

Nanoanalytical Electron Microscopy Of Cobalt Ferrite Thin Films

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Declaration

I declare that the work contained in this thesis is my own work and any references to other work are appropriately cited. Some of the work contained in this thesis has been published in the following journal article.

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Abstract

Electron energy-loss spectroscopy (EELS) is a powerful method for providing detailed information on the bonding, chemical structure and electronic structure of materials. In this work, EELS has been used to correlate variations in magnetic properties of cobalt ferrite films with film thickness and post-processing conditions. Magnetometry performed on as-deposited and oxygen post-annealed films has shown saturation magnetization (M_s) to be strongly affected by post processing. This has been attributed to an enhancement in superexchange by reoxidation and cation ordering processes during post-anneal. To date this has not been confirmed using nanoanalytical techniques. This work addresses this issue. In particular, it is of interest to determine local changes in the degree of inversion of the ferrite spinel in order to link local chemical changes to bulk magnetic properties.

Two sample preparation techniques were used to produce electron transparent sections – conventional ion beam milling and focussed ion beam (FIB) milling using a dual beam system. The suitability of each technique is discussed in terms of, sample damage, thickness, reproducibility and reliability.

Aberration corrected HRTEM was used to investigate the microstructure of the thin films. Lattice strain and defect strain were quantified at increasing distance from the substrate/interface in as-deposited and oxygen post-annealed cobalt ferrite films and structural defects responsible for misfit accommodation were characterised. Local variation in cation valence and coordination cobalt in an oxygen post-annealed film was investigated by monochromated EELS of the iron and cobalt $L_{2,3}$ -edges in the electron energy-loss spectrum. A method to determine the spinel degree of inversion (λ) by multiple linear least squares fitting was developed using data acquired from reference materials. A commercially available full multiple scattering code (FEFF 8.2) was used to aid interpretation of reference spectra and the fitting technique used to determine λ was applied to the cobalt ferrite thin film in order to identify variations in λ .

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Chapter 1 - Background

1.1. Introduction

Magnetic materials have found widespread application as data storage media and components of hard disk heads used to read and write information to and from a magnetic hard disc [1]. Due to increasing demand for high-density data storage and portable electronics, there is a trend toward miniaturization and nanostructured magnetic materials are now commonplace in many technologies. As well as data storage applications, magnetic nanomaterials are found in applications ranging from drug delivery to catalysis and cancer treatment [2].

The ferrite class of materials may be used in microwave devices [3] though bulk ferrites are not suitable for operating at high frequency [4]. Ferrite thin films give advantages of high frequency capability in addition to compatibility with planar circuit design [4,5]. Magnetic ferrites are of particular technological interest as they have a complex and relatively open structure. The magnetic properties depend on the distribution of magnetic cations within this structure giving the possibility of tuneable magnetic properties.

Epitaxial thin films have advantages over bulk materials as their properties can be tailored by varying growth parameters, giving increased flexibility for optimization [4,5]. Understanding the structure property relationships of ferrite films is essential to achieve this optimization. It is of particular importance to understand the role of interfaces in thin films of thickness < 100 nm. The functional properties of nanomaterials are known to differ from bulk materials due to a large increase in surface to volume ratio associated with reduced dimensionality. This gives rise to a significant increase in the importance of the properties of interfaces compared to those of the bulk.

The $\text{SrTiO}_3/\text{CoFe}_2\text{O}_4$ (STO/CFO) system is of particular interest as CoFe_2O_4 (CFO) is a potential component of a magnetoelectric (ME) composite. In a

magnetoelectric (ME) material, ferroelectric and magnetic orders coexist. ME materials may consist of a single phase where the ME effect is intrinsic or many phases where the ME effect is extrinsic, typically resulting from the strain coupling of piezoelectric and magnetostrictive phases such as BaTiO₃ (BTO) and CFO [6]. Single-phase magnetoelectrics suitable for application in devices are rare so there is increased interest in thin film ME composites [7].

A clear understanding of the microstructural and electronic properties of the perovskite/spinel interface in the STO/CFO is an essential starting point for the future design of a BTO/CFO composite. Understanding the microstructure and electronic structure of CFO thin films is also beneficial for promoting development in the wider field of ferrite thin films and magnetic nanomaterials.

1.2. Fundamentals of Magnetism

Magnetic fields may be produced by the movement of charge and by variations in an electric field with time. Magnetic fields also originate from the intrinsic spin and angular momentum of fundamental particles.

The magnetic flux density (**B**) is defined in the Lorentz force law as,

$$\mathbf{F} = q(\mathbf{E} + \mathbf{v} \times \mathbf{B}) \quad (1.1)$$

where **F** is the force felt by a charge **q** moving at velocity **v** in an electric field (**E**).

The torque (**τ**) exhibited on a current carrying loop by a magnetic field is expressed in terms of the magnetic dipole moment (**μ**).

$$\boldsymbol{\tau} = \boldsymbol{\mu} \times \mathbf{B} \quad (1.2)$$

When a magnetic field passes through a magnetic material it is common to redefine **B** in terms of the magnetization (**M**), which is the net dipole moment in the material, and in terms of magnetic field strength (**H**) defined as

$$\mathbf{B} = \mu_0 (\mathbf{H} + \mathbf{M}) \quad (1.3)$$

where μ_0 is the permeability of free space.

The bulk magnetic characteristics of a magnetic material are conventionally described by a plot of the magnetization against magnetic field strength known as a M-H loop. An example M-H loop is shown in figure 1.1.

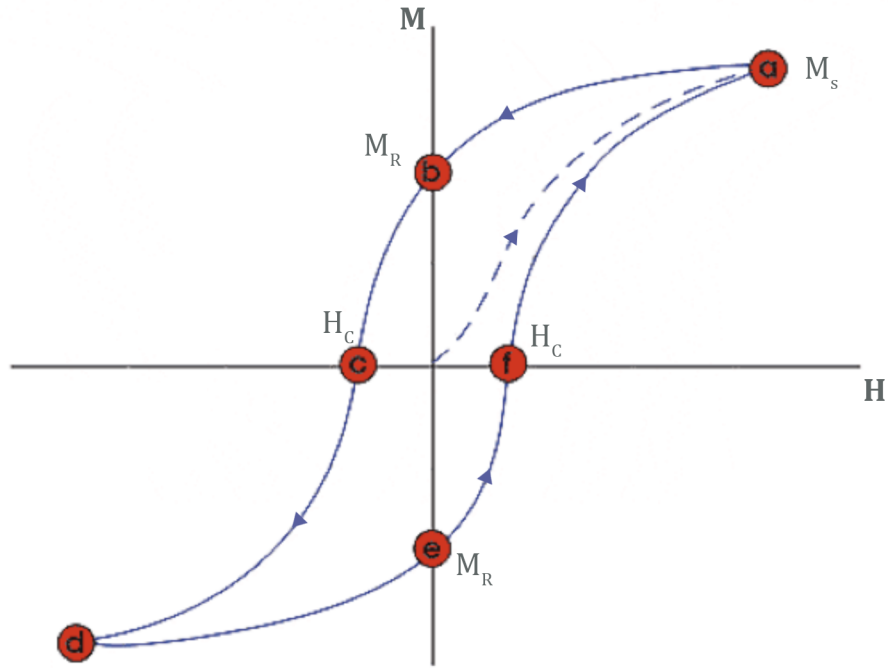


Figure 1.1 – General M-H loop showing: (a, d) saturation magnetization (M_s), (b, e) remanent magnetization (M_r) and (c, f) coercive field (H_c)^[8].

Due to hysteresis, the magnetic response of a magnetic material depends on the polarity of applied external field. From figure 1.1 it is clear that there is a saturation magnetization (M_s) corresponding to the situation in which all magnetic moments are aligned with the externally applied field. If an applied field is removed then a remanent magnetization is left in the magnetic material (M_r). The coercivity is the magnetic field strength (H_c) that must be applied to achieve a magnetization of zero. If a material is magnetically anisotropic then the M-H response for different crystallographic directions in the material is different. A magnetic easy direction is a direction in which saturation magnetization is achieved at lower applied magnetic field strength^[9,10].

