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To cite this version:

S. R. Bland, Carsten Detlefs, S. B. Wilkins, T. A. W. Beale, Claudio Mazzoli, et al.. Resonant x-ray scattering and full polarisation analysis of forbidden half-integer reflections in magnetite. Journal of Physics: Conference Series, 2010, 211, pp.012009. 10.1088/1742-6596/211/1/012009 . hal-00689231

HAL Id: hal-00689231

https://hal.science/hal-00689231

Submitted on 19 Apr 2012

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2010 J. Phys.: Conf. Ser. 211 012009

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Journal of Physics: Conference Series **211** (2010) 012009 doi:10.1088/1742-6596/211/1/012009

Resonant x-ray scattering and full polarisation analysis of forbidden half-integer reflections in magnetite

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Abstract. Magnetite is one of the oldest known magnetic materials, but questions still surround both its crystal and electronic structures at low temperature. The most debated of these low temperature properties regard the presence, or lack of, of charge and orbital order. Using resonant x-ray diffraction at the iron K-edge to probe the long range order present on the iron sites, we have studied $(0\ 0\ \frac{2n+1}{2})_C$ type reflections. By using the technique of full linear polarisation, we have shown that the key features of the reflections can be described merely using the simplified $Pmca$ structure, without invoking orbital order.

1. Introduction

Magnetite, Fe_3O_4, is the oldest known magnetic material, but despite its long history, a number of mysteries still surround it. The high temperature system is well understood; magnetite is ferrimagnetic with an inverse spinel structure, with Fe ions sitting at tetrahedral (A) and octahedral (B) co-ordinated sites. Upon cooling below the Verwey transition, ∼120 K, the system undergoes a first-order phase transition, accompanied by a change in structure[1], resistivity[2], specific heat[3] and magnetisation[4] properties. Verwey[5, 6] proposed that this transition is also accompanied by a transformation to a charge ordered state. Specifically he proposed an alternate layering along the c-axis of Fe^{2+} and Fe^{3+} ions on the octahedral iron sites. It now appears that this simple explanation is not correct, although it has not stopped magnetite often being described as the classic charge ordered system. It is in this low temperature state where the remaining mysteries lie. Perhaps the most surprising problem is that the low temperature crystal structure is still not fully understood. There have been indications the structure is in fact triclinic[7], however the best refinements to date have been obtained using monoclinic $P2/c$[8] and Cc constraints[9]. However, the further simplified orthorhombic $Pmca$ low temperature

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structure provides a useful framework, reducing the problem to 4 inequivalent octahedral B sites and 2 inequivalent tetrahedral A sites.

The next most pressing problem regards the charge ordered structure of magnetite. While it has become clear that Verwey's initial model is not correct[10, 11, 12, 13] debate still continues as to the correct arrangement and magnitude of the charge disproportionation (see *e.g.* [14, 15, 16, 11]). An extra level of complexity is then added, when the possibility of orbital order is included[12, 13, 17]. Recently both hard[18] and soft[19] resonant x-ray diffraction experiments have claimed to observe orbital ordering in magnetite. In order to investigate these claims of orbital order we have used the technique of full polarisation analysis[20, 21, 22] to study the origins of these reflections. The most common way to assess such reports is to study the azimuthal dependencies of the reflections, so allowing any anisotropy to become evident. However, this can prove problematic in high quality crystals of magnetite, as the sample is frequently rotated into positions where multiple scattering dominates over the resonant diffraction signal. The solution is to position the sample at an azimuthal position relatively free of multiple scattering, and instead rotate the incident polarisation of the linearly polarised light. This is then followed by post scattering polarisation analysis via the use of the more commonplace analyser crystal.

2. Experimental Results and Discussion

The sample was a synthetic magnetite crystal, produced using the floating zone method. The high quality of the sample was confirmed using heat capacity measurements. These measurements showed the sample to be of high quality, with a purity above $\delta < 0.0007$ (where $Fe_{3(1-\delta)}O_4$), and a Verwey transition of 120.4 ± 0.3 K [23, 24]. In this paper we have studied the low temperature phase, but index the reflections using the high temperature cubic lattice. Thus $(0\ 0\ 1)_C \equiv (0\ 0\ 2)_O$, where C and O refer to *cubic* and *orthorhombic* respectively.

