Direct Observation of t_{2g} Orbital Ordering in Magnetite

J. Schlappa,[1] C. Schüßler-Langeheine,[1] C. F. Chang,[1] H. Ott,[1] A. Tanaka,[2] Z. Hu,[1] M. W. Haverkort,[1] E. Schierle,[3]
E. Weschke,[3] G. Kaindl,[3] and L. H. Tjeng[1]
[1]*II. Physikalisches Institut, Universität zu Köln, Zülpicher Strasse 77, D-50937 Köln, Germany*
[2]*Department of Quantum Matter, ADSM, Hiroshima University, Higashi-Hiroshima 739-8530, Japan*
[3]*Institut für Experimentalphysik, Freie Universität Berlin, Arnimallee 14, D-14195 Berlin, Germany*
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Using soft-x-ray diffraction at the site-specific resonances in the Fe $L_{2,3}$ edge, we find clear evidence for orbital and charge ordering in magnetite below the Verwey transition. The spectra show directly that the $(00\frac{1}{2})$ diffraction peak (in cubic notation) is caused by t_{2g} orbital ordering at octahedral Fe^{2+} sites and the (001) by a spatial modulation of the t_{2g} occupation.

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Magnetite, Fe_3O_4, is one of the most fascinating materials in solid state physics. Besides being the first magnetic material known to the mankind, see e.g. [1], it is also the first example for an oxide to show a first order anomaly in the temperature dependence of the electrical conductivity at $T_V \approx 120$ K, the famous Verwey transition [2]. It is accompanied by a structural phase transition from the cubic inverse spinel to a distorted structure, leading to the appearance of superstructure diffraction peaks mainly characterized by the wave vectors (001) and $(00\frac{1}{2})$ (the notation throughout this Letter refers to the cubic high-temperature unit cell with $a = 8.396$ Å). One usually connects this transition with charge ordering of Fe^{2+} and Fe^{3+} ions on the octahedrally coordinated, so-called, B sites [3].

Very recently, Wright, Attfield, and Radaelli found from their neutron and synchrotron-x-ray diffraction measurements an intriguing pattern of shorter and longer bond lengths between B-site Fe and oxygen ions below T_V, which they interpreted in terms of a particular charge order [4,5]. This result has triggered a flurry of new theoretical and experimental efforts. Particularly important hereby are the LDA + U band structure studies by Leonov *et al.* and Jeng *et al.* who made the conjecture that it is the t_{2g} orbital occupation and order which are the characteristic order parameters of the system [6,7] rather than the order of the total charge itself as its variation is rather small. Yet, most of the follow-up experimental investigations [8,9] are still focused on the charge-order issue. In a soft-x-ray diffraction study of Huang *et al.* the importance of the orbital and charge-order issue was recognized [10], but the experiments at the oxygen $1s \rightarrow 2p$ (K) resonance are not specific to the Fe t_{2g} orbital order.

Here we report on our resonant soft-x-ray diffraction (RSXD) study on Fe_3O_4 using photons in the vicinity of the Fe $L_{2,3}$ absorption edges. This technique directly probes the $3d$-electronic states of the transition-metal ion via the dipole allowed Fe $2p \rightarrow 3d$ $(L_{2,3})$ excitation involved in the scattering process [11–14]. This has enabled us to obtain clear evidence for the presence of the Fe t_{2g} orbital and charge order, thereby providing experimental support for the ideas brought forward by the LDA + U studies [6,7].

For this study we chose a magnetite film rather than a bulk crystal for two reasons. First, diffraction features in a thin film are broadened along the surface normal. This broadening allows us to study the resonance of the (001) peak, whose peak maximum cannot be reached at the $L_{2,3}$ resonance. Second, the volume probed by the scattering experiment is determined by the film thickness rather than by the photon penetration depth. Since the latter changes strongly across resonances in the soft-x-ray range, this change may obscure the resonance effect. A 40-nm film of Fe_3O_4 was grown *ex situ* by molecular-beam epitaxy (MBE) on epipolished MgO. In order to separate the specular reflectivity from the c direction of Fe_3O_4, a substrate with about 6° miscut was used. The film was characterized by resistivity measurements and shows a sharp Verwey transition at 115 K. RSXD experiments were carried out at the BESSY beam line UE52-SGM using the UHV diffractometer built at the Freie Universität Berlin. The sample was oriented such that two of the cubic axes of the room temperature structure were parallel to the diffraction plane. The incoming light polarization was either perpendicular (σ polarization) or parallel (π polarization) to the diffraction plane.