The bulk magnetic properties of a magnetic material originate from the electronic structure of its constituent atoms. Atomic electrons have an intrinsic orbital angular momentum and spin. An atom will have a net magnetic moment if the total angular momentum is non-zero. In a paramagnetic material, the

atoms of the material have a net magnetic moment but the moments are non-interacting. In the absence of an external $\mathbf{B}$ field, atomic moments are aligned randomly so that paramagnetic materials and there is no net magnetic moment. In the case of ferromagnets, atomic moments interact. Below the Curie temperature (T_c) the atomic moments of nearest neighbour atoms in a ferromagnet are parallel in the ferromagnetic phase. Ferromagnetic ordering is short range with moments tending to align in small volumes known as domains. The dipole moments of the magnetic domains in a bulk ferromagnet naturally align so that the net dipole moment is zero. Above T_c the moments are aligned randomly due to thermal fluctuations and the ferromagnetic material is in a paramagnetic phase [10].

Magnetic coupling between atomic moments is mediated by the exchange interaction due to overlap between the wavefunctions of atomic electrons of adjacent atoms [10]. The nature of this coupling is described by an exchange integral (J_{ex}). If the exchange integral is positive then adjacent moments are parallel and a material is ferromagnetic. If J_{ex} is negative the adjacent moments are antiparallel and a material is antiferromagnetic.

In the antiferromagnetic transition metal oxides, the coupling between magnetic cations is mediated through intermediate oxygen anions by superexchange [10]. Due to partial overlap between the metal 3d and the oxygen 2p orbitals the 3d and 2p electrons may interact through the exchange interaction. Shown in figure 1.1 is a simplified illustration showing a 3d orbital of metal site M_A , an oxygen 2p orbital and a metal 3d orbital of metal site M_B . A 3d electron from site M_A and the closest 2p electron from the oxygen atom must have antiparallel spin, as the wavefunctions of the two electrons cannot be identical by the Pauli principle. The electrons occupying the p-orbital must also have opposite spin by the same principle which results in an antiparallel spin arrangement for the 3d electrons shown for site M_A and M_B . The superexchange coupling is maximised if the cations and anions are present in a collinear arrangement [9,10]. In an antiferromagnet, the antiparallel spin arrangement occurs below the Neel

temperature (T_N). For temperatures above T_N the antiferromagnet is in a paramagnetic state.

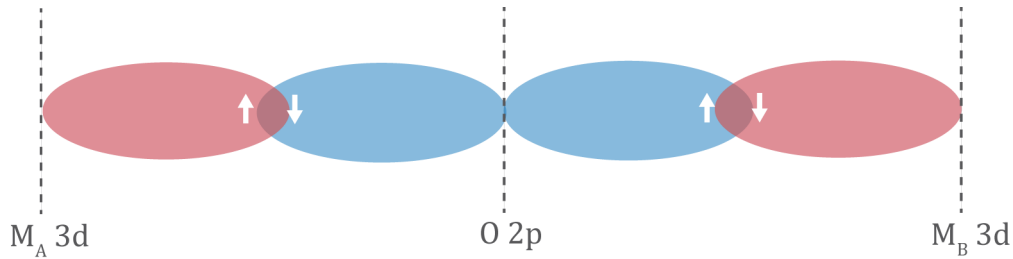


Figure 1.2 - Illustration of superexchange in a system of two metal cations (M_A , M_B) and an intermediate oxygen anion.

The simple two electron model is suitable in a description of insulating narrow band systems but inaccurately describes wide band systems in which there is significant spin degeneracy ^[11]. In this case the magnetic characteristics are better predicted by the Stoner model in which a net spin moment is attributed to an energy splitting between spin bands in the magnetic material ^[10,11].

1.3. Magnetic Ferrites

1.3.1. Magnetic Ferrites

The general formula for a spinel is AB_2O_4 [12,13]. The unit cell consists of a face centred cubic oxygen lattice of in which cations are distributed amongst the tetrahedral (T_d) and octahedral (O_h) sites. In a normal spinel, 8 of the A-type cations occupy tetrahedral interstices and 16 B-type cations occupy octahedral interstices. The formula may be written as $(A)[B]_2O_4$ where round and square brackets denote the tetrahedral and octahedral interstices respectively. In an inverse spinel, 8 tetrahedral interstices are occupied by B-type cations and the remaining A and B cations occupy octahedral interstices so that the general formula becomes $(B)[AB]O_4$ [9,12,13]. The unit cell for $CoFe_2O_4$ is shown in figure 1.3.

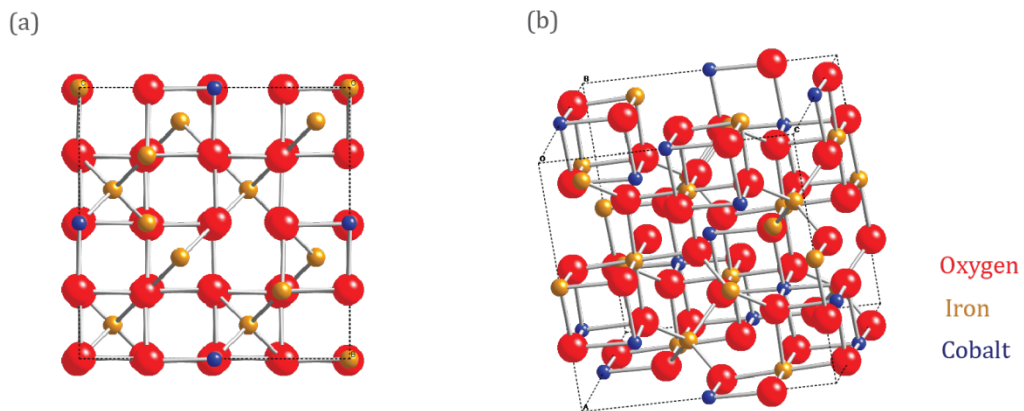


Figure 1.3 – Unit cell for fully inverse $CoFe_2O_4$ in: (a) (100) projection and (b) off-axis projection.

The spinel degree of inversion (λ) indicates the fraction of tetrahedral interstices occupied by B-type cations. For a normal spinel is $\lambda = 0$ and for an inverse spinel, $\lambda = 1$. The oxygen parameter (u) defines structural deviation from cubic symmetry. For $u = 0.250$, oxygen anions form a perfect cubic close packed lattice. As u increases, oxygen anions displace along the $[111]$ direction causing the tetrahedral site to enlarge and the symmetry of the octahedral site to degenerate

to $\bar{3}m$ [13,14]. CoFe_2O_4 is reported to have a u parameter of 0.25641 [15]. Magnetic ferrites of hexagonal structure are reported in the literature but a discussion of their structure is beyond the scope of this thesis [16].

1.3.2. Cation Distribution

If λ is between 0 and 1 the structure of a spinel lies between the inverse and normal and the formula can be rewritten as $(\text{A}_{1-\lambda} \text{B}_\lambda)[\text{A}_\lambda \text{B}_{2-\lambda}]\text{O}_4$ [12]. The site preference energy of the A and B cations was predicted from crystal field theory by comparing the crystal field stabilization energies of the cations in the tetrahedral and octahedral sites but the accuracy of this method was found to be limited and unable to predict site preference energies of a number of cations, in particular cations of d^0 , d^5 and d^{10} electronic structure [12,13].

Verwey found a normal structure was more stable than the inverse for $u > 0.379$ [17]. Glidewell *et al.* later argued that the total electrostatic energy was more important than the crystal field splitting in determining the spinel structure [18]. Grimes and Thompson and O'Neill and Navrotsky also argued the significance of the electrostatic energy and O'Neill and Navrotsky calculated a critical value for the oxygen parameter of $u > 0.2555$ for a spinel to be of normal structure [13].

