Spin moment over 10-300 K and delocalization of magnetic electrons above the Verwey transition in magnetite

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In order to probe the magnetic ground state, we have carried out temperature dependent magnetic Compton scattering experiments on an oriented single crystal of magnetite (Fe\textsubscript{3}O\textsubscript{4}), together with the corresponding first-principles band theory computations to gain insight into the measurements. An accurate value of the magnetic moment $\mu_S$ associated with unpaired spins is obtained directly over the temperature range of 10-300K. $\mu_S$ is found to be non-integral and to display an anomalous behavior with the direction of the external magnetic field near the Verwey transition. These results reveal how the magnetic properties enter the Verwey energy scale via spin-orbit coupling and the geometrical frustration of the spinel structure, even though the Curie temperature of magnetite is in excess of 800 K. The anisotropy of the magnetic Compton profiles increases through the Verwey temperature $T_v$ and indicates that magnetic electrons in the ground state of magnetite become delocalized on Fe B-sites above $T_v$.

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Magnetite was known to the ancient Greeks and its “magical” properties have been a source of fascination for millenia. In recent years, magnetite has become an archetype of complex correlated materials which display competing orders and interesting charge and orbital ordering effects in a solid state setting. This complexity is accentuated by the expectation that Fe in the inverse spinel crystal structure of magnetite will assume a mixed valence. Simple chemical arguments suggest that on the tetrahedral sites Fe occurs as ferric cations (Fe\textsuperscript{3+}), while the octahedral sites are populated equally by ferric and ferrous (Fe\textsuperscript{2+}) cations. Also, magnetite is important for technological applications because it magnetizes spontaneously like a ferromagnet but possesses low electrical conductivity so that it can be used at high frequencies where eddy currents make the use of iron impossible.

Magnetite has also drawn considerable attention because it displays a first order phase transition—the Verwey transition—at $T_v=120K$, below which the resistivity increases by a factor of $\sim100$\textsuperscript{[1, 2]} \textsuperscript{[1, 2]}. The earliest interpretation was that this is an order-disorder transition where the Fe\textsuperscript{2+} and Fe\textsuperscript{3+} cations on the octahedral sites become ordered below $T_v$. However, this interpretation and various pictures of electronic ordering on different Fe sites still are quite hotly debated issues \textsuperscript{[3, 4, 5, 6, 7, 8]}. Band computations based on the local density approximation (LDA) show that the bonding electrons are shared in states that cannot be assigned solely to iron or oxygen \textsuperscript{[8, 9, 10]} and predict magnetite to be a half-metal above $T_v$ where the minority spin electrons are conducting, but the majority spins are insulating.

It is clear that the behavior of magnetic Fe 3$d$ electrons in magnetite is the key to understanding the properties of this material. With this motivation, we have carried out a magnetic inelastic x-ray scattering investigation of an oriented single crystal of magnetite in the deeply inelastic (Compton) regime. In this way we obtain a direct measurement of the magnetic moment associated with unpaired spins in magnetite over the wide temperature range of 10–300 K. Notably, magnetic Compton scattering (MCS) is a genuine bulk probe which can detect the spin magnetic moment ($\mu_S$) with a sensitivity of $\sim0.1\%$ (1 $\mu_B$ per 1000 electrons) \textsuperscript{[11]}. Previous estimates of $\mu_S$ are less direct, being based on the application of sum rules for extracting orbital moments ($\mu_O$) from x-ray magnetic circular dichroism (XMCD) spectra \textsuperscript{[12]}. Moreover, a recent XMCD study \textsuperscript{[13]} of magnetite reports a nearly vanishing $\mu_O$ and an integral value of $\mu_S$, which is in sharp contrast to the earlier XMCD results \textsuperscript{[12]} of a large value of $\mu_O$ and a non-integral $\mu_S$ \textsuperscript{[14, 15]}. It is important therefore to determine independently whether $\mu_S$ is integral or not and $\mu_O$ is small or large in order to understand the role of spin-orbit coupling in magnetite.