Figure 1 shows a q scan along the [001] or L direction of the reciprocal space taken at 83 K (open symbols), i.e., below T_V, with 708.5 eV photons, revealing the $(00\frac{1}{2})$ diffraction peak, and the onset of the (001). Even though the maximum of the (001) cannot be reached at the Fe-$L_{2,3}$ resonance, where the maximum momentum transfer is $L = 0.96$ as indicated by the vertical line in Fig. 1, the broadening of the (001) peak transfers some intensity into the reachable momentum space. The solid line through the data points is a simulation including two peaks of the same shape but different intensity and the Fresnel reflectivity, which causes the increasing background at low L values. This model describes the data reasonably well, even though the oscillations of the Laue profile are not resolved in the data. The intensity of the (001) peak is about 10 times

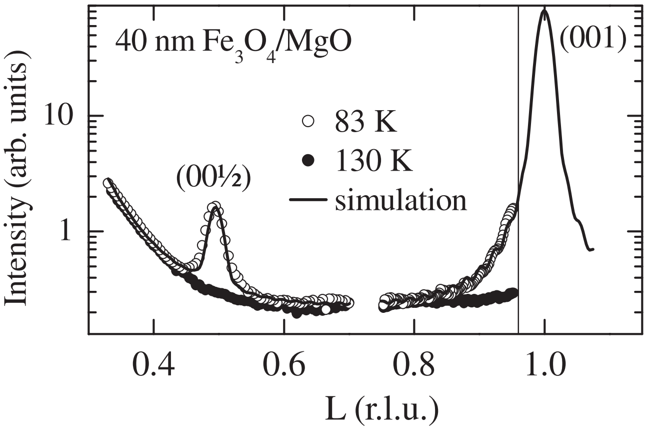

FIG. 1. Scan along L below (open symbols) and above (filled symbols) T_V recorded at 708.5 eV photon energy with σ polarization. The solid line through the data points is a simulation. The vertical line at $L = 0.96$ denotes the maximum possible momentum transfer at this energy.

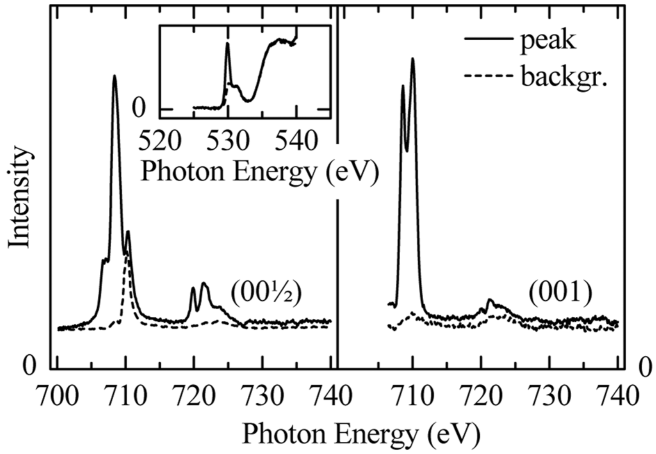

FIG. 2. Spectra of the $(00\frac{1}{2})$ (left) and (001) (right) diffraction peaks (solid lines) and the corresponding backgrounds (dashed lines) recorded with π polarized light. The inset shows the $(00\frac{1}{2})$ spectra recorded at the oxygen K edge for comparison. All spectra are plotted on the same vertical scale.

that of $(00\frac{1}{2})$. Both peaks disappear when the sample is heated to 130 K (filled symbols), i.e., above T_V. From the peak widths we determine the correlation length perpendicular to the surface to be 37 nm, which is essentially the full film thickness. The in-plane correlation length of 10 nm is most probably limited by the formation of crystalline domains [15]. The influence of the stepped substrate on the structure of the film seems to be weak, since the in-plane correlation length is about 2.4 times larger than the MgO terrace width.

In order to identify the origin and nature of the two diffraction peaks, we recorded their intensity as a function of photon energy. The background below the $(00\frac{1}{2})$ peak was interpolated from the resonance behavior at $L = 0.35$, 0.4, 0.6, and 0.7. The spectrum for the (001) peak was recorded at $L = 0.95$ with the background intensity taken at $L = 0.8$.

The spectra obtained from the peaks and backgrounds are presented in Fig. 2. The shapes of the spectra for the two peaks are distinctly different: the L_3 part of the $(00\frac{1}{2})$ spectrum has a sharp resonance maximum at 708.4 eV, while the spectrum of the (001) peak shows a double-peak structure, one peak at 708.6 eV, i.e., almost the same energy as the maximum of the $(00\frac{1}{2})$ spectrum, and the second one at 710.1 eV. The L_2 parts of the spectra, on the other hand, are more similar with two maxima at 720 and 721.4 eV. The inset shows the corresponding data from the oxygen-K edge as a reference.