Grimes *et al.* later used a modified atom superposition and electron delocalization molecular orbital (ASED-MO) model to calculate the anion and cation preference energies for 50 spinels [12]. By this approach, the inversion parameters were successfully predicted and explained in terms of electronic structure. Oxygen bonding stabilization was argued to depend on the surrounding cation environment. An increase in stabilization was identified with increasing overlap between metal and oxygen orbitals, though stabilization decreased with the separation of metal and oxygen energy levels. Oxygen bonding stabilization considerations were reported to be relatively unimportant compared to the cation preference energy where the atomic number of the A and B cations are similar [12]. Trends in cation preference energy calculated by Grimes *et al.* were found to be analogous to crystal field preference energies

previously determined empirically by Dunitz and Orgel [19]. Grimes *et al.* [12] predicted a fully inverse structure for CoFe_2O_4 .

In contrast to modelling results, CFO was generally found to be partially inverse by experiment. Vaingankar *et al.* [20] report a partial degree of inversion for CFO prepared by a standard ceramic route. Rieck and Thijssen [21] also report partial inverse in CFO of $0.63 < \lambda < 0.67$ for specimens prepared by ceramic synthesis at temperatures of 1200°C and 1400°C. Specimens were quenched or annealed though a trend in λ with processing conditions was not observed [21]. Sawatzky *et al.* [22] report a partial degree of inversion for CFO and further report the dependence of λ on the heat treatment of the CFO. Murray and Linnett [23] later report a negligible site preference between Co^{2+} and Fe^{3+} in reasonable agreement with Grimes *et al.* [12,23]. Docherty found CFO to be partially inverse with the inversion parameter reported to be $\lambda = 0.82$ [15].

1.3.3. Magnetic Structure

In the magnetic ferrites, the magnetic moments of the A and B sites are coupled by superexchange [22]. Superexchange coupling occurs between magnetic cations on octahedral sites (J_{BB}) and magnetic cations on tetrahedral and octahedral sites (J_{AB} , J_{BA}). J_{AB} , J_{BA} interactions are strongest as the A-O-B bond angles are closest to collinear (125 °C and 154 °C in undistorted spinel) [16]. If the magnetic moments of the A and B cations differ then the spinel is ferrimagnetic. A ferrimagnet possesses a net dipole moment due to the antiparallel alignment of the uncompensated spin moments of the A and B cations.

The net moment depends on the type of magnetic cations present in the spinel and their relative distribution over the tetrahedral and octahedral sites [22]. The magnetic moments for Co^{2+} , Fe^{3+} and Co^{2+} cations are given in table 6.1 for cations in octahedral complexes and tetrahedral complexes in table 6.2.

Table 1.1 - Magnetic moments for octahedral coordinated cobalt and iron cations [24]

Ion	μ (μ_B)	
	<i>high spin</i>	<i>low spin</i>
Co ²⁺	4.3 – 5.2	1.8
Fe ³⁺	5.6 – 6.1	1.8 – 2.1
Fe ²⁺	5.1 – 5.7	

Table 1.2 - Magnetic moments for tetrahedral coordinated cobalt and iron cations [24].

Ion	μ (μ_B)
	<i>high spin</i>
Co ²⁺	4.2 – 4.8
Fe ²⁺	5.3 – 5.5

Cobalt ferrite is a room temperature ferrimagnet ($T_N = 870$ K) [25], the magnetic moment reported to be $3.7 \mu_B$ [16]. Sawatzky *et al.* [22] report a net moment of $3.45 \mu_B \pm 0.05$ for cooled CFO and $4.00 \mu_B \pm 0.05$ for quenched CFO. Taking Co²⁺ and Fe³⁺ as high spin Axelsson *et al.* previously calculated theoretical moments for perfectly inverse and disordered CFO of the of $3 \mu_B$ and $4 \mu_B$ respectively [3]. A net moment of $3 < \mu < 4$ would therefore correspond to partial inversion, in agreement with the findings of Sawatzky *et al.* [22]. The net moment of cobalt ferrite is less than the magnetic moment of the Co²⁺ and Fe³⁺ cations due to antiparallel magnetic coupling between the A and B sites.

Cobalt ferrite is unique among the magnetic ferrites in that it is highly magnetostrictive and magnetically anisotropic. Magnetostrictive materials undergo changes in volume as the magnetization increases. The magnetostriction coefficient (K) is defined as the fractional change in length as

the magnetization increases from 0 to M_s ^[10]. Magnetostriction constants of $K_{100} \sim -590 \times 10^{-6}$ and $\lambda_{111} \sim 120 \times 10^{-6}$ were reported by Hu *et al.* ^[26] for CFO.

1.4. Epitaxial Thin Films

Where a thin film is grown on a crystalline substrate and the film is crystallographically matched to the substrate, the film is said to be epitaxial. Epitaxial thin films are commonplace in many modern technologies as they often display enhanced functional properties compared to bulk materials due to the highly ordered structure of the film. Epitaxial multilayers provide additional benefits for use in devices, such as extrinsic functional properties that arise from coupling between monolayers.

In order to grow an epitaxial thin film, a supply of source material is required in addition to a crystalline substrate to act as a growth surface and growth template. A flux of source material is typically provided by breaking down a target material into atomic or ionic species under vacuum. The source flux is then transported to the substrate, where the atoms and/or ions condense on the growth surface [27-29].

PLD is a popular technique for thin film research as it is relatively straightforward in application and versatile due to a large number of deposition parameters that may be varied [27]. An overview of the PLD technique is provided in the section 1.4.1. Reports of oxide thin films grown by a wide variety of deposition techniques are found in the literature but an in depth discussion of oxide thin film growth techniques is beyond the scope of this thesis. A number of reviews are present in the literature and the text by Kelsall *et al.* [30] is recommended for further reading.

1.4.1. Pulsed Laser Deposition

In PLD, a high-energy laser is focussed on a rotating ablation target that is housed in a vacuum chamber [27]. The ablation target is subject to short laser pulses which cause the ejection of atomic, diatomic, molecular and ionic species from a small surface volume of the ablation target into a plasma plume, which travels towards the substrate surface [27]. On striking the substrate, the energetic

plasma species condense on the substrate surface, forming a thin film. Thin film thickness increases with the total number of laser pulses. A schematic of a PLD chamber is shown in figure 1.4.

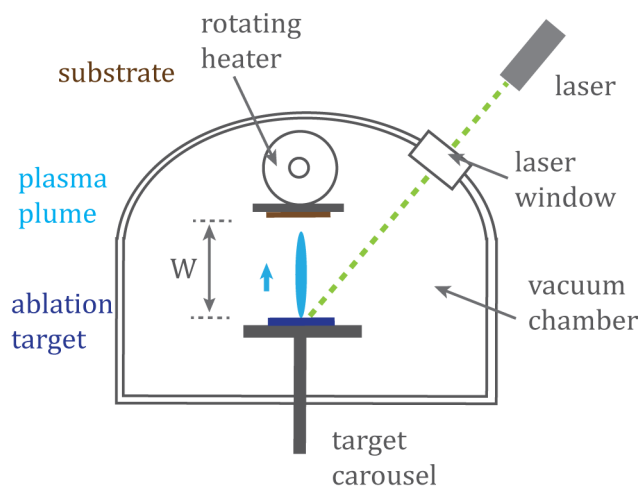


Figure 1.4 – Simplified schematic of a PLD chamber showing the laser source, vacuum chamber, ablation target and target substrate [27].

PLD thin film growth is a non-equilibrium deposition technique. Laser pulses are typically supplied at high fluence rates so that the energy density supplied to the specimen surface is high [27]. As the laser is tightly focussed, a high energy density is supplied to a small volume of surface material. Vaporization of target material under these conditions does not depend on vapour pressure so that PLD gives stoichiometric transfer of material from the ablation target to the target substrate [28]. The PLD technique is compatible with chamber pressures ranging from ultra high vacuum to 1 Torr as the energy source is outside of the vacuum chamber [27,31]. This gives advantages over other deposition techniques as film growth can be performed in reactive atmospheres [31].