An MCS experiment is well known to couple directly to the wavefunction of magnetic electrons in the ground state of the system \textsuperscript{[11, 13, 17]}. The present MCS measurements over the 10-300K range thus allow us to compare the characteristics of the magnetic states in magnetite above and below the Verwey transition. In particular, we show that the anisotropy of the MCS spectrum be-
comes significantly larger as the system goes through $T_v$. In order to help interpret our measurements, we report extensive computations of the magnetic momentum density within the first-principles band theory framework. These and other model computations enable us to deduce that the anisotropy of the MCS provides a handle for ascertaining the localized vs delocalized nature of the magnetic electrons in the ground state of magnetite.

In an MCS experiment one measures the magnetic Compton profile (MCP), $J_{mag}(p_z)$, for momentum transfer along the scattering vector $p_z$, which is defined by

$$J_{mag}(p_z) = J^\uparrow(p_z) - J^\downarrow(p_z),$$  

where $J^\uparrow$ ($J^\downarrow$) is the majority(minority) spin Compton profile. $J_{mag}$ can be expressed in terms of a double integral of the spin density, $\rho_{mag}(p)$:

$$J_{mag}(p_z) = \int \int \rho_{mag}(p) dp_x dp_y,$$

where $\rho_{mag}(p) \equiv \rho^\uparrow(p) - \rho^\downarrow(p)$ is the difference of the majority and minority spin densities. We emphasize that the area under $J_{mag}(p_z)$ gives the spin moment $\mu_S$. In contrast, the information about the nature of the ground state wavefunction is described by the shape of $J_{mag}(p_z)$.

Experiments were performed on beamline 11-B at the Advanced Photon Source [18] using an elliptical multipole wiggler to generate circularly polarized photons. A high quality single crystal of Fe$_3$O$_4$ was used and MCPs were measured along the [100] and [110] crystal directions at temperatures of 10K, 100K, 140K, and 300K. The Verwey transition temperature of the sample was determined via resistivity measurements to be 120 ± 1 K. The incident photon energy was 125 keV. The scattering angle $\theta$ was 170°. All measurements were made under an external magnetic field of 7T oriented along the direction of the scattering vector. The momentum resolution is estimated to be 0.4 a.u. (full-width-at-half-maximum). Magnetic calibration measurements [18] were performed using a crystal of Fe oriented along [110].

The electronic structure was computed for the high temperature (Fd3m) phase of Fe$_3$O$_4$ within an all-electron, fully charge and spin self-consistent LDA-based band theory framework [19]. All computations were carried out to a high degree of accuracy, e.g., the crystal potential was converged to better than $10^{-5}$ Ry. Our band structure is in good overall accord with the few available studies [8, 9, 10]. Various calculations argue on a half-metallic ferromagnetic band structure with the Fermi level crossing the minority spin $t_{2g}$ bands originating from the octahedral Fe sites. The computed band structure and wavefunctions were used to obtain spin-resolved momentum densities $\rho^\uparrow(p)$ and $\rho^\downarrow(p)$. These quantities were computed over a fine mesh of $855 \times 10^6$ points within a sphere of radius $\sim 13$ a.u. in $p$ space [20] in order to properly account for the fine structure in $\rho^\uparrow$ and $\rho^\downarrow$, and provided the dataset from which various projections of the spin-resolved momentum density and the MCPs along the high symmetry directions were computed.

The experimental spectra are summarized in Fig. 1. The area under the MCPs yields the magnetic moment of unpaired spins (per formula unit) obtained from the area under the MCP [11].