In order to determine to what extent our results are influenced by film properties, we have carried out experiments using a film twice as thick as the one presented above and grown on a flat MgO substrate. We have seen that the reflectivity background below the $(00\frac{1}{2})$ peak was larger and that the onset of the much narrower (001) peak was less well defined. These findings, however, justify precisely our motivation to use thin films on a miscut substrate rather than a bulk crystal with a low index surface as outlined in the experimental paragraph above. The key data of this thicker film are identical to those of the 40 nm film: both the $(00\frac{1}{2})$ and (001) diffraction peaks can be observed below T_V and both disappear above T_V; the energy dependence of their intensities are very similar to the ones shown in Fig. 2. This indicates that the results presented are not a particularity of a magnetite film, but that they are indeed representative for the bulk material.

In Fig. 3 we present the resonance spectra of the two diffraction features after background subtraction together with the Fe $L_{2,3}$ x-ray-absorption spectroscopy (XAS) spectrum. The spectral line shapes for the two diffraction peaks are clearly different from the XAS spectrum [symbols in Fig. 3(a)]. To interpret the spectroscopic results, we resort to the existing literature on the XAS of Fe_3O_4 [16–18] with emphasis on the strong magnetic circular and linear dichroism [17,18] effects therein. The sharp structures in the dichroic spectra allow for a clear decomposition of the XAS spectrum in terms of contributions coming from the different Fe sites in magnetite. This decomposition is given in Fig. 3(a): the spectrum from the B-site Fe^{2+} ion is shown by the red thick solid line, the A-site Fe^{3+} by the green dotted line, and the B-site Fe^{3+} by the blue dashed line. The maximum in the L_3 white line of each of these ions occurs at quite different energies, an aspect which we will utilize next to interpret the spectra (001) and $(00\frac{1}{2})$ diffraction peaks.

The maximum of the $(00\frac{1}{2})$ diffraction peak spectrum occurs at essentially the same energy as that of the B-site Fe^{2+} XAS. This means that the $(00\frac{1}{2})$ diffraction peak is due to an order, which involves *only* B-site Fe^{2+} ions. This in turn implies that orbital order of the t_{2g} electrons is at play here, since this is the only degree of freedom available

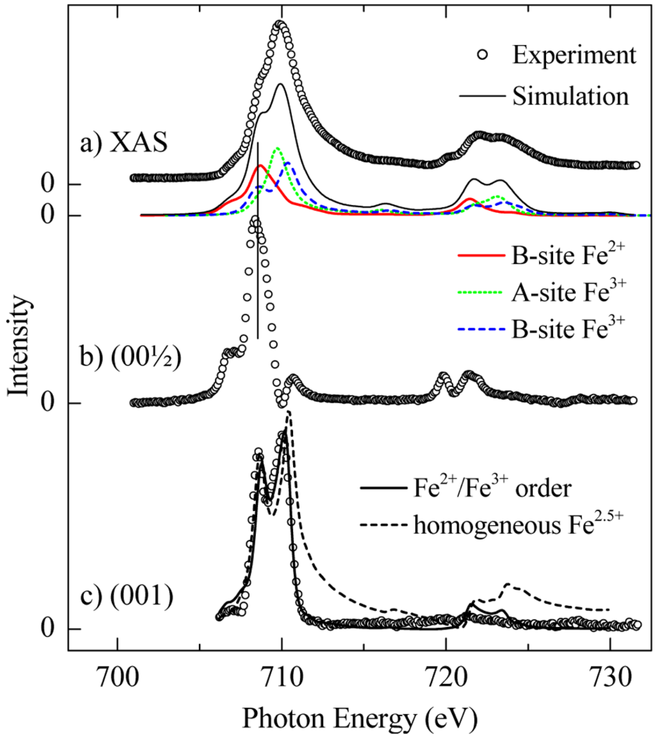

FIG. 3 (color online). (a) Experimental Fe $L_{2,3}$ XAS spectra of Fe_3O_4 (symbols). The black thin solid line is a simulation, which is constructed as the sum of the spectra from the B-site Fe^{2+} (red thick solid line), A-site Fe^{3+} (green dotted line), and B-site Fe^{3+} (blue dashed line) ions; (b) energy dependence of the $(00\frac{1}{2})$ diffraction peak intensity; (c) energy dependence of the (001) intensity (symbols), the solid line is a simulations for a charge-order scenario and the dashed line for a homogeneously mixed-valent scenario, both scaled to the height of the first resonance peak.

