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To cite this version:

H Elnaggar, Ph Sainctavit, A. Juhin, S. Lafuerza, F. Wilhelm, et al.. Non-collinear ordering of the orbital magnetic moments in magnetite. Physical Review Letters, American Physical Society, In press. hal-02349259

HAL Id: hal-02349259
https://hal.archives-ouvertes.fr/hal-02349259

Submitted on 5 Nov 2019

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Non-collinear ordering of the orbital magnetic moments in magnetite

H. Elmaggar,1,a Ph. Sainctavit,2 A. Juhin,2 S. Lafuerza,3 F. Wilhelm,3 A. Rogalev,3 M.-A. Arrio,2 Ch. Brouder,2 M. van der Linden,1 Z. Kakol,4 M. Sikora,5 M. W. Haverkort,6 P. Glatzel,3 and F. M. F. de Groot1,4

1Debye Institute for Nanomaterials Science, Utrecht University, 3584 CA Utrecht, The Netherlands.
2Institute de Minéralogie de Physique des Matériaux et de Cosmomachie, Sorbonne Université, CNRS, 4 place Jussieu, Paris, France.
3European Synchrotron Radiation Facility, CS2B 02000 Grenoble Cedex 9, France.
4Faculty of Physics and Applied Computer Science, AGH University of Science and Technology, Mickiewicza 30, 30-059 Krakow, Poland.
5Academic Centre for Materials and Nanotechnology, AGH University of Science and Technology, Mickiewicza 30, 30-059 Krakow, Poland.
6Institut für Theoretische Physik, Universität Heidelberg, Philosophenweg 19, 69120 Heidelberg, Germany.

(Dated: July 16, 2019)

The magnitude of the orbital magnetic moment [1–9] and its role as a trigger of the Verwey transition [10–17] in the prototypical Mott insulator, magnetite, remain contentious. Using 1s2p resonant inelastic X-ray scattering magnetic linear angular distribution (RIXS-MLAD), we prove the existence of non-collinear orbital magnetic ordering and infer the presence of dynamical distortion creating a polaronic precursor for the metal to insulator transition. These conclusions are based on a subtle angular shift of the RIXS-MLAD spectral intensity as a function of the magnetic field orientation. Theoretical simulations show that these results are only consistent with non-collinear magnetic orbital ordering. To further support these claims we perform Fe K-edge X-ray magnetic circular dichroism (XMCD) in order to quantify the iron average orbital magnetic moment.

Magnetite ([Fe3+][Fe3+, Fe2+]O4) is the most abundant iron bearing mineral on Earth and it finds many applications in areas such as palaeomagnetism, medicine, data recording, and engineering [18]. Ever since Verwey’s pioneering work [19], an immense amount of research has been dedicated to Fe3O4 in view of its importance as a reference for systems exhibiting the metal to insulator transition [11, 20, 21]. In Fe3O4, the Verwey transition occurs at TV ~ 125 K and results in a spontaneous change of both, the lattice symmetry and the electric conductivity. Above TV, Fe3O4 has a cubic inverse spinel crystal structure containing two different Fe sites. Fe3+ ions reside in tetrahedral (T) interstices (the A sites) while both Fe2+ and Fe3+ ions reside in octahedral (O) interstices (the B sites). The A and B sublattices are antiferromagnetically coupled while the Fe ions in the same sublattice are ferromagnetically coupled (Fig. 1a).

In ferromagnets and ferrimagnets, the spin and orbital magnetic moments of the transition metal ions can be directly quantified by applying the sum rules on the L2,3 XMCD signal [22]. In spite of the great success of sum rules, the experimental and analysis procedures were shown to be prone to huge uncertainties due to surface effects [1]. Orbital magnetic moments as small as 0.01 µB [2] and as large as 0.33 µB [3] were reported for Fe3O4. In addition, large orbital magnetic moment contributions that are of equal absolute values but with antiparallel coupling between the Fe A and B sublattices were also suggested [4] (for a unit formula of Fe3O4: FeB µB = 1 µB and FeA µL = −1 µB). A summary of the orbital and spin magnetic moments reported in literature using various techniques is shown in Fig. S1. These large discrepancies regarding an essential quantity to many Mott insulators [23] ask for a new approach.

