Magnetite, a Model System for Mixed-Valence Oxides, Does Not Show Charge Ordering

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We have investigated the charge ordering (CO) in magnetite below the Verwey transition. A new set of half-integer and mixed-integer superlattice reflections of the low-temperature phase have been studied by x-ray resonant scattering. None of these reflections show features characteristic of CO. We demonstrate the absence of CO along the c axis with the periodicity of either the cubic lattice $\mathbf{q} = (001)$ or the doubled cubic lattice $\mathbf{q} = (001/2)$. This result suggests that the Verwey transition is caused by strong electron-phonon interaction instead of an electronic ordering on the octahedral Fe atoms.

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The metal-insulator transition in magnetite (Fe_3O_4) at $T_V \sim 120$ K, the so-called Verwey transition [1,2], has been argued to be a charge ordering (CO) transition of Fe^{3+} and Fe^{2+} ions on the octahedral sites whose nature has not been clarified yet [3]. Oxides are generally considered to be rather ionic in character so the electronic states are described as nearly atomic [4]. Thus, CO is considered to be an essential ingredient for the description of metal-insulator transitions in mixed-valence oxides although an adequate model has not been given yet. Therefore, the experimental verification of the possible CO modulations below T_V in magnetite, prototype of CO oxides, is of fundamental relevance to give a realistic description of the insulating and metallic states in transition-metal oxides.

The diffraction techniques are the most suitable to determine periodic arrangements in crystals. However, neither conventional x-ray nor neutron diffraction can directly discriminate between two close valence states. This lack of sensitivity of the atomic Thomson scattering factor to valence states can be solved nowadays by means of the x-ray resonant scattering technique [5]. A strong contrast in the atomic anomalous scattering factors between ions with different valence states is accessible at energies close to an absorption edge. These resonant effects are especially important for forbidden or weak-allowed Bragg reflections because of the out of phase interference scattering of identical or nearly identical sites, originated by the difference between either the atomic anomalous scattering factors of defined valence states [6,7] or the local anisotropy (ATS) reflections [8,9]). This technique has recently been applied to study the charge and orbital ordering phenomena in several mixed-valence oxides [6,7,10,11]. These studies succeed in demonstrating the sensitivity of the technique to this kind of phenomena, although none of them have detected a difference of one electron (denoted as ionic CO) [10–14].

Magnetite is the oldest known magnetic material and the original Néel ferrimagnet ($T_N = 851$ K). It has the inverse spinel cubic structure AB_2O_4 above T_V (space group $Fd\bar{3}m$). The oxygen lattice has an almost perfect fcc close-packed structure where A and B sites are the tetrahedral $8a$ and octahedral $16d$ interstitial sites, respectively. The B-site lattice (where CO was claimed) can be regarded as a diamond lattice of tetrahedra of nearest-neighbor octahedral Fe atoms, sharing alternate corners (see the inset of Fig. 3). The low-temperature monoclinic cell (Cc) corresponds to $\sqrt{2}a \times \sqrt{2}a \times 2a$ of the cubic unit cell, consisting of a stacking of eight planes of B sites along the c axis [15–17]. Different refinements of this low-temperature structure have shown that small atomic displacements give rise to the appearance of two main types of superlattice reflections (using cubic index) below T_V: (I) Half-integer $(h\,k\,l + 1/2)$ arising from the doubling of the c axis and (II) even-odd mixed-integer characterized by a wave vector $\mathbf{q} = (001)$ resulting from the loss of the fcc translation. Any further distortions are found to be very small. Hence, a plausible model should relate the CO to the atomic displacements so charge modulations parallel to c are the most likely [15,17]. In fact, CO models proposed in magnetite have either the periodicity of the cubic lattice $\mathbf{q} = (001)$ [17] or the periodicity of the doubled cubic lattice $\mathbf{q} = (001/2)$ [15]. If this were true, a resonant effect should be observed at the Fe K edge for (00 *odd*) and (00 *half-integer*) reflections, respectively. Moreover, two special classes of fundamental reflections also deserve attention: (III) the forbidden $(0\,k\,l)$ $k + l = 4n + 2$ due to the diamond glide plane in the spinel structure, and (IV) the weak $(h\,h\,l)$ $h + l = 2n$ reflections that are forbidden for iron atoms but allowed for the oxygen.