Axelsson *et al.* [3,32] previously grew as-deposited and oxygen post-annealed STO/CFO by PLD in film thickness range 25 – 200 nm [3,32]. Films were grown using a KrF excimer laser (248 nm) with spot size 2 x 10 mm, repetition rate 8 Hz and laser energy density of 2.6 Jcm⁻². The working distance (W) as shown in

figure 1.4, was 50 mm. Films were grown at an oxygen pressure of 20 Pa. The substrate and ablation target were rotated during deposition and the substrate temperature maintained at 700 °C. Post-annealed specimens were annealed for 1 hour at 0.1 MPa oxygen pressure.

1.4.2. Growth Mechanisms

Thin film growth by PLD occurs as a result of condensation of the plasma plume onto the substrate surface. At an atomic level, the film growth process is initiated as the atomic, diatomic, molecular and ionic species of the plasma are adsorbed onto the growth surface [28,31]. Adsorption is followed by surface diffusion and chemical binding at nucleation sites, followed by growth of the thin film [28]. The thin film growth mechanism depends on the relative surface energies of the adsorbed species and the substrate material.

If the adsorbates are more strongly bound to the substrate material than other adsorbates, the nucleation layer forms as a complete monolayer over the substrate [28]. Film growth proceeds in a layer by layer fashion as shown in figure 1.5a if the surface energy of subsequent layers decreases monotonically toward the value for the bulk crystal [28,29]. If the adsorbates are more strongly bound to other adsorbates than the substrate, small islands nucleate on the substrate surface that grow in size as more source material adsorbs on to the growth surface [28]. This is known as island growth and is shown schematically in figure 1.5c.

The layer-island growth mechanism is observed where a change in surface energy conditions occurs during film growth, from initial conditions that favour layer growth, to final conditions favouring island growth [28]. This is typically observed in systems in which a lattice mismatch is present between the substrate and film layers [29]. The elastic strain energy per unit area of interface increases with thickness (chapter 4) and at a critical thickness (h_c), a change in growth mechanism occurs from a strained layer growth to island growth [28,29].

Islanding increases the film surface area which decreases the elastic strain energy per unit area [33]. Strain may also be accommodated by misfit dislocation formation, which is discussed in detail in chapter 4. A schematic showing the nucleation and growth phases of layer-island growth is shown in figure 1.5b. The thin film growth mechanism is highly dependent on the adsorbate type and substrate, but is also strongly influenced by the chosen deposition conditions [28,34].

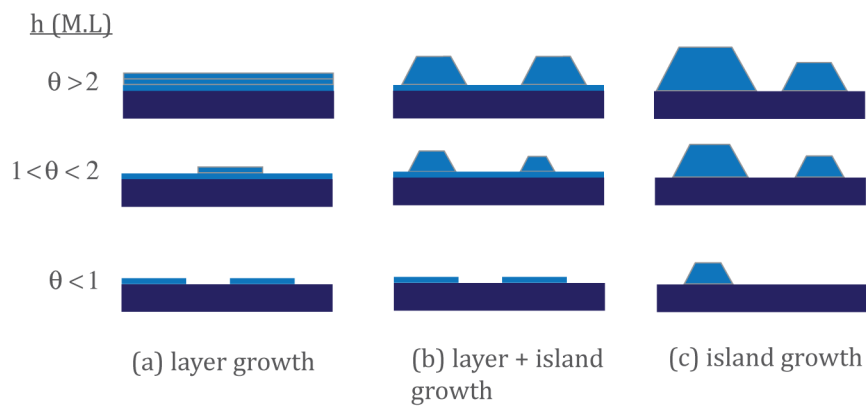


Figure 1.5 – Schematic showing thin film growth mechanisms at different film thickness (h) in monolayers for: (a) layer growth, (b) layer + island growth and (c) island growth [28].

1.4.3. Perovskite/Spinel Thin Films

The perovskite structure is of general formula ABO_3 where A and B correspond to different cation species. The ideal perovskite structure is a simple cubic structure. The basis vector ($\mathbf{R}$) for the A and B cations in a cubic perovskite are $\mathbf{R} = 0$ and $\mathbf{R} = 0.5a_1 + 0.5a_2 + 0.5a_3$ respectively. Oxygen anions are found at unique crystallographic positions with basis vectors $\mathbf{R} = 0.5a_2 + 0.5a_3$, $\mathbf{R} = 0.5a_1 + 0.5a_2$ and $\mathbf{R} = 0.5a_2 + 0.5a_3$.

$SrTiO_3$ is a cubic perovskite with lattice parameter $a_0 = 3.905 \text{ \AA}$ [3]. A spinel film such as CFO ($a = 8.387 \text{ \AA}$) [15] may be grown epitaxially due to a close match

between the oxygen sublattices of the perovskite and spinel materials, as shown in figure 1.6a and 1.6b.

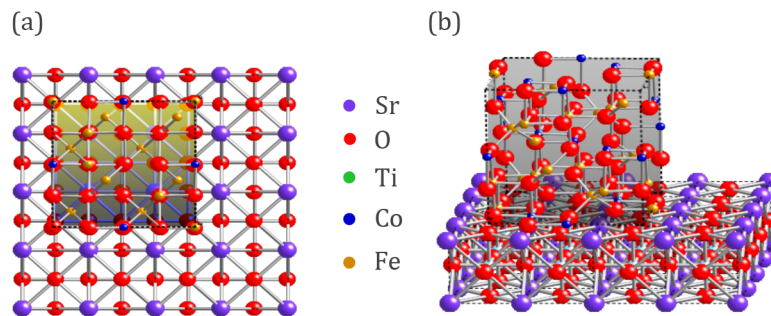


Figure 1.6 – Illustration of epitaxial growth of a spinel film (CFO) on a perovskite substrate (STO) with orientation relationship $(001)_{STO} // (001)_{CFO}$ [28]. Images are shown in (a) (001) projection and (b) off-axis projection.

CFO thin films were previously grown epitaxially on (001) by PLD [3,32], molecular beam epitaxy (MBE) [35] and laser assisted molecular beam epitaxy (LMBE) [34]. Huang *et al.* found that the film growth mechanism depended on deposition conditions. The structural and magnetic properties of ferrite thin films are widely reported to strongly depend on film deposition conditions.

CFO is able to grow epitaxially on STO (001) due to a close match between the oxygen sublattices of the two phases, the oxygen cell sizes 3.905 Å and 4.195 Å for STO and CFO respectively [3], giving a value for the lattice mismatch in (001) STO/CFO of -7.4%.

1.5. Characterisation of Ferrite Thin Films

The magnetic properties of ferrite thin films have been found to vary with deposition parameters such as post-annealing conditions and substrate temperature. Variations in magnetic properties of CFO thin films were also observed that were attributed to the inter relation between the lattice mismatch, magnetostriction and anisotropy. The presence of microstructural defects in CFO thin films is also reported to affect the magnetic properties [4,26,34,36-38].

Margulies *et al.* observed anomalous magnetic behaviour in Fe_3O_4 films grown by sputter deposition that was independent of film thickness, substrate choice and post deposition annealing conditions [39]. In an investigation by TEM, Rudee *et al.* identified antiphase domain boundaries in Fe_3O_4 thin films that were later attributed to the origin of the anomalous magnetic behaviour in Fe_3O_4 previously reported by Margulies *et al.* [40,41]. Hibma *et al.* grew Fe_3O_4 on (100) MgO by MBE and performed bright field imaging of plan view TEM specimens under the (220) two beam condition, identifying antiphase boundaries of shift vector $\mathbf{a}_0/4[011]$ [42]. The presence of antiphase boundaries in CFO grown on MgO is reported by Hu *et al.*, though dark field TEM images presented are in poor agreement with previous reports by Hibma *et al.* [36].