![FIG. 1: (Color online) $J_{mag}(p_z)$ for $p_z$ along [100] (blue dots) and [110] (red dots) as a function of temperature. Different datasets are offset vertically with respect to one another. Symbol size is representative of error bars. Inset gives the magnetic moment of uncompensated electronic spins (per formula unit) obtained from the area under the MCP [11].](image)

In general, band theory can accommodate non-integral $\mu_S$ since bands can be occupied partially. But, if spin is assumed to be a good quantum number, it is straightforwardly argued that $\mu_S$ in a half-metallic system must also be strictly integral. However, a non-integral $\mu_S$ value can be obtained if the spin-polarized band calculation is supplemented by spin-orbit interactions. The spin-orbit coupling has been estimated to be of the order of 10 meV [22], so that we would expect a substantial orbital moment due to Fe$^{2+}$. 
Bulk magnetization measurements in magnetite reveal a significant magneto-crystalline anisotropy. This anisotropy is relatively small above $T_v$ with [111] being the easy axis, while below $T_v$, the anisotropy is larger with [001] being the easy axis. However, the maximum saturation field is about 2T, so that under the field of 7T used in the present measurements, we would not normally expect anisotropic effects. Therefore, changes in the spin moment with the direction of the magnetic field seen in the inset to Fig. 1 which are especially striking at 140K, are anomalous and do not fit within the standard picture. The origin of this anomaly is unclear, but it may be related to the effect of geometrical frustration on magnetic properties above $T_v$ [29]. Notably, Ref. [29] considers a Hamiltonian for the pyrochlore B lattice with a spin-orbit interaction. In this model, several complex orbital ordered states with noncollinear orbital moments are found as a possible ground state for the high-temperature phase. This degeneracy of the lowest energy states can be broken by an external magnetic field in a manner which depends on the field direction. Since the energy differences between these states are very small, a magnetic field of 7T can be sufficient to switch between the states [28]. Further MCS measurements of the spin moment in magnetite over a range of temperatures around $T_v$ should prove worthwhile in this connection. Here a note should also be made of the role of magnons, which will reduce the moment below the canonical value of 4 $\mu_B$ at high temperatures [27].

Some insight into the shape of the MCPs can be obtained through the LDA-based first-principles band theory computations. This is illustrated in Fig. 2 which shows a good level of agreement between the shapes of the computed and measured [110] MCPs. The LDA correctly reproduces the overall width of the measured MCP as well as the pronounced peak at 1.3 a.u. The shallow bumps in the experimental MCP at momenta between 2 – 3 a.u. and 4 – 5 a.u. are similar to features in the theoretical MCP. This fine structure is the hallmark of interference terms that cannot be explained within a purely atomic picture.

In order to extract wavefunction localization features, we now discuss the anisotropy of the MCP defined as the difference between the two directional MCPs [28],

$$\Delta J_{\text{mag}} = \left(J_{\text{mag}}^{[100]}\right) - \left(J_{\text{mag}}^{[110]}\right),$$

where the brackets $\langle...\rangle$ denote an average over temperature. $\left(J_{\text{mag}}^{[100]}\right)$ is normalized at each temperature to the integral of the corresponding $J_{\text{mag}}^{[110]}$, so that $\Delta J_{\text{mag}}$ integrates to zero. The average $\left(J_{\text{mag}}^{[100]}\right)$ provides a temperature-independent "background" for highlighting changes in the shape of $J_{\text{mag}}^{[110]}$ as a function of temperature [29].

