Spin and orbital moments in Fe_3O_4

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We report a study of the spin moment in Fe_3O_4 as a function of temperature using spin-dependent Compton scattering. Magnetic Compton profiles and spin moment values were obtained either side of the Verwey transition for applied magnetic fields of 2.5 and 7 T. The orbital moments, determined by comparison with bulk magnetometry, are almost fully quenched. No evidence of any anomalies in the spin or orbital moments at the Verwey transition was observed. The magnetic Compton profiles have the characteristic shape for Fe 3*d* electrons at all temperatures with no changes in the degree of anisotropy across the Verwey transition. Our data are consistent with the highly spin-polarized electronic structure expected for bulk Fe_3O_4.

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Owing to its electronic and magnetic properties, Fe_3O_4, or magnetite, has been the subject of research for many years, and most recently because of its potential for use in spintronic devices. Fe_3O_4 is ferrimagnetic with a Curie temperature of 850 K. At room temperature it has a cubic inverse spinel structure, AB_2O_4, with the *A* site occupied by Fe^{3+} and the *B* sites having an equal mix of Fe^{3+} and Fe^{2+}. This straightforwardly leads to a simple model for the spins, with the *A* site contributing $+5\mu_B$, and the *B* sites contributing $-5\mu_B$ and $+4\mu_B$, respectively, resulting in a total spin moment of $4\mu_B$ and no orbital moment. Most interestingly, however, Fe_3O_4 exhibits a metal-insulator transition, widely known as the Verwey transition, at a temperature $T_V \approx 120$ K, below which the resistivity increases by 2 orders of magnitude.[1,2] This is accompanied by a transition to a low symmetry structure, the precise nature of which is still being discussed.[3–5] Above this transition, band-structure calculations predict that Fe_3O_4 should be a half metal, with conduction only associated with the minority spin electrons[6,7] and thus possess 100% spin polarization. Experimentally somewhat lower values have been reported [for example, 40% (Ref. 8) and 80% (Ref. 9)]. The proposed high spin polarization, together with the magnetoresistive properties, have generated interest in using Fe_3O_4 in various spintronic applications such as spin-polarized current injection.[10,11]

There are still conflicting reports concerning the magnetism, orbital ordering, and the degree of spin polarization in Fe_3O_4. For example, while charge and orbital ordering have been reported,[12–14] recent work suggests that charge order is not necessarily present.[5] A key issue, and one which has proven controversial, is that of the orbital magnetic moment. A number of studies have been performed to investigate the spin and orbital moments in Fe_3O_4. Most theoretical work is consistent with the picture of bulk Fe_3O_4 possessing a spin moment of $4\mu_B$ and very little orbital moment. Leonov[6] and Szotek[7] calculated the orbital moment to be $0.07\mu_B$ and $0.05\mu_B$, respectively, although these small values arise in part from the cancellation of larger orbital moments on the different Fe sites. However, the x-ray magnetic circular dichroism (XMCD) data of Huang *et al.*[15] indicated a large unquenched orbital moment of typically $0.67 \pm 0.07\mu_B$ (together with a spin moment $3.68 \pm 0.09\mu_B$) at all temperatures measured, both above and below the Verwey transition. Based on further experiments, Goering *et al.*,[16,17] suggested that this conclusion was erroneous, and that there was in fact a vanishingly small orbital moment with a spin moment of $3.8\mu_B$ on the Fe sites, although it should be noted that Huang *et al.*[18] stood by their conclusions. In their subsequent work, Goering *et al.*[19] demonstrated the importance of the surface state in these XMCD measurements, finding that the spin moment may be reduced by up to 50% from the bulk value. Although the O 2*p* states play an important role in the electronic structure, with evidence of their orbital ordering observed below T_V,[13] the magnetic moment associated with these states is generally calculated to be less than $0.1\mu_B$.[6]

There have been two recent reports of spin-polarized Compton scattering studies of magnetite, one of which addressed the issue of the spin and orbital moments.[20] The technique provides a measurement of the spin moment only and it is unambiguously sensitive to the bulk rather than the surface. The authors reported that they had found a significant orbital moment.[20] Specifically, at $T=10$ K and in a 7 T magnetic field, the spin moment was measured to be $3.54 \pm 0.05\mu_B$ and, using literature magnetization data, they inferred the orbital moment to be $0.51 \pm 0.05\mu_B$. These findings are largely consistent with those of Huang *et al.*,[15] rather than with the more recent work.[17] Furthermore, along the [100] crystallographic direction, they observed an enhanced spin moment at the Verwey transition temperature, with diminished moments along the two other directions measured. It was concluded that the ground state was sensitive to the direction of the applied magnetic field at temperatures near the Verwey transition. It is indeed known that cooling through the Verwey transition while applying a magnetic field may suppress the formation of different domains.[21] However, no signature of an anomaly in the net magnetization has been reported at T_V in bulk magnetization measurements or in the moments deduced from the XMCD data discussed above.