An antiphase boundary is a structural boundary between two antiphase domains. The crystal structures of two antiphase domains are the same but the types of atom occupying equivalent sites differs so that an antiphase boundary is present where the domains meet [33]. Antiphase boundaries in Fe_3O_4 films grown on MgO were argued to be a consequence of the 2:1 pairing between the MgO and Fe_3O_4 lattice parameters by [41,42]. Hibma *et al.* propose a layer by layer growth mechanism for Fe_3O_4 with the initial layer forming from the coalescence of separate layer nucleation sites [42]. The oxygen sublattice would be continuous though Hibma *et al.* predict discontinuities in the cation sublattice, due to a number of inequivalent start positions for the initial islands [42]. Parallel or perpendicular displacement of the B-site cations planes between APB domains was reported to depend on the shift vector ($\mathbf{R}$) for equivalent cations across an

antiphase boundary. A full list of possible shift vectors is provided in the literature [42].

In a microstructural study of topotaxial films of spinel structure grown on MgO, Sieber and Hess found that antiphase domains were only present in systems of small lattice mismatch [43]. Misfit dislocations were observed in place of antiphase boundaries for systems of significant mismatch. Under compression, dislocations were observed with Burgers vector parallel to the interface plane [43]. A summary of structural defect types for ferrite thin films grown on MgO found in the literature is given in table 1.3.

Table 1.3 - Summary of structural defects for different spinel films grown on MgO.

Spinel Film	a_0 (Å)	Mismatch (%)	Structural Defect
Fe ₃ O ₄	8.380	0.5	APB [40,42]
CoFe ₂ O ₄	8.387	0.4	APB [36,44]
MgAl ₂ O ₄	8.086	-4.1	misfit dislocation [43]
MgCr ₂ O ₄	8.333	-1.1	misfit dislocation [43]
MgFe ₂ O ₄	8.390	-0.4	APB [43]
TiMg ₂ O ₄	8.44	+0.17	APB [43]
MgIn ₂ O ₄	8.81	+4.5	misfit dislocation [43]

Hu *et al.* identified Frank dislocations ($\mathbf{b} = 1/3 \langle 111 \rangle$) in CFO grown on CrCo₂O₄(CCO) buffered (100) MgAl₂O₄(MAO) and claimed that the films are antiphase boundary free, supporting wider literature reports that antiphase boundaries are specific to systems in which the substrate unit cell parameter is half the film cell parameter [26].

Mitchell *et al.* [44] report the favoured slip system in bulk stoichiometric MAO as $\{111\} \langle 110 \rangle$. Dislocations of Burgers vector for dislocations of $\mathbf{b} = a_0/2 \langle 110 \rangle$ are reported to dissociate into partial dislocations as

$$\frac{a_0}{2} \langle 110 \rangle \rightarrow \frac{a_0}{4} \langle 110 \rangle + \frac{a_0}{4} \langle 110 \rangle \quad (1.4)$$

The $a_0/4 \langle 110 \rangle$ partial dislocation is described as a stacking fault that only appears in the cation lattice [44].

Both Hibma *et al.* and Margulies *et al.* attribute poor magnetic behaviour of Fe_3O_4 relative to bulk Fe_3O_4 to disrupted magnetic coupling at the antiphase boundaries. Saturation was not achieved by applying a H-field strength that would saturate bulk Fe_3O_4 [41,42]. Hu *et al.* report a similar dependence of the magnetic properties of as-deposited CFO films on antiphase boundaries, also not achieving saturation at the in CFO films when the expected saturation field strength was applied [36].

Both Huang *et al.* and Axelsson *et al.* report an epitaxial growth relationship for (001) STO/CFO grown by PLD in spite of the high lattice mismatch of $\sim 7\%$ [3,34]. Both authors found the film to be under compressive strain. Axelsson *et al.* [3] found a magnetic easy axis parallel to the film surface and a hard direction normal to the film. The film growth mode at 700 °C was found to depend on the PLD laser repetition rate by Huang *et al.* who report layer-layer growth at 1 Hz, Stranski-Krastanov growth at 1-3 Hz and island growth at 3-5 Hz [34]. In an investigation of the interface structure and chemistry of (001) STO/CFO, Xie *et al.* [35] also confirmed an epitaxial growth relationship by cross sectional TEM; misfit dislocations of spacing ~ 4 nm were identified by Fourier filtering performed on HRSTEM images acquired from (001) STO/CFO though Burgers vectors were not given. Xie *et al.* [35] also investigated variations in the oxidation state of iron across the (001) STO/CFO interface by STEM EELS. An oxidation state of 3+ was determined from the Fe L_2/L_3 white line ratio. No variation in valence over the interface was reported.

Both Dorsey *et al.* and Lisfi and Williams found the magnetic properties of (100) CFO films to vary with substrate temperature [45,46]. Dorsey *et al.* found a magnetic easy direction normal to the film surface for deposition temperatures of 200 °C - 800 °C [45]. Lisfi and Williams found the magnetic properties of films grown at 300 °C varied with thickness. This variation was attributed to an increase in the significance of magnetocrystalline anisotropy compared to stress anisotropy with increasing film thickness. At high temperature magnetic properties were independent of thickness, stress anisotropy was argued to be less significant in high temperature deposition due to thermal expansion of the substrate and film lattice [46].

Post processing conditions were also found to have a strong effect on the magnetic properties of ferrite thin films. Axelsson *et al.* [3] observed variations in the M_s of as-deposited and oxygen post-annealed (001) STO/CFO that were attributed to post deposition cation ordering and reoxidation (section 1.6.2). Both Axelsson *et al.* and Hu *et al.* argued the likelihood of structural disorder in as-deposited films grown by PLD due to the non-equilibrium conditions under which films are grown [3,26]. Extended x-ray absorption fine structure (EXAFS) measurements carried out by Hu *et al.* on as-deposited CFO grown on (100) MgO suggest 23% of the Co^{2+} cations occupy tetrahedral sites, confirming a deviation from perfect inversion in as-deposited films [26]. The site occupancy reported by Hu *et al.* corresponds to an inversion parameter of $\lambda = 0.77$, which is in close agreement with the value previously reported by Docherty for bulk CFO ($\lambda = 0.82$) and wider reports of the partially inverse structure of CFO [15,20-23].

Axelsson *et al.* [3] also observed variations in the M_s of post-annealed CFO films with thickness in comparison to as grown films. An increase in M_s with respect to as-deposited films was observed for films of thickness 7 – 25 nm though for films of thickness 100 nm, M_s was found to decrease. These variations are discussed in detail in section 1.6.2 and section 6.6. Hu *et al.* observed a decrease in M_s of post-annealed CFO grown on (100) MgO in films of thickness 140 nm – 420 nm [36]. In contrast to Axelsson *et al.* [3], Hu *et al.* [36] attributed the decrease in M_s to

secondary phase formation during the post-annealing stage. Interdiffusion processes during annealing were also observed for CFO grown on CrCo_2O_4 - buffered MgAl_2O_4 substrates by Hu *et al.* [36] and for CFO grown on MgO by Schnittger *et al.* [47]. Hu *et al.* [36] also observed a change in the magnetic easy direction of CFO grown on MAO and CFO grown on CCO buffered MgAl_2O_4 after annealing in 1000 °C in air. EXAFS measurements performed on as-deposited films showed that $22.57 \pm 2\%$ of Co^{2+} occupied tetrahedral sites. Post-annealing films did not lead to any noticeable change in overall cobalt coordination. Interdiffusion of Cr^{3+} was reported to prevent Co^{2+} diffusion to octahedral sites. Secondary phases were not observed and the change in easy direction was attributed to structural relaxation and cation distribution [26].