In this work we employed a combination of Fe K-edge XMCD and 1s2p RIXS-MLAD measurements to investigate the orbital magnetic moment of Fe in Fe3O4. Experiments at the Fe K-edge (1s → 3d + 4p excitations) have a probing depth of few µm and hence surface effects are negligible offering a valuable advantage over L2,3-edge XMCD measurements. We quantified the average orbital magnetic moment by performing K-edge XMCD. The accurately measured 1s2p RIXS-MLAD signal was used to determine the average square orbital magnetic moment which complements the average quantity obtained from XMCD. A difference between the orbital magnetic moments predicted by both experiments indicates compensation: the orbital magnetic moments of the Fe ions must be either antiparallel or non-collinear.

Guided by theoretical calculations, we show that the only possibility to explain both of our experimental results is the existence of a non-collinear magnetic orbital ordering that can tilt the orbital magnetic moment as large as 82° away from the spin magnetic moment. We proposed a model for this non-collinear orbital magnetic ordering and inferred the presence of a dynamical distortion related to the X3 phonon mode in the high temperature phase. Our model imposes strong restrictions on the candidate mechanisms for the Verwey transition [10, 24].

We investigated highly stoichiometric (001), (110) and (111) Fe3O4 single crystals at room temperature. The average orbital magnetic moment projected along the magnetic field direction can be quantified by performing Fe K pre-edge XMCD measurements [22]. Three main dichroic features can be seen at E∥ = 7112.7 eV, E⊥ = 7114 eV and E⊥⊥ = 7115.1 eV with only significant angular de-
The experimental XMCD signal and its angular dependence can be best interpreted to arise from a partially quenched orbital magnetic moment at the formal $\text{Fe}^{3+}$ ions. An excellent agreement between the calculated and the experiment is observed (compare spectra labelled Exp and Calc 1 in Fig. 1b). This partial quenching is a result of the octahedral symmetry accompanied by a small trigonal distortion ($D_3 = 67 \pm 10 \text{meV}$). The Fe environment is not perfectly $O_h$ since the point group symmetry of the B site is rhombohedral ($D_{3d} = 3m$).

We found that the average orbital magnetic moment is $0.26 \pm 0.03 \mu_B$ per unit formula of $\text{Fe}_2\text{O}_4$. It is important to note that feature I is theoretically predicted to be completely suppressed in the case that $\mu_L = 0 \mu_B$ (see Fig. 1b Calc 2) strongly supporting the presence of a finite orbital magnetic moment in bulk $\text{Fe}_2\text{O}_4$.

To investigate possible non-collinearity of the orbital magnetic moment, we performed comprehensive $1s^22p$ RIXS-MLAD measurements. This complements the average projected result obtained from XMCD. The RIXS-MLAD was measured by rotating the sample about the incident wave-vector direction ($\mathbf{k}_{\text{inc}}$) aligned with the $[110]$ direction (refer to Fig. 2a). This implies that the RIXS-MLAD includes contributions from both structural and magnetic dichroism signals. We focus in this work on the effect of the magnetic dichroism on the linear angular distribution of RIXS. We initially measured the RIXS-MLAD with the magnetic field nearly parallel to $\mathbf{k}_{\text{inc}}$ as a reference measurement. In this case the magnetic field is oriented along a high symmetry crystallographic direction and the angle between the linear incident polarization ($\epsilon_{\text{inc}}$) and the magnetic field nearly does not change as a function of the sample rotation. These choices simplify the angular dependence and serve as a benchmark for the full 360° experimental (theoretical) angular dependence of the three main spectral features can be seen in Fig. 2c. The angular dependence is twofold and a $90^\circ$ angular shift is observed between the first feature and both the second and third features. A first explanation of the general angular dependence can be provided by analysing the $1s^33d^7$ intermediate states. Projections of the intermediate states associated with non-zero transition matrix elements onto cubic crystal field to analyze the RIXS spectra.

Although the experimental RIXS planes measured in the horizontal ($\phi = 0^\circ$) and vertical ($\phi = 90^\circ$) configurations show a broad single pre-edge peak (Fig. S9a, angular shifted w.r.t. the second and third features and b), it is possible to identify three main features in responding to excitations dominantly into the $e_g$ orbitals.
An energy shift of ~ 0.2 eV was found between the two subclasses.