The results of a second, more recent spin-polarized

Compton scattering experiment are reported by Kobayashi *et al.*,[22] but without a discussion of the values of the spin and orbital moments. The authors reconstructed [from one-dimensional (1D) to two-dimensional] the spin density at both 300 and 12 K from measurements along six crystallographic directions in the (010) plane. A substantial redistribution of spin density was observed to occur between these temperatures and was attributed to the localization of minority-spin bands below the Verwey transition. In contrast to the study by Li *et al.*[20] and our current work, Kobayashi *et al.*[22] tackled the issue of twinning in the single crystals at temperatures below the Verwey transition by using a specially designed sample holder.

In this paper, we report a systematic spin-dependent Compton scattering study specifically of the spin and orbital magnetic moments of Fe_3O_4 and examine the previously reported anomaly at the Verwey transition[20] in detail. Measurements were made in applied magnetic fields of both 2.5 and 7 T. The spin moment was determined to be $\approx 4\mu_B$ for all temperatures and crystallographic directions, and there appears to be only a small orbital moment of $\leq 0.1\mu_B$. There was no evidence for a large orbital moment nor of any anomalies near T_V.

Magnetic Compton scattering is an ideal technique for studying spin moments. The 1D projection of the spin-polarized momentum density distribution is measured and the incoherent nature of Compton scattering means that all local and itinerant contributions to the spin moment are observed. It is important to note that the magnitude of the magnetic scattering observed straightforwardly provides an accurate value for the net spin moment of the sample. The orbital moment is not observed[23] and its value can be determined simply by comparison with a bulk magnetization measurement. The high x-ray energies used in the experiments, typically well above 100 keV, mean that the bulk electronic structure is measured. The Compton effect is observed when high-energy photons are inelastically scattered by electrons. The scattered photon energy distribution is Doppler broadened since the electrons have a finite momentum distribution. If the scattering event is described within the impulse approximation,[24] the measured Compton spectrum is directly related to the scattering cross section.[25] The Compton profile is defined as a 1D projection (onto the scattering vector) of the electron momentum distribution, $n(\mathbf{p})$, where the z direction is taken parallel to the scattering vector,

$$J(p_z) = \int\int n(\mathbf{p})dp_x dp_y. \tag{1}$$

The integral of $J(p_z)$ is taken over occupied electron states. If the incident beam has a component of circular polarization, the scattering cross section contains a term which is spin dependent.[26] The spin dependence is isolated by either flipping the direction of magnetization or the photon helicity parallel and antiparallel with respect to the scattering vector. Either method results in a *magnetic* Compton profile (MCP), $J_{mag}(p_z)$, that is only sensitive to the net spin moment of the sample, and is defined as the 1D projection of the spin-polarized electron momentum density,

$$J_{mag}(p_z) = \int\int [n^{\uparrow}(\mathbf{p}) - n^{\downarrow}(\mathbf{p})]dp_x dp_y. \tag{2}$$

Here $n^{\uparrow}(\mathbf{p})$ and $n^{\downarrow}(\mathbf{p})$ are the momentum densities of the majority- and minority-spin bands. Since the MCP is the difference between two measured Compton profiles, components arising from spin-paired electrons cancel, as do most sources of systematic error.