After mounting the sample on a 0.3 T magnet, in order to fix the monoclinic c-axis, the sample was cooled to 20 K. A scan was conducted at the Fe K-edge along the $[0\ 0\ L]$ direction in reciprocal space in the unrotated σ-σ channel, locating the superlattice reflections. Figure 1, shows reflections at integer and half-integer positions along the c-axis. By contrast in the high temperature structure only the $(0\ 0\ 4)_C$ Bragg reflection and the $(0\ 0\ 2)_C$ ATS[25, 26] (Anisotropic Tensor of Susceptibility) reflection are seen[27, 28]. ATS reflections are forbidden off-resonance due to compound symmetry operations, but at the absorption edge the anisotropic terms in the scattering factors become significant and they can be detected. The $(0\ 0\ \frac{1}{2})_C$, $(0\ 0\ 1)_C$, $(0\ 0\ \frac{9}{2})_C$ and $(0\ 0\ 5)_C$ reflections were all found to resonate close to the iron K-edge;

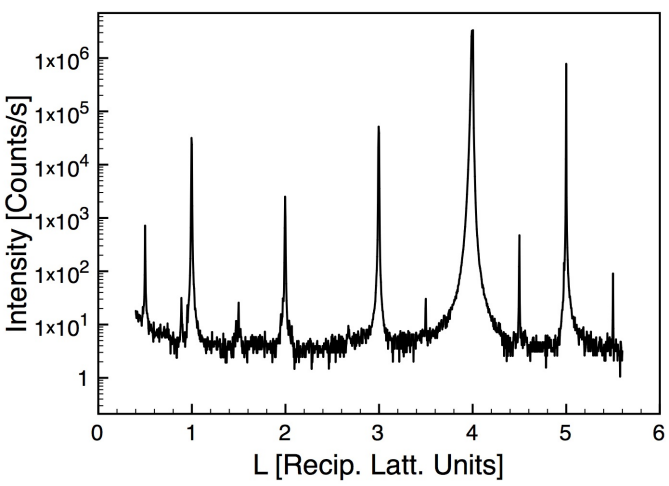

Figure 1. Scan along the L-axis in reciprocal space, at 20 K, with an incident energy of 7.120 keV.

the spectrum of the $(0\ 0\ \frac{9}{2})_C$ reflection is shown in Figure 2. Both half-integer and integer type resonant reflections were found to show the same width, which was of the same order of magnitude as the allowed Bragg reflections.

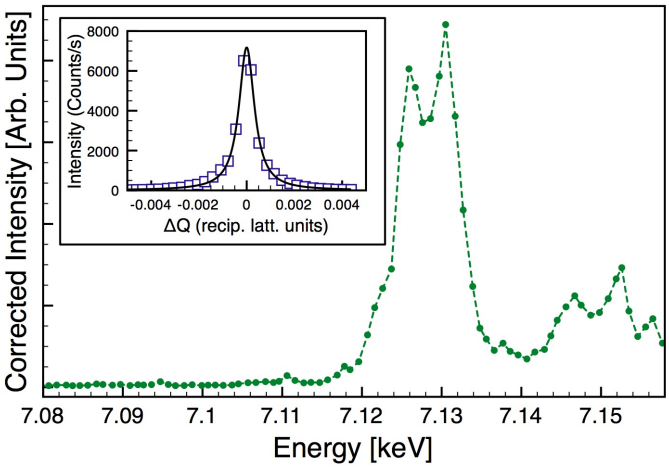

Figure 2. Energy scan of the $(0\ 0\ \frac{9}{2})_C$ reflection at 20 K, measured with fixed wavevector. The scan has been corrected for multiple scattering and absorption effects. Inset: corresponding scan along the L-axis, of the $(0\ 0\ \frac{9}{2})_C$ reflection.

In order to explore the origin of the half-integer type reflections, we then subjected the $(0\ 0\ \frac{9}{2})_C$ reflection to full linear polarisation analysis, the results of which can be seen in Figure 3. Presented in the form of the self-normalising Stokes' Parameters (see *e.g.* [29]), the results demonstrate that the polarisation of the incident light is almost entirely rotated upon scattering. The model shown in Figure 3 represents the expected behaviour of an E1-E1 scattering process for an ATS reflection in the *Pmca* structure, which corresponds to a full rotation of the incident light. In this case the scattering tensor, for all contributing iron sites, is given by

$$\hat{S}_{Pmca} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & Q_{yz} \\ 0 & Q_{yz} & 0 \end{pmatrix}, \tag{1}$$

in the basis of the *Pmca* structure. We note that while comparing to the Stokes' parameters it is not necessary to consider the absolute value of Q_{yz}. There is clearly a strong agreement with the experimental data, although it is obvious that the model does not fully explain the

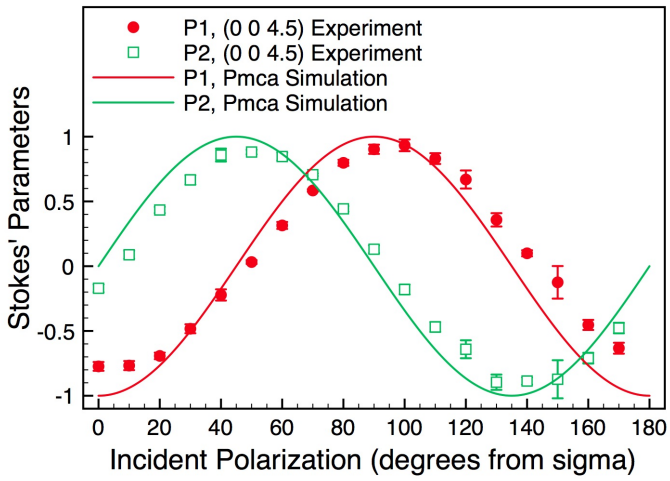

Figure 3. Polarisation dependence of the $(0\ 0\ \frac{9}{2})_C$ reflection at 20 K, tuned to 7.120 keV. The simulations show the expected result for ATS scattering using the *Pmca* structure.