Fig. 3 which focuses on the 140K and 300K data above the Verwey transition, shows that although the LDA reproduces the overall features in the measured anisotropy, the amplitude of the anisotropy given by the LDA is too large by about a factor of 4 (note that plotted LDA curve is scaled down). In order to gain insight into the shape and amplitude of $\Delta J_{\text{mag}}$, we have considered this quantity for a variety of clusters of Fe A- and B-site atoms and their nearest neighbor (NN) Fe atoms, using linear combinations of Slater type orbitals (STOs) where the cluster wavefunction is constructed by allowing STOs on NN Fe atoms to mix via a small admixture parameter $f$ [30]. Our results show that the shape of the experimental $\Delta J_{\text{mag}}$, including the location of the peak at 1.12 a.u., can only be reproduced for a B-site Fe cluster in which the NN Fe atoms are situated at a NN distance $d_{BB}=5.61$ a.u. (2.97 Å) along the [110] direction [31]. In this case, the momentum wavefunction obtained by Fourier transforming the cluster wavefunction contains an oscillating factor of $[1+2f\cos\{d_{BB}(p_x+p_y)/\sqrt{2}\}]$, which yields the correct shape, and as Fig. 3 shows, for $f = 0.1$ the computed curve (dashed) gives a good agreement in shape and amplitude with the 140K and 300K measurements in the low momentum region. We note that $\Delta J_{\text{mag}}$ is rather insensitive to the inclusion of covalency with O atoms, and furthermore, the lack of oscillations in the cluster model at $p_z > 2$ a.u. is related to inaccuracy in our STOs near the nucleus and is of little interest in the present context of solid state effects.

In order to delineate the temperature dependence of $\Delta J_{\text{mag}}$ the results for the 10K and 100K datasets below $T_v$ are presented in Fig. 4. The peak located at
110 mag decreases with temperature. In other words, the Verwey transition parameter $f$ also increases systematically in going from the 10K to the 300K dataset. Interestingly, this behavior of $A$, the parameter $f$ also increases with temperature. In other words, the Verwey transition is accompanied by a change in the character of the ground state wavefunction such that the wavefunction becomes significantly more delocalized on Fe B-sites above $T_v$. Notably, the present analysis suggests that the B-site is involved in the change in valence across the Verwey transition as in Ref. [35], and not the A-site as argued in Ref. [36] recently. Positron annihilation experiments [37, 38], which also give information on spin-resolved momentum density, have revealed covalency effects between Fe and O atoms but have failed to detect significant changes at $T_v$. This result however may reflect the tendency of the positron to sample mostly O-ions and interstitial spaces rather than the Fe-ions.

In conclusion, we have presented magnetic Compton scattering measurements on a magnetite single crystal, together with corresponding predictions of the MCP within the conventional band picture. An accurate value of the unpaired spin moment $\mu_S$ is thus obtained directly over a wide temperature range. For example, at 10K $\mu_S$ has clearly a non integer value of $3.54 \pm 0.05 \mu_B$ per formula unit for the magnetic field along [100] demonstrating a non vanishing spin-orbit coupling. The ground state of magnetite is shown to be remarkably sensitive to the direction of the external magnetic field around the Verwey transition and to display an anomalous magnetic moment, which may be a manifestation of a large degeneracy and associated geometrical frustration in the spinel lattice. The amplitude of the anisotropy of the MCP is shown to increase with temperature. We argue on this basis that the ground state wavefunction in the system...
becomes delocalized on Fe B-sites above $T_\text{p}$.

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[29] We have also obtained $\Delta J_{mag}$ where the average $\langle J_{mag}^{[100]} \rangle$ was taken over just the two high (140K and 300K) or the two low (10K and 100K) temperature datasets. The resulting anisotropy is quite similar to that shown in Figs. 3 and 4 where all four datasets are employed in the averaging process, indicating that our use of $\langle J_{mag}^{[100]} \rangle$ as background does not introduce any spurious features in the anisotropy defined by Eq. 3.
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[32] The error in our values of f is estimated to be $\pm 0.02$.
[33] The temperature dependence of $A$ shown in Fig. 5 is not sensitive to the value of the cut-off momentum $p_{max}$.
[34] The factor of 1/2 in Eq. 4 accounts for the presence of positive excursions in $\Delta J_{mag}(p)$ (in particular the peak at 1.12 a.u.) which involve the same area as the negative contributions.
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![FIG. 5: Amplitude $A$ of the MCP anisotropy obtained from Eqs. 3 and 4 as a function of temperature.](image)
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