1.6. X-ray Diffraction Analysis and Magnetometry of PLD Grown (001) SrTiO₃/CoFe₂O₄

(001) STO/CFO thin films grown by Axelsson *et al.* [3,32] using growth parameters previously given in section 1.4.1, form the core specimen set for the experimental work discussed in this thesis. X-ray diffraction and magnetometry results previously reported by Axelsson *et al.* [3,32] are summarised in the following sections.

1.6.1. X-Ray Diffraction

In order to identify the orientation relationship of CFO thin films grown on (001) STO, Axelsson *et al.* [3,32] acquired normal incidence and grazing incidence x-ray diffraction scans from all films grown. ϕ -scans on (103) STO and (206) CFO planes were acquired to verify epitaxy and reciprocal space mapping was performed to verify the cubic structure of CFO.

Shown in figure 1.7a are normal incidence and grazing incidence (GID) scans acquired from 100 nm (001) STO/CFO by Axelsson *et al.* [32]. From figure 1.7a it is clear that reflections are only present in the normal and GID scans for the {400} and {800} families of planes for CFO, suggesting a cube on cube growth and an orientation relationship to (001) STO. Axelsson *et al.* [3,32] confirmed the epitaxial growth relationship of (001) STO/CFO by ϕ -scan on (103) STO and (206) CFO planes as shown in figure 1.7b.

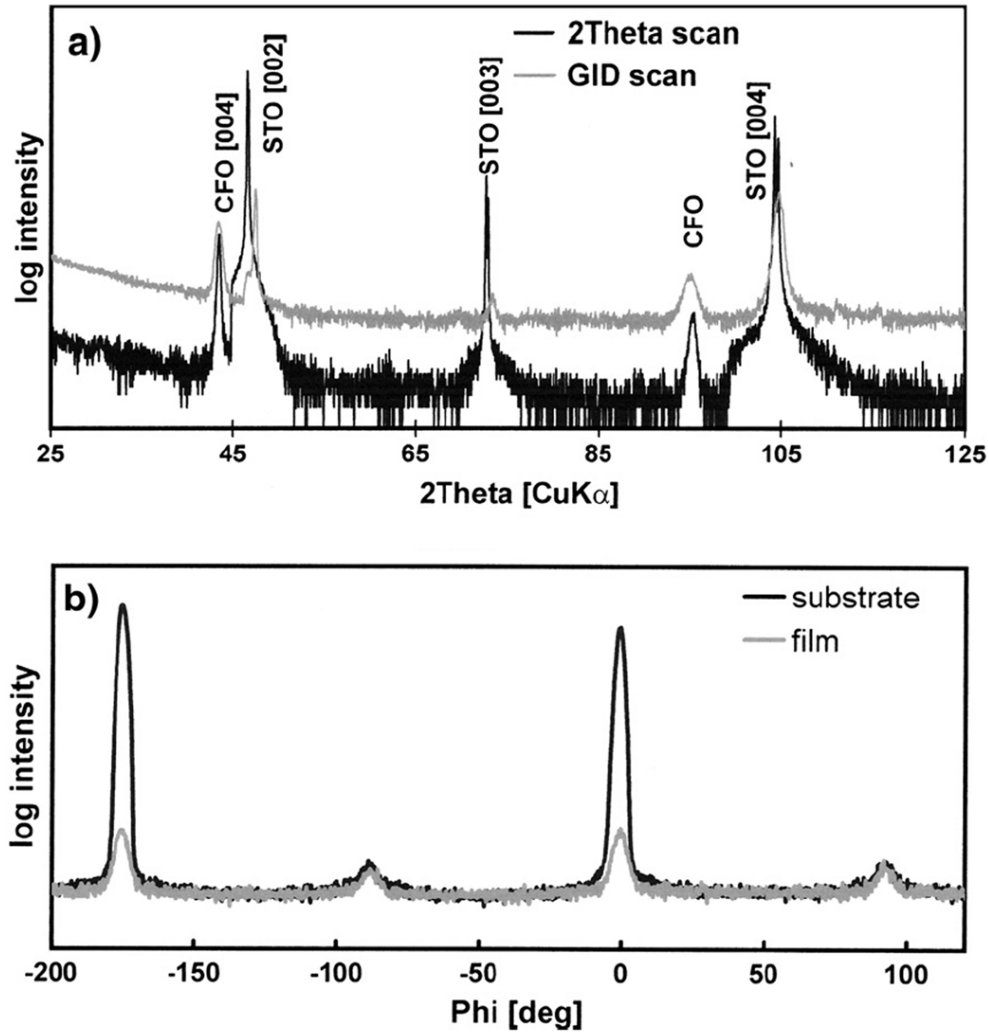


Figure 1.7 –X-ray diffraction analysis of 100 nm (001) STO/CFO: (a) normal and grazing incidence scans; (b) ϕ -scan on (103) STO and (206) CFO planes, confirming an epitaxial growth relationship [3,32].

Shown in figure 1.8 are plots of the reciprocal space maps around the (202) STO and (404) CFO peaks for the as-deposited and oxygen post-annealed specimen sets. Axelsson *et al.* found clusters of peaks around $\mathbf{q}_x = \mathbf{q}_y$ suggesting a cubic structure for both as-deposited and oxygen post-annealed (001) STO/CFO [32]. A greater spread in spot position was observed in the reciprocal space map for as-deposited films, suggesting higher microstrain relative to oxygen post-annealed films.

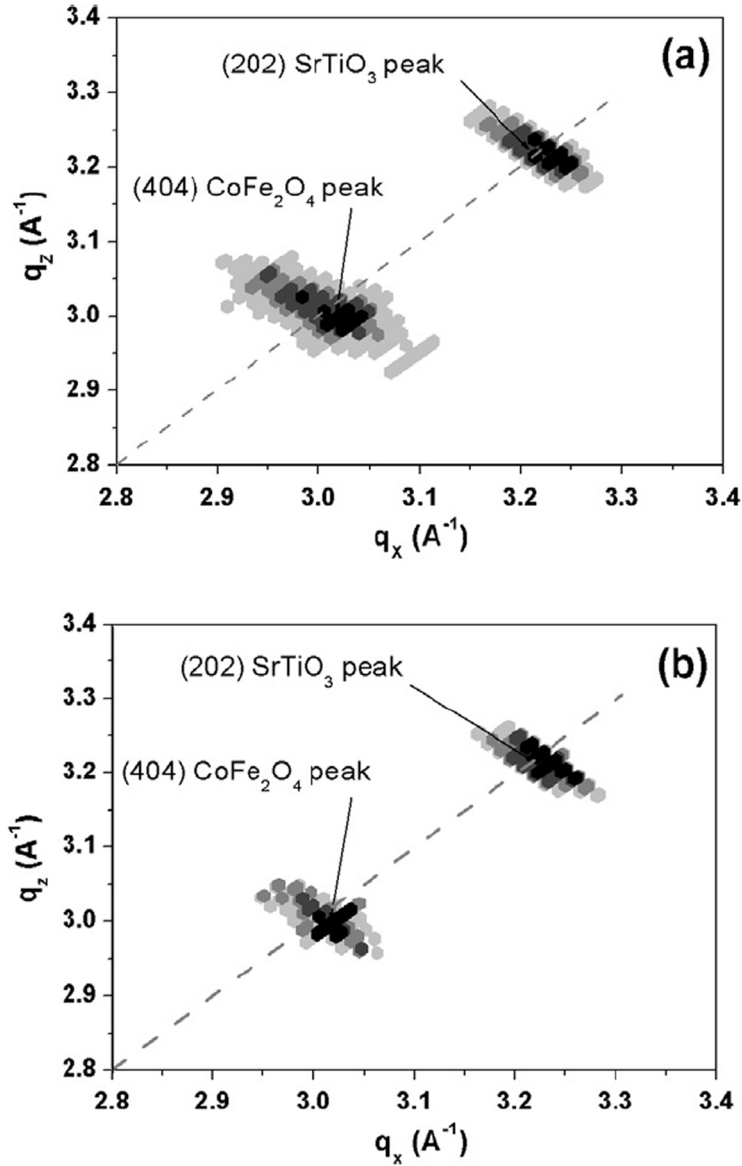


Figure 1.8 –Reciprocal space maps around (202) STO and (404) CFO: (a) as-deposited films and (b) oxygen post-annealed films. $q_z/q_x = 1$ corresponds to a cubic structure, represented by the dashed line [3,32].