results, as there is a small disagreement with the experiment. There is a slight offset between the simulation and the model, and the experimental results clearly show that, at least initially, the incident light is not fully rotated; indeed, the signal was easily detectable in the unrotated channel in Figures 1 and 2. However, to simulate the ATS reflection in the true low temperature space group goes beyond the scope of this paper, and requires the full crystallographic structure. This remains unknown at present.

Figure 4 shows the temperature dependence of a forbidden half-integer $(0\ 0\ \frac{9}{2})_C$ reflection, as well as the $(0\ 0\ 4)_C$ Bragg reflection, which is allowed in all phases. The transition is clearly first order, and does not appear to show any sign of the continuous transition as measured in other samples [18]. Our temperature dependence of the Bragg reflection also shows a clear first order transition at the same temperature, highlighting the structural change at the transition. Our results in this regard are in agreement with those of García *et al.* [30], who also observed sharp transitions for all reflections. Combined with our full polarisation analysis, it is thus clear that the origin of the $(0\ 0\ \frac{9}{2})_C$ reflection is structural rather than orbital in our high quality sample.

3. Conclusions

The appearance of the $(0\ 0\ \frac{9}{2})_C$ reflection below the Verwey transition can be explained as a consequence of a structural transition to the lower symmetry space group. The appearance of the ATS reflection indicates that there is local anisotropy associated with the iron sites, but this is not a direct indication of orbital order, merely of the structural anisotropy. It is often tempting to attribute ATS reflections (in materials besides magnetite) to orbital order, as they appear at an absorption edge, display the expected anisotropy and appear at the appropriate temperature. Indeed, if the system is orbitally ordered, these reflections are indeed tied to the corresponding electron distribution and associated structural Jahn-Teller distortion. However, the *presence* of an ATS reflection is merely an indication that the scattering factors are neither spherically symmetric or forbidden, whether that be for orbital and/or structural reasons.

In order to definitively explain the results it is necessary to go beyond the *Pmca* approximation, and consider the true low temperature charge ordered structure, and consider the effects of the different scattering factors associated with each of the inequivalent iron sites. It is emphasised that our results do not suggest that magnetite is not orbitally ordered. Rather that the claims of orbital order based on the observation of the $(0\ 0\ \frac{2n+1}{2})_C$ type reflections are not conclusive of orbital order. These reflections arise due to the structural anisotropy of the low-symmetry crystal structure. Further definitive crystallographic studies are needed to

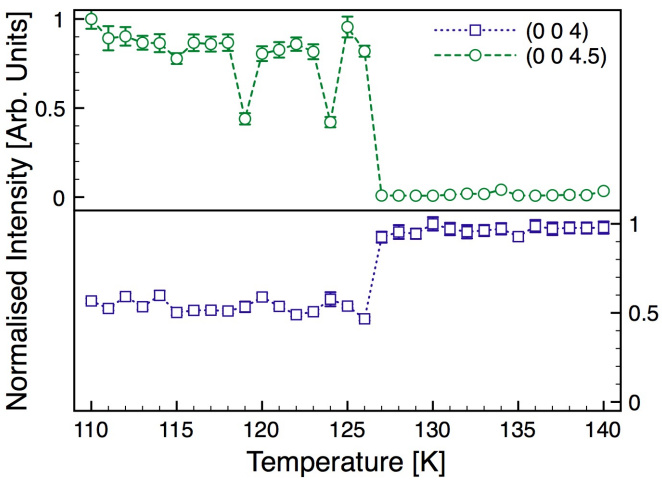

Figure 4. Temperature dependence of the forbidden $(0\ 0\ \frac{9}{2})_C$ and $(0\ 0\ 4)_C$ Bragg reflections. The temperature shown is slightly offset, due to the placement of the temperature sensor. The transition lies at 123.5 K, as revealed by specific heat measurements.

confirm the structure of the low temperature system before conclusive claims of orbital order can be confirmed.

Acknowledgments
The authors wish to thank the ESRF and ID 20 for the beamtime and experimental support. SRB and PDH would like to thank EPSRC for funding. The work at Brookhaven National Laboratory is supported by the Office of Science, U.S. Department of Energy, under contract no. DE-AC02-98CH10886. TAWB and PDH would like to thank STFC for financial support. Part of this work was performed on the EPSRC-funded XMaS beamline at the ESRF, directed by M.J. Cooper and C.A. Lucas. We are grateful to the beam line team of S.D. Brown, P. Normile, O. Bikondoa, L. Bouchenoire and P. Thompson for their invaluable assistance, and to S. Beaufoy and J. Kervin for additional support.

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