does not display that sharp increase in the intensity but an abrupt change of slope at T_V to follow an identical temperature dependence as the lattice distortion below T_V. At this temperature, we observe a decoupling of the CO and OO degrees of freedom as indicated in the different temperature dependencies of the associated order parameters.

To conclude, our data reveal new features of the charge and orbital orderings in magnetite, not observed in previous experiments nor predicted by any current theory of the Verwey transition in magnetite. The charge and orbital orders develops concomitantly with the spin-reorientation that occurs at $T_K \approx 130$ K, i.e., 10 degrees above the actual Verwey transition. The three electronic degrees of freedom charge, orbital, and spins are coupled. The lattice distortions developing below T_V share the same symmetry as the orbital fluctuations, and therefore the Verwey transition can be viewed as a sort of Jahn Teller transition. The evolution of the charge ordering on decreasing temperature appears to be quenched by the lattice distortions, as manifested in the levelling off of the temperature dependence of the order parameters (see Fig. 3). We conclude that the Verwey transition at T_V arises as a need to exhaust the development of long range charge correlations and to prevent the growth of the charge disproportionation beyond a certain value $\delta = 0.1e^-$.

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