In order to carry out a thoughtful analysis of the CO problem in magnetite, we have performed x-ray resonant scattering experiments at the Fe K edge in a single crystal of magnetite at $T \sim 20$ K at the beam line D2AM at the

ESRF (European Synchotron Radiation Facility, Grenoble, France) [18]. The single crystal was grown by the floating zone method, showing a sharp discontinuity in the electrical resistance and magnetization at 121 K, which guarantees a right oxygen stoichiometry of the sample [19,20]. Two pieces were cut and polished to obtain flat (001) and (420) surfaces. Total (σ–σ + σ–π polarization components) intensity versus photon energy is reported for the following reflections: class (I) superlattice (441/2); class (II) superlattice (003) and (210); and class (IV) fundamental (442). Class (III) reflections were the subject of previous studies [19,20]. Allowed Bragg reflections have been also measured for the sake of comparison. The superlattice reflections were studied at different azimuthal angles. Energy-dependent spectra were alike, indicating the lack of azimuthal dependence and the homogeneity of the twinning structure of the probing region.

Figure 1 shows the intensity profiles of a (00*l*) scan at two fixed energies of the x rays, $E_P = 7.112$ keV and $E_W = 7.125$ keV, corresponding to the prepeak and the white line in the absorption spectra, respectively, (see left inset in Fig. 1). We observe the Bragg-allowed (004) reflection together with the superlattice (003) reflection of the low-T phase and the forbidden (002) reflection. The forbidden (002) reflection shows the maximum intensity at the Fe absorption K edge, in agreement with the presence of an intense resonance at the threshold. On the other hand, the superlattice (003) reflection clearly appears to have much less intensity at the energy of the absorption edge than at the prepeak energy, opposite to the behavior of the resonant (002) reflection. If $\mathrm{Fe}^{2.5+\delta/2}$ and $\mathrm{Fe}^{2.5-\delta/2}$ ions were periodically ordered in the lattice with a [001] modulation, a strong resonance at the energy of the Fe absorption K edge would be expected. Therefore, this characteristic suggests the absence of a resonant effect for the (003) reflection and the lack of CO modulation with this periodicity. Neither the (005/2) nor the (007/2) superlattice reflections were detected (see the right inset of Fig. 1) although other half-integer reflections such as $(0\,4\,l + 1/2)$ and $(4\,4\,l + 1/2)$ have previously been observed [20,21]. We note that the Thomson scattering for the $(0\,0\,l/2)$-type reflections is zero. Therefore, the extinction of this kind of reflections at $E = 7.125$ keV (Fe absorption K edge) also implies the lack of resonant effects, and consequently the absence of CO modulation with this periodicity.

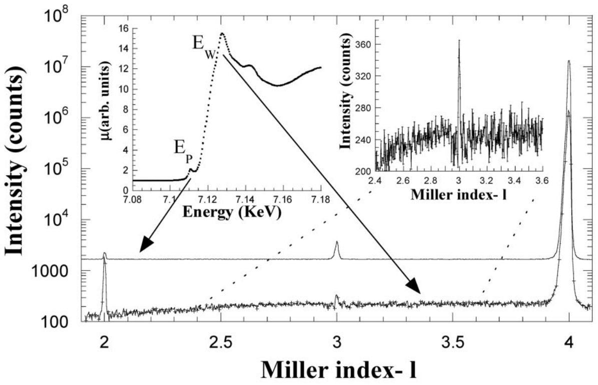

FIG. 1. Logarithmic intensity vs the momentum transfer around the $(0\,0\,l)$ reflection of magnetite measured at energies of $E_P = 7.112$ keV (solid line) and $E_W = 7.125$ keV (line + crosses) at $T = 20$ K. Left inset: x-ray absorption spectra of magnetite at the Fe K edge. Arrows indicate the two selected energies for the l scans. Right inset: detail of the l scan around the (003) reflection of magnetite at $E_W = 7.125$ keV.

We examine now the limit for the possible charge disproportionation (δ) along the c axis given by the sensitivity of the x-ray resonant scattering technique. The energy dependence in diffracted intensity for both fundamental (Bragg-allowed and forbidden) and superlattice reflections is reported in Fig. 2 compared to the self-absorption contribution. The variation of the intensity with energy for all the reflections, except for (002), mainly reflects an absorption profile due to the strong self-absorption of magnetite. Resonant effects are clearly seen for the forbidden (002) reflection where the Thomson contribution is zero and even for the weak-