Because only those electrons that contribute to the spin moment of the sample contribute to the integral of this MCP, it is then possible to determine the spin magnetic moment. This can be done with knowledge of the scattering cross sections and the polarization of the incident x-ray beam. However, it is usually determined by comparison with a measurement, under the same experimental conditions, of a sample with known moment. Previous measurements in a range of other materials have shown that the magnitude of the spin moment of the system may be determined unambiguously, and by comparison with theoretical calculations, the band origin of the magnetic species in the system can be found.[27,28] In metals, features associated with the Fermi surface arising from bands crossing the Fermi level are even visible, as has been described by Dixon *et al.*[29]

The spin-polarized Compton profiles presented in our report were measured on the beam line BL08W at the SPring-8 synchrotron and on ID15 at the ESRF. The SPring-8 measurements were made using a superconducting solenoid to provide the applied magnetic field of 2.5 T which was reversed every 60 s in order to obtain the difference profile. An incident x-ray energy of 175 keV was used. The energy spectrum of the scattered flux was measured using a ten-element Ge detector at a mean scattering angle of 173°. The momentum resolution of the magnetic Compton spectrometer, taken as the full width at half maximum of the instrument response function, was 0.50 a.u. of momentum (where 1 a.u.$=1.99\times10^{-24}$ kg m s^{-1}). At the ESRF, an Oxford Instruments Spectromag cryomagnet was used to obtain fields of 7 T. Here a 13-element Ge detector was used. The incident energy of 220 keV and scattering angle of 172° resulted in a resolution of 0.44 a.u. In both experiments, the data were corrected for energy-dependent detector efficiency, sample absorption, and the relativistic scattering cross section. The profiles were then corrected for multiple scattering using the technique described by Felsteiner.[30]

In order to determine the spin moment from the experimental data, first the so-called flipping ratio, R, of the integrated Compton profiles was determined, where

$$R = \frac{\int J_{mag}(p_z)dp_z}{\int J(p_z)dp_z}. \tag{3}$$

The spin moment was then found by comparison with the flipping ratio for Ni, which was measured under the same conditions on both synchrotron beamlines. Since the spin moment of Ni ($0.56\mu_B$) is well known,[29] the spin moment of the sample being studied can be determined accurately. Although the background contribution cancels out for the mag-

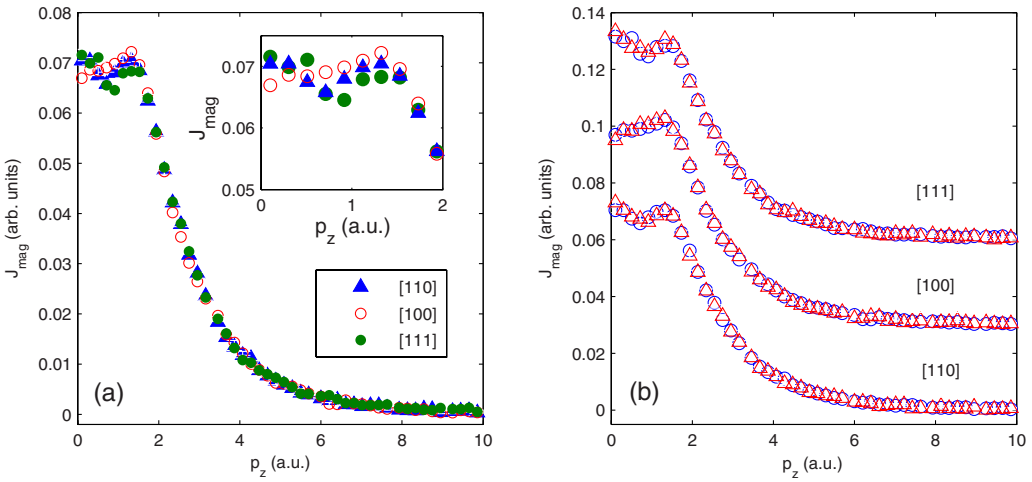

FIG. 1. (Color online) (a) The experimental MCPs at a temperature of $T=100$ K, for a magnetic field of 2.5 T applied along the [100], [110], and [111] crystallographic directions in Fe_3O_4, represented by open red circles, solid blue triangles, and solid green circles, respectively. The inset shows the low momentum region in more detail. (b) Profiles at $T=100$ K (blue circles) and $T=300$ K (red triangles) for the three directions. The statistical error is smaller than the size of the symbols.

netic profile, $J_{mag}(p_z)$, itself, it can still contribute to the charge scattering and hence affect the flipping ratio used to determine the spin moment. Hence, when calculating the spin moment, sources of systematic error, such as changes in the degree of circular polarization of the incident x rays, and especially background scattering contributions must be considered. This is important for comparing calculated spin moments measured for different crystallographic directions, and especially for different temperatures, where any sample movement in the cryostat must be accounted for. Each of our measurements was carefully setup to ensure the scattering geometry was identical, and several Ni measurements were made both at SPring-8 and at the ESRF during the experiments in order to ensure consistency.