Using the Nelson Riley formula, Axelsson *et al.* [3,32] calculated the in-plane and out of plane CFO lattice parameters from (400) and (800) peaks in GID and normal incidence x-ray diffraction scans respectively. The in and out of plane lattice strain was determined from the shift of (400) and (800) peaks with respect to bulk CFO. Axelsson *et al.* [3,32] defined lattice strain as strain resulting from uniform compressive stress. Using Scherrer's formula, Axelsson *et al.* [3,32] determined the broadening of the (400) and (800) peaks which was attributed to

the microstrain in CFO films. Microstrain was defined as non-uniform strain resulting from locally generated stress. A summary of the lattice strain and microstrain calculated for (001) STO/CFO by Axelsson *et al.* is given in table 1.4.

Table 1.4 – Lattice strain and microstrain for PLD grown as-deposited and oxygen post annealed (001) STO/CFO films in thickness range 13 – 100 nm. Lattice strain and microstrain were calculated from x-ray diffraction scans using the Nelson Riley formula and Scherrer's formula by Axelsson et al. [3,32].

Post Processing	h (nm)	Microstrain (%)	Lattice strain (%)	
			<i>in-plane</i>	<i>out of plane</i>
As-deposited	13	-	-	-0.33
	25	0.24	-	-0.34
	50	0.41	-	-0.37
	100	0.49	-	-0.33
Oxygen post annealed	13	-	-0.40	-0.29
	25	0.21	-0.43	-0.37
	50	0.25	-0.48	-0.40
	100	0.30	-0.53	-0.45

For as-deposited CFO, Axelsson *et al.* [32] found that the lattice strain was independent of film thickness. For oxygen post-annealed films, lattice strain was found to increase with film thickness. Microstrain was found to increase with film thickness in both as-deposited and oxygen post-annealed films. For all films investigated, Axelsson *et al.* [3,32] found that the total strain calculated did not account for the lattice mismatch.

1.6.2. Magnetometry

Using superconducting quantum interference device (SQUID) magnetometry, Axelsson *et al.* [3] determined the field dependent magnetisation in as-deposited and oxygen post-annealed (001) STO/CFO films at room temperature. Both the parallel and perpendicular components of $\mathbf{M}$ were determined up to 2.4 MA m^{-1} in order to achieve saturation in all films. Shown in figure 1.9 are the hysteresis loops collected by Axelsson *et al.* [3] for as-deposited CFO films.

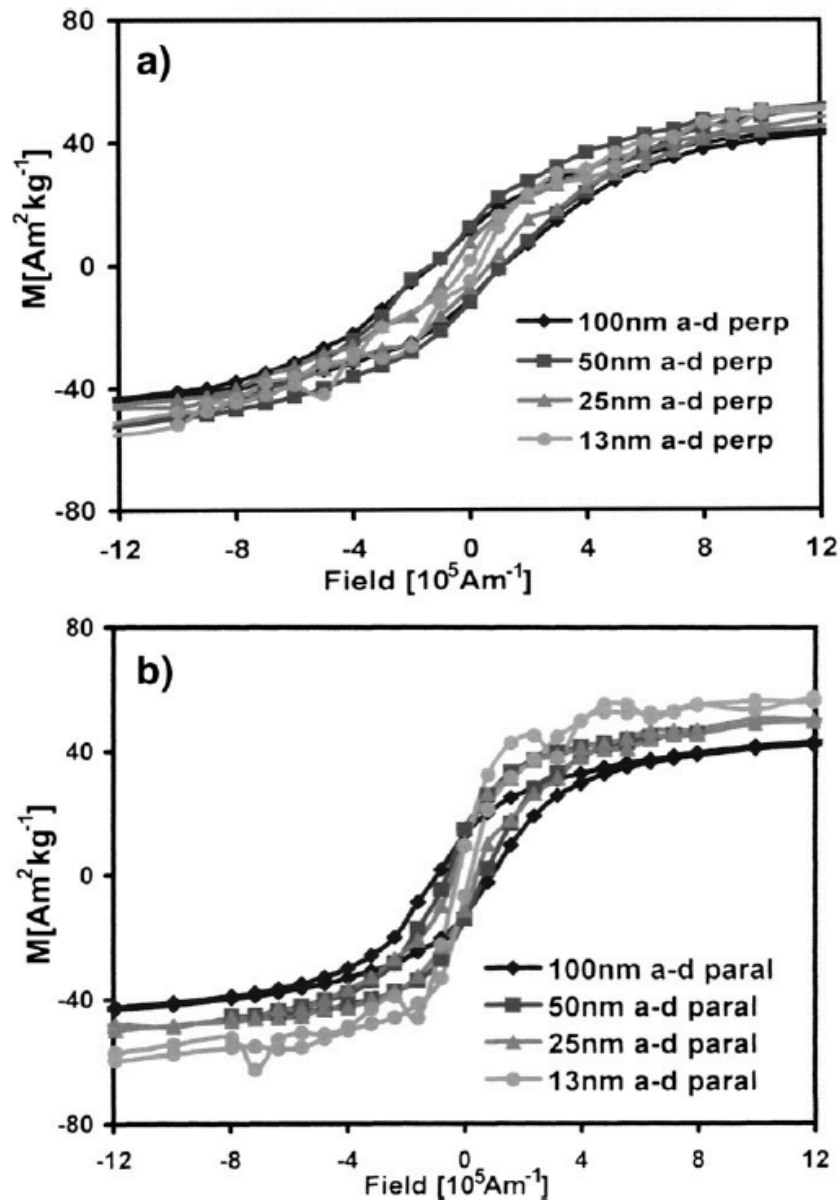


Figure 1.9 –Magnetic hysteresis loops for as-deposited CFO films with field applied (a) parallel to the film (in-plane) and (b) perpendicular to the film (out of plane) [3].

Axelsson *et al.*^[3] found a value of M_s in all as-deposited films of $\sim 50\%$ that of bulk CFO ($M_s = 80 \text{ Am}^2\text{kg}^{-1}$ [48]). H_c was found to decrease with film thickness and no directional dependence or significant change in M_s was observed. Shown in figure 1.10 are the hysteresis loops collected by Axelsson *et al.* [3] for oxygen post-annealed CFO films.