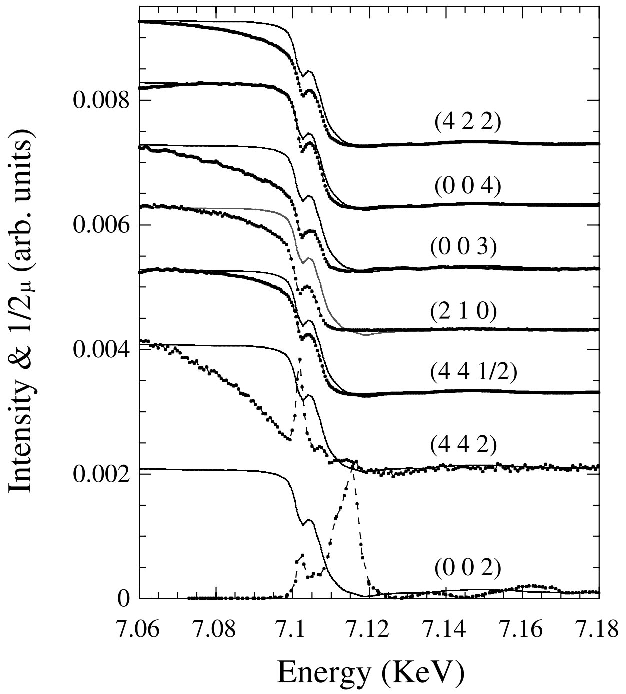

FIG. 2. Energy dependence of the diffracted intensity around the Fe K absorption edge of selected Bragg-allowed [(004), (422)-tetrahedral, and (442)], superlattice [(003), (210), and (441/2)], and fundamental forbidden (002) reflections of magnetite at $T = 20$ K. The self-absorption contribution ($1/2\mu$) is shown for comparison (solid curve).

allowed (442) reflection with nonresonant intensity relative to the fundamental (004) reflection of $\sim 3 \times 10^{-4}$. However, none of the superlattice reflections studied show any resonance at the absorption edge.

Actually, the resonant scattering at the forbidden $(004n + 2)$ reflections (Verwey model) has previously been studied [19,20,22]. We demonstrated that the main resonance arises from the structural anisotropy of the octahedral Fe atoms because of the trigonal point symmetry of the B sites ($\bar{3}m$) [19,22]. This result implied that the four octahedral Fe atoms of each oriented tetrahedra averaged in the cubic unit cell are electronically equivalent [20]. It is obvious that the equivalence among the octahedral Fe atoms belonging to a tetrahedral cluster does not guarantee the lack of ionic CO (or a charge density wave) between different tetrahedral units with either (001) or (001/2) periodicities of the cubic unit cell. The absence of resonant scattering at the half-integer reflections of $(0\,0\,l/2)$ type (Fig. 1) implies that the charge modulation with this double periodicity should be lower than $\delta = 0.05e^-$. This value is inferred from the minimum intensity in the azimuthal evolution of the forbidden (002) reflection [20]. Moreover, the observation of (401/2)-type (see Ref. [20]) and (441/2)-type (Fig. 2) reflections whose energy dependence is essentially a self-absorption profile together with the lack of (001/2)-type reflections indicate that these half-integer reflections arise from the atomic displacements in planes perpendicular to the c axis below T_V [15].

Finally, concerning the CO modulation with $\mathbf{q} = (001)$, we have simulated the energy-dependent spectra for the (003) reflection assuming a charge-ordered sequence along the [001] direction to establish the limit for the observation of a resonant signal. The structure factor for the (003) reflection has been calculated on basis of the Cc structure given by Zuo *et al.* [16] considering three contributions: First, an energy-independent f_0 term which accounts for the Thomson scattering. The value of f_0 has been estimated as the nonresonant intensity of the Bragg-allowed reflection (004) scaled by the experimental intensity ratio (003)/(004), 3×10^{-4}, measured from the l scan (Fig. 1). Second, an energy-dependent nonresonant contribution arising from the average of the atomic anomalous scattering factors of nonordered tetrahedral and octahedral Fe atoms. Third, a resonant contribution that arises from the ordering of Fe^{3+} and Fe^{2+} ions. The CO scheme proposed by Wright *et al.* [17] has been considered. The respective imaginary parts of the atomic scattering factors f'' for Fe^{3+} and Fe^{2+} have been obtained from the experimental absorption spectrum of $MnFe_2O_4$ (Fe occupies only the octahedral B sites) shifting the spectra by a chemical shift of 4 eV [23]. The real part f' is related to f'' by the Kramers-Kronig transformation. We note that the intensity of the resonance depends on either the number of pairs Fe^{3+}/Fe^{2+} ordered or the chemical shift between the two Fe ions. In this sense, the limit we obtain for the CO modulation can be interpreted either in terms of a number of electrons ordered or of a charge disproportionation δ. The ionic CO model ($\delta = 1$) corresponds to 32 electrons ordered in the low-T unit cell, the total number of octahedral Fe atoms being 64. We also want to note that the lower the Thomson scattering intensity, the higher the sensitivity to the resonant effect [18], as it is clearly shown in Fig. 2. The resonant effect is emphasized in the forbidden (002) reflection, for which the Thomson scattering cancels out, and the weak (442) reflection whose intensity is a factor of 3×10^{-4} lower than that of (004). Instead, the absorption factor $(1/2\mu)$ dominates the energy-dependence spectrum for strong Bragg reflections such as (422) and (004).