While the objective of our experiments was to address the issue of the spin and orbital moments in Fe_3O_4, in light of Kobayashi's recent paper[22] we first discuss the shape and anisotropy of the spin-dependent Compton profiles. Examples of our results are presented in Fig. 1, measured in a field of 2.5 T at SPring-8. The profiles have the characteristic distribution expected for Fe 3*d* electrons in all cases. Figure 1(b) shows the temperature dependence of the profiles and little change in the anisotropy at different temperatures. There is a small degree of anisotropy at low momentum, which is typical of 3*d* ferromagnets. However, the main 3*d* contribution to the profiles, for momentum values greater than 2 a.u. is unchanged.

There are a number of subtle, yet significant differences between our experimental data sets and those of Li *et al.* and Kobayashi *et al.* Our data agree well with those of Kobayashi at low temperature, in spite of the fact that our sample would most likely have been twinned at low temperatures. Specifically, in the region of $p_z=0$, we observe a "dip" in the [100] profile and a small peak in the [110] direction. However, in Li *et al.*, a peak was observed for both directions. Indeed, below T_V they observe very little anisotropy. At 300 K both our data and those of Li *et al.* show the same features observed below T_V, albeit with some subtle differences in Li *et al.*'s data. However, Kobayashi *et al.* observed a significantly different MCP along the [100] (and at four angles between [100] and [110]) at 300 K with a very pronounced dip appearing. Along the [110] direction (and for projections at 9° and 18° toward the [110]) they, like us, observed little change with temperature. The distinct change in anisotropy at 300 K was attributed, by Kobayashi *et al.*,[22] to a delocalization of the minority-spin band electrons at high temperature. The reason for the difference is not clear but our data do not show evidence for the significant change in localization of the spin moment that they observed. It should also be noted that this significant discrepancy between the results actually occurs in the cubic phase, where twinning is not relevant.

Now we turn to the spin and orbital moments in Fe_3O_4. Our data for the spin moments measured at $B=2.5$ T are presented in Fig. 2 as a function of temperature (near T_V) for the [100], [110], and [111] crystallographic directions. The mean spin moment was found to be $3.98\pm0.03\mu_B$ with no significant directional or temperature variation. The bulk magnetic moment in the sample was $4.09\pm0.14\mu_B$ at this field [the bulk moment as measured in the superconducting quantum interference device (SQUID) was essentially saturated for fields above 1 T]. The error associated with this value is dominated by the systematic error in the SQUID measurement due to inherent uncertainties in calibration, rather than the much smaller statistical point-to-point accuracy. Hence the orbital moment was determined to be $0.11\pm0.14\mu_B$. The data show clearly that there is no indication of any anomaly in the spin and orbital moments near the Verwey transition for any crystallographic direction in the sample. This is again consistent with the SQUID magnetometry, where no evidence of any anomaly in the total (i.e., spin and orbital moments) was observed.

Since the previous magnetic Compton study of the spin moments was performed in an applied magnetic field of 7 T, a second measurement was performed at 7 T at the ESRF. Data were collected for the field applied along the [110]

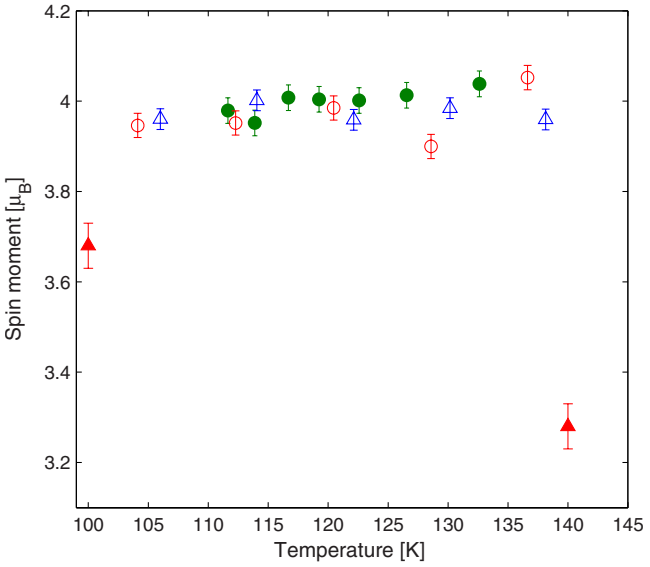

FIG. 2. (Color online) The experimental spin moment observed with a magnetic field of 2.5 T applied along the [100], [110], and [111] crystallographic directions in Fe_3O_4. The directions are indicated by red circles, blue triangles, and green circles, respectively. The Li *et al.* (Ref. 20) data, measured in a 7 T magnetic field, for the [110] direction are shown as filled triangles.