which could make one B-site Fe^{2+} ion to be different from another B-site Fe^{2+} ion. In $P2/c$ or Cc symmetry the $(00\frac{1}{2})$ diffraction peak is glide-plane forbidden with the consequence that only off-diagonal elements of the scattering tensors contribute. These elements can be expected to be much stronger for the Fe^{2+} (d^6) ions than for the more spherical Fe^{3+} (d^5) ions, explaining indeed why the resonant enhancement of the $(00\frac{1}{2})$ peak occurs only for photon energies which are characteristic for the Fe^{2+} sites. Our result that the resonant enhancement of the $(00\frac{1}{2})$ peak occurs only for photon energies which are characteristic for the Fe^{2+} sites thus provides direct experimental proof for orbital order as predicted in Refs. [6,7]. We note that this orbital-order finding does not exclude the existence of charge order associated with other, not glide-plane forbidden peaks related to the doubling of the unit cell along c as observed in Ref. [9].

In contrast to $(00\frac{1}{2})$, the (001) spectrum shows two peaks which essentially occur at the energies of the maxima of the two B-site resonances. Such a double-peak structure is exactly the resonance shape to be expected from charge order involving the two B-site ions. The experiment is sensitive to differences in the scattering amplitudes of the different ions. For two resonances well separated in energy, as it is the case for the B-site Fe^{2+} and Fe^{3+} ions, this difference is large near the two resonance maxima leading to such a two-peak feature. To illustrate this we show as the solid line in Fig. 3(c) the result of a simulation using the complex scattering amplitudes for the B-site ions, which we have extracted from the subspectra in Fig. 3(a). We find a very good agreement between experiment and simulation.

We would like to remark that the (001) is a structurally allowed Bragg peak, so that it should be visible even in the case of a homogeneously mixed-valent system, i.e., if there were no charge order. Since the scattering amplitude of the Fe sites changes across resonance, even a pure structural peak will show a resonance effect. In the structure proposed by Wright *et al.* the B-site contribution to the amplitude for (001) is $\approx 4.1 f_{2+}(\omega) - 3.7 f_{3+}(\omega)$ [5] with the f's describing the scattering amplitudes for the different ions. In a charge-ordered case $f_{2+}(\omega) \neq f_{3+}(\omega)$ and for energies where one resonance is dominating the charge order contribution to the observed intensity would be of the order of $16|f|^2$. The structural contribution is the one that would remain even if all sites were identical. It gives an intensity of the order of $(4.1 - 3.7)^2|f|^2$, i.e., about 100 times weaker than the intensity expected in the case of charge ordering.

Since (001) is stronger than $(00\frac{1}{2})$, the charge-order scenario appears to be more plausible, but a quantitative comparison requires one to know the absolute sizes of the scattering tensor elements. The identification of (001), however, is possible even without intensity reference from its spectral line shape. The resonant scattering amplitudes consist of a complex energy-dependent part $f'(\omega) + if''(\omega)$ plus an energy-independent part f_0. The scattering amplitude for the charge-order scenario is dominated by the difference between f_{2+} and f_{3+}. In this difference the f_0 term, which is essentially the same for both iron valences, cancels out. It does, however, contribute to the structurally scattered intensity. The latter is $|f_0 + f' + if''|^2$ and thus contains a mixed term $2f_0f'$. Since f' is asymmetric going through a minimum at the low-energy side of the absorption maximum, the mixed term is asymmetric too; its relative contribution to the total intensity depends on the ratio between f_0 and f', f''. We estimated this ratio by scaling the edge jump in the XAS data to the tabulated values for f'' [19]. A simulation of the spectral shape for a no-charge-order scenario including the mixed-term contribution is presented as the dashed line in Fig. 3(c). The B-site part of the absorption spectrum of this hypothetical homogeneous system was taken as the average of the two B-site spectra in Fig. 3(a). For better comparison the two simulated spectra were scaled to the same intensity at the low-energy peak. The asymmetry in the simulated no-charge-order spectrum is considerable and clearly not observed in the experimental data. We therefore conclude that (001) is dominated by B-site charge order.