Figure 3 compares the simulations, including the self-absorption contribution, for two degrees of CO. For instance, 25% CO corresponds to $\delta = 0.25e^-$ in terms of charge disproportionation or to $8/32e^-$ in terms of the number of Fe^{3+}/Fe^{2+} pairs ordered. We can deduce that CO modulations correspondent to $\delta > 0.1e^-$ should be

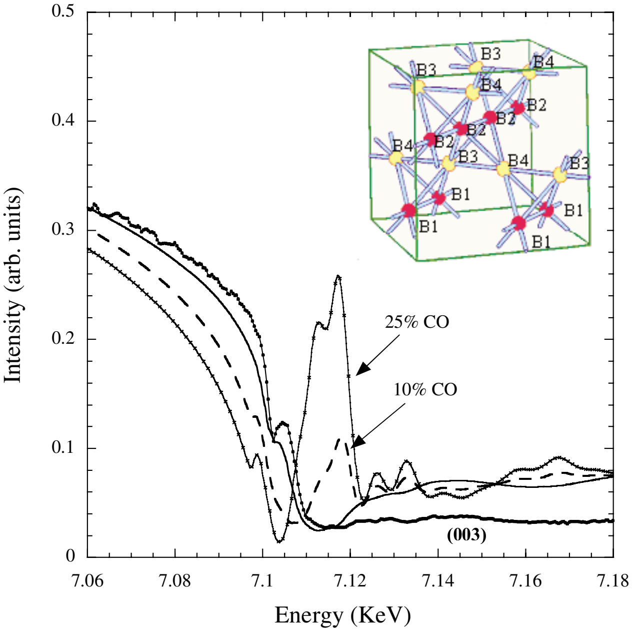

FIG. 3 (color online). Simulations of the energy dependence of the intensity of the superlattice (003) reflection, including self-absorption, for (a) no CO modulation solid line, (b) $0.1e^-$ CO modulation (dashed line), and (c) $0.2e^-$ CO modulation (line + crosses). The experimental spectrum (line + dots) is shown for comparison. The resonant intensity has been calculated on basis of the crystallographic CO model given by Wright *et al.* [17]. Inset shows the B-site lattice of the spinel cubic unit cell consisting of four tetrahedral of Fe atoms sharing corner with each other. Two models, Verwey (● Fe^{2+} and ∘ Fe^{3+}) and Wright [large ($B1$ and $B4$) and small ($B2$ and $B3$) octahedral sites] are schematized.

detectable. Therefore, we can conclude that no CO modulation correspondent to more than $0.1e^-$ exists with the periodicity given by $\mathbf{q} = (001)$. The same results can be applied for the superlattice (210) reflection.

In summary, we present a complete set of data to assure the lack of ionic CO modulation in magnetite below T_V. First, the extinction of the $(00l + 1/2)$ reflections and the absence of resonant effects on the $(h\,k\,l + 1/2)$, h or $k \neq 0$ reflections indicate that the two halves of the low-T unit cell (doubled along the c axis) are equivalent in terms of charge distribution and even in terms of the anisotropy of the octahedral sites. In other words, the charge density on one half of the unit cell is exactly the same as on the other. Second, the absence of resonant effects on the (003) reflection [and on other class (II) reflections] proves that there is no difference in the charge density between planes containing tetrahedra of octahedral Fe atoms, i.e., between octants of the cubic unit cell. Finally, the ATS character of the forbidden $(0\,0\,4n + 2)$ and fundamental (442) reflections demonstrates that no CO occurs between consecutive planes of octahedral Fe atoms within each tetrahedron (one octant of the cubic unit cell). We estimate the limit for the maximum charge disproportionation to be $0.1e^-$ and $0.05e^-$ for $\mathbf{q} = (001)$ and $\mathbf{q} = (001/2)$ modulations, respectively. Within this result, the CO scheme proposed by Wright *et al.* is completely discarded [17,24].

In conclusion, we have demonstrated that the metal-insulator (Verwey) transition in magnetite is not originated by pure electronic ordering on the octahedral Fe atoms as it has been believed for over 60 years. Taking into account that the structural change is the main effect at the metal-insulator transition, we proposed that a conduction mechanism assisted by phonons would be a more reliable origin for this transition. This proposition is strongly supported by previous neutron scattering works [15], which suggest that the atomic displacements at the phase transition result from the condensation of phonons. As magnetite is considered the prototype of CO in oxides, this work demonstrates that the theoretical framework for mixed-valence transition-metal oxides accepted so far has to be reconsidered.

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