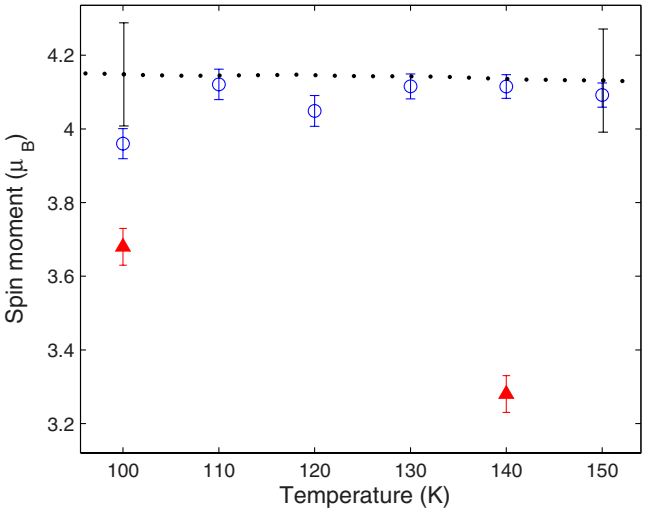

FIG. 3. (Color online) Spin moment in Fe_3O_4 for a magnetic field of 7 T applied along the [110] crystallographic direction (open circles), together with the Li *et al.* (Ref. 20) data as filled triangles. Also shown is the total magnetization at 7 T as measured in a SQUID (black). The error bars shown for the magnetization indicate the overall systematic error rather than a point-to-point statistical error.

crystallographic direction, as this was the crystallographic direction where the anomaly was reported. Our results are presented in Fig. 3, together with the corresponding results taken from Ref. 20. As at a field of 2.5 T, our data follow the SQUID measurement of the total magnetic moment. There is no apparent temperature dependence of the spin moments measured. Over the temperature range shown, the mean spin moment is $4.08 \pm 0.03 \mu_B$, leading to an orbital moment of $0.06 \pm 0.14 \mu_B$.

Our data disagree with those of Li *et al.*[20] who reported a significant orbital moment at all temperatures. None of our data, either at 2.5 or 7 T applied fields indicate the existence of such an orbital moment. Furthermore, we see no evidence of the anomaly that they observed near the Verwey transition. They reported a diminished spin moment and consequentially an enhanced orbital moment of $0.77 \mu_B$ for their measurement along the [110] direction at $T = 140$ K. We did not find any evidence for a reduced spin moment at T_V, finding instead that the orbital moment remains nearly fully quenched. It is difficult to reconcile our results with those of Li *et al.*, and one partial explanation might be that those authors compared with a literature magnetization value to infer the orbital moments. However, this would not explain the anomalous behavior with temperature or direction. On the other hand, we have obtained results at two magnetic fields, at two synchrotrons, using different experimental setups, and have reproduced results consistent with magnetization data collected on the same sample. Furthermore, it is clear that our results are consistent with the values obtained using XMCD by Goering *et al.*,[17] and with recent theoretical predictions.[6,7]

In conclusion, our experiments have found that there is a spin moment of approximately $4 \mu_B$ for all temperatures and for the three principal crystallographic directions. Consequentially, the orbital moment, determined by comparison with bulk magnetometry, is therefore nearly fully quenched, in agreement with Goering *et al.*[17,19] We do not observe the significant orbital moments reported by Huang *et al.*[15] or Li *et al.*[20] No evidence of any anomalies in the spin or orbital moments at the Verwey transition is observed. The magnetic Compton profiles have the characteristic shape expected for Fe $3d$ electrons at all temperatures. We do not find any significant changes in the localization of the electrons that contribute to the magnetic moment across the Verwey transition. Our data are consistent with the highly spin-polarized electronic structure expected for bulk Fe_3O_4.

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