As indicated by the LDA + U band structure calculations, the charge modulation is rather in the t_{2g} count and not so much in the total d-electron count on the Fe sites. The reason is that modulation of the t_{2g} occupation is partially screened by charge transfer from oxygen neighbors to the empty e_g states [6]. For the t_{2g} states LDA + U finds that the modulation amounts to 0.7 electron, i.e., almost a full electron, while the total 3d modulation is only 0.23 electrons. As a check of our analysis, in which we have used the cluster model calculations [20] to simulate the XAS spectra in Fig. 3, we have looked at the t_{2g} occupations in the FeO_6 clusters constructed for the Fe^{2+} and Fe^{3+} ions: we find a t_{2g} occupation difference of 0.86 electron. This is also close to unity, i.e., very consistent with the LDA + U results. In fact, one must expect the cluster calculation to slightly overestimate the occupation difference since intercluster hopping or band-formation effects are not included.

Summarizing, using resonant soft-x-ray diffraction at the Fe-$L_{2,3}$ threshold from a film of magnetite grown on stepped MgO we were able to establish directly that there is t_{2g} orbital order on the B-site Fe^{2+} ions as predicted by LDA + U calculations, and that this is reflected in the existence of the $(00\frac{1}{2})$ diffraction peak. We also showed that charge order of the B-site ions is the dominant reason for the appearance of the (001) diffraction peak, thereby settling the contradicting claims from Fe K-edge resonant diffraction studies.

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[1] D.C. Matthis, *Theory of Magnetism* (Springer, Berlin, 1981).
[2] E.J.W. Verwey, Nature (London) **144**, 327 (1939).
[3] N. Tsuda, K. Nasu, A. Yanase, and K. Siratori, *Electronic Conduction in Oxides* (Springer, Berlin, 1991).
[4] J.P. Wright, J.P. Attfield, and P.G. Radaelli, Phys. Rev. Lett. **87**, 266401 (2001).
[5] J.P. Wright, J.P. Attfield, and P.G. Radaelli, Phys. Rev. B **66**, 214422 (2002).
[6] I. Leonov, A.N. Yaresko, V.N. Antonov, M.A. Korotin, and V.I. Anisimov, Phys. Rev. Lett. **93**, 146404 (2004).
[7] H.-T. Jeng, G.Y. Guo, and D.J. Huang, Phys. Rev. Lett. **93**, 156403 (2004).
[8] G. Subías, J. García, J. Blasco, M.G. Proietti, H. Renevier, and M.C. Sánchez, Phys. Rev. Lett. **93**, 156408 (2004).
[9] E. Nazarenko, J.E. Lorenzo, Y. Joly, J.L. Hodeau, D. Mannix, and C. Marin, Phys. Rev. Lett. **97**, 056403 (2006).
[10] D.J. Huang, H.-J. Lin, J. Okamoto, K.S. Chao, H.-T. Jeng, G.Y. Guo, C.-H. Hsu, C.-M. Huang, D.C. Ling, W.B. Wu, C.S. Yang, and C.T. Chen, Phys. Rev. Lett. **96**, 096401 (2006).
[11] I.S. Elfimov, V.-I. Anisimov, and G.A. Sawatzky, Phys. Rev. Lett. **82**, 4264 (1999).
[12] C.W.M. Castleton and M. Altarelli, Phys. Rev. B **62**, 1033 (2000).
[13] K.J. Thomas, J.P. Hill, S. Grenier, Y.-J. Kim, P. Abbamonte, L. Venema, A. Rusydi, Y. Tomioka, Y. Tokura, D.F. McMorrow, G. Sawatzky, and M. van Veenendaal, Phys. Rev. Lett. **92**, 237204 (2004).
[14] C. Schüßler-Langeheine, J. Schlappa, A. Tanaka, Z. Hu, C.F. Chang, E. Schierle, M. Benomar, H. Ott, E. Weschke, G. Kaindl, O. Friedt, G.A. Sawatzky, H.-J. Lin, C.T. Chen, M. Braden, and L.H. Tjeng, Phys. Rev. Lett. **95**, 156402 (2005).
[15] W. Eerenstein, T.T.M. Palstra, T. Hibma, and S. Celotto, Phys. Rev. B **66**, 201101(R) (2002).
[16] J.-H. Park, Ph.D. thesis, University of Michigan, 1994.
[17] P. Kuiper, B.G. Searle, L.-C. Duda, R.M. Wolf, and P.J. van der Zaag, J. Electron Spectrosc. Relat. Phenom. **86**, 107 (1997).
[18] J. Chen, D.J. Huang, A. Tanaka, C.F. Chang, S.C. Chung, W.B. Wu, and C.T. Chen, Phys. Rev. B **69**, 085107 (2004).
[19] B.L. Henke, E.M. Gullikson, and J.C. Davis, http://www.cxro.lbl.gov/optical_constants/sf/fe.nff.
[20] A. Tanaka and T. Jo, J. Phys. Soc. Jpn. **63**, 2788 (1994).