We interpret the formation of these two subclasses as a result of a dynamical Jahn-Teller distortion at the Fe B sites. The magnitude of the static trigonal distortion lies close within the phonon energies of Fe$_3$O$_4$ [30, 31], the magnetic exchange interaction and spin-orbit coupling, leading to a situation where electron-phonon interaction, dynamical Jahn-Teller and Kugel-Khomskii interactions all play a role in determining the low energy state. We treat this dynamical variation of the distortion in a first approximation as a small change in the bond lengths over the four sites giving rise to a small energy shift. This is a reasonable approximation because the electronic structure adapts almost instantaneously to the crystallographic structure (i.e. the electronic motion is much faster than the nuclear motion). In this case, the effect of phonons could be simulated as a static distribution of bond lengths leading to a shift in energy between the four sites. This is a common practice in XAS theory as can be found in the paper by Nemeu et al. [32] where thermal fluctuations are simulated by a well chosen series of configurations. Although theoretical studies that treat simultaneously the electronic and the lattice degrees of freedom are required to comprehend the precise effect of the dynamical distortion, we point out that numerous theoretical works concluded the essential role of the strong electron-phonon coupling in the presence of strong electron correlations leading to dynamical Jahn-Teller distortion and the creation of polarons [33–36]. In particular, Piekarcz et al. [33, 34] identified the highly dispersive $X_3$ phonon mode as a primary order parameter of the Verwey transition which splits the four Fe B sites into two subclasses. This agrees rather well with our observation.

Theoretical calculation of the angular dependences are presented in Fig. 3c. The model captures the essential aspects of the angular dependence and in particular the 10° angular shift of the maximum intensity. The angular shift ($\Omega$) quantified by fitting the angular dependence to a $\cos^2(\phi + \Omega)$ of the three features is reported in Tab. S4. The anisotropy of the angular dependence is not well reproduced, likely due to a small misalignment of the magnetic field that has not been included in the calculations (see Supplementary). It is now important to highlight the key ingredients responsible for this angular shift. The first factor is the static trigonal distortion.

The relative orientation of the exchange interaction with respect to the local trigonal distortion varies between the four sites leading to anisotropy effects and generates four sub-classes.

The presence of four non-equivalent Fe B sites in the non-equivalent Fe B sites. The theoretical RIXS-MLAD for the four sites are shown in Fig. S12. The second factor is the effect of dynamical distortion that produces two subclasses of the Fe B sites, namely, sites 1 and 2 forming one subclass and sites 3 and 4 forming the other (see Fig. 4b). It is only when the dynamical distortion effect is taken into consideration that the experimental RIXS-MLAD angular shift can be reproduced (see Fig. S13).
ordering arising from the interplay between trigonal dis-
tortion effects (static and dynamical), spin-orbit coupling
and exchange interaction at the formal Fe$^{2+}$ ions. The
orbital magnetic moment per Fe$^{2+}$ ion is predicted to
have a strong dependence on the magnetic field in con-
trary to the spin magnetic moment which is collinear to
the magnetic field. Fig. 4 illustrates the dependence of
the orbital magnetic moments on the orientation of the
magnetic field when we rotate it about the [110] direc-
tion for the four sites independently. Large non-collinear
orbital contributions that tilt as much as 82° away from
the magnetic spin moment orientation are present. Fur-
thermore, the collinear contribution per site ranges from
0 to 150% of the average quantity as a function of the
orientation of the field. Remarkably, the average orbital
magnetic moment for the four sites remains nearly con-
stant (Fig. 4f).

The large discrepancies regarding the orbital magnetic
moment of Fe in Fe$_3$O$_4$ can now be understood in light of
the large non-collinear contribution, the site dependency
and the magnetic field angular dependence. Experiments
sensitive to the effective orbital magnetic moment yield
different results to those sensitive to the projected av-
"arage quantity, or the average of the squared projected
quantity. Moreover, variations as a function of the ori-
entation of the magnetic field are expected for experi-
ments sensitive to the non-averaged quantity. This or-

FIG. 4. The angular dependence of the orbital momentum ($M_L$) of the four Fe$^{3+}$ ions as a function of the rotation of the magnetic field ($B_{Field}$) about the [110] orientation. (a) Sketch of the rotation geometry. The angular dependence of the orbital magnetic moment projected along the direction of $B_{Field}$ and two perpendicular non-collinear contributions are shown in panel (b), (c), (d) and (e). The average orbital magnetic moments of the four Fe$^{3+}$ ions are shown in (f).

...ing and assisting us to use the program CTM4DOC. We thank A. Bosak and M. Hussein for their help with the X-ray diffraction measurements and sample characterisation. Many thanks to R.-P. Wang for the discussions and suggestions. We acknowledge financial support from COST Action MP1306 (EUSpec). M. Sikora acknowledges support from National Science Center of Poland (2014/14/E/ST3/00026). This work was financed by the ERC advanced Grant XRAYonACTIVE No. 340279.

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