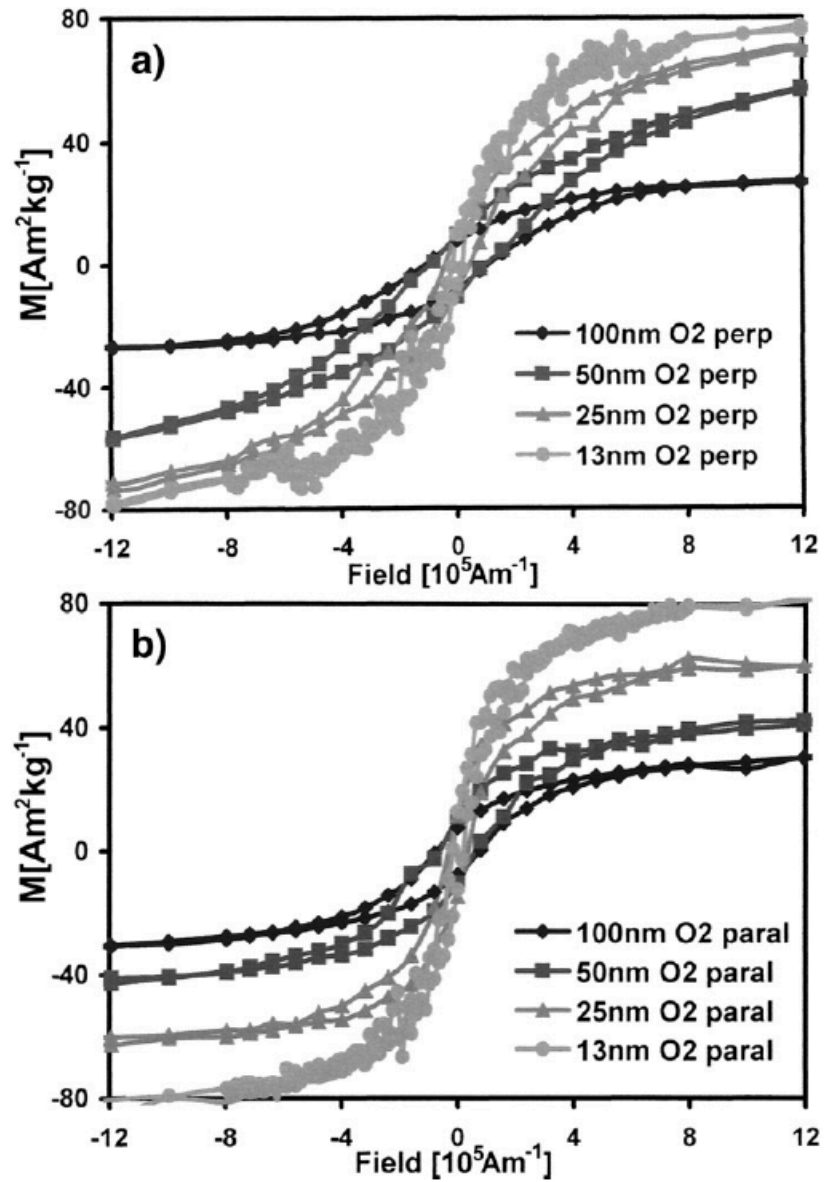


Figure 1.10 –Magnetic hysteresis loops for oxygen post-annealed CFO films with field applied (a) parallel to the film (in-plane) and (b) perpendicular to the film (out of plane)^[3].

M_s in oxygen post-annealed films was found to vary strongly with film thickness. With respect to the as-deposited films, M_s in the thickest post-annealed film (100 nm) was found to decrease though in thinner films (25 nm, 13 nm) increased significantly. A summary of the magnetic properties of CFO films grown by Axelsson *et al.* [3] is given in table 1.5.

Table 1.5 – Magnetic properties of CoFe_2O_4 films as a function of film thickness, orientation and annealing [3].

Film Orientation	t (nm)	M_s ($\text{Am}^2\text{kg}^{-1}$)		M_r ($\text{Am}^2\text{kg}^{-1}$)		H_c (MAm^{-1})		Appl. H for M_s (MAm^{-1})	
		AD	OA	AD	OA	AD	OA	AD	OA
Parallel	13	50	81	9.5	13.0	0.022	0.021	0.4	0.7
	25	51	59	10.5	11.7	0.047	0.033	0.8	0.8
	50	46	43	14.8	11.1	0.065	0.051	0.9	1.2
	100	44	33	13.1	8.0	0.095	0.080	1.4	1.4
Perpendicular	13	57	78	4.0	10.0	0.023	0.017	1.0	0.5
	25	52	68	7.6	10.4	0.051	0.040	1.0	1.0
	50	57	60	12.4	9.7	0.096	0.095	1.2	1.4
	100	47	24	11.4	7.8	0.096	0.080	1.2	0.6

In order to explain variations in the M_s of CFO thin films, Axelsson *et al.* [3] suggest a random cation arrangement in as-deposited CFO that becomes modified by post-annealing. The observed variations in M_s were argued to be a result of simultaneous cation reordering and reoxidation processes taking place during the oxygen post-annealing.

Cation ordering was argued to occur simultaneously across the film volume and lead to a decrease in the net magnetic moment due to the redistribution of Co^{2+}

and Fe^{3+} over O_h and T_d interstices in the spinel structure. Reoxidation is thought to occur by vacancy diffusion from within the film to the film surface and is thought to enhance the degree of superexchange coupling therefore leading to an increase in M_s [3]. Axelsson *et al.* [3] report a decrease in the oxygen and vacancy diffusion rate with increased annealing time associated with increasing thickness of a surface reoxidation layer (d_{ox}) as shown in figure 1.11. The difference in the M_s observed for the post-annealed films was argued to be a consequence of the relative thickness of the re-oxidised layer and total film thickness (h) as shown in figure 1.11. For the thinnest films, the re-oxidised and ordered layer represents a greater fraction of the total film volume leading to an increase in M_s with respect to as-deposited CFO. In thicker films, the re-oxidised layer is a less significant fraction of the total thickness layer leading to decreased M_s with respect to as-deposited CFO. A detailed discussion of the chemistry of post-annealing in CFO thin films is provided in section 6.6.

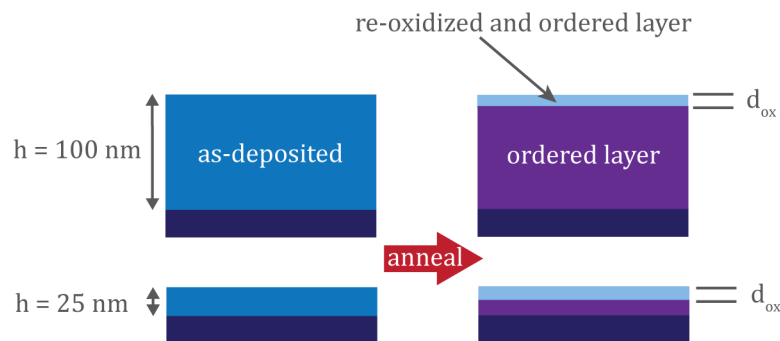


Figure 1.11 – Schematic showing as-deposited films of different thickness and the corresponding reoxidation and cation ordering layers following oxygen post-annealing [3].

1.7. Project Overview

The structure property relationships of a number of ferrite thin film systems have been widely investigated using bulk characterisation techniques such as XRD and magnetometry. Basic TEM analysis has been performed though typically using plan view specimens, which give no information about interface structure or chemistry. Xie *et al.* [35] have presented a preliminary investigation of the interface structure of as-deposited STO/CFO by HRSTEM, enabling misfit dislocations to be identified indirectly through Fourier filtering. Iron valence was determined from the iron $L_{2,3}$ white line ratio though detailed fine structural analysis and assessment of the inversion parameter was not performed.

1.7.1. Aims and Objectives

The primary objectives of the work contained in this Thesis are given below.

- (i) Develop a TEM specimen preparation route capable of producing ultra thin (~ 30 nm) and contamination free cross sections reproducibly.
- (ii) Identify the misfit accommodation mechanisms in as-deposited and oxygen post-annealed (001) $\text{SrTiO}_3/\text{CoFe}_2\text{O}_4$ thin films grown by PLD and determine variations in the accommodation of misfit associated with post processing conditions.
- (iii) Investigate local chemistry in as-deposited and oxygen post-annealed CoFe_2O_4 thin films grown on (001) SrTiO_3 by monochromated STEM-EELS in order to identify local variations in transition metal valence and coordination environment.
- (iv) Correlate local chemistry in CoFe_2O_4 thin films with bulk magnetic behaviour determined by SQUID magnetometry and validate the chemical model for this magnetic behaviour previously proposed by Axelsson *et al.* [3].

1.7.2. Thesis Outline

Fundamentals of magnetism have been introduced and the structural and magnetic properties of the spinel class of materials discussed. A review of previous investigations of the microstructure, and chemistry of ferrite thin films has been presented in order to rationalise the novelty and relevance of this thesis.

An overview of the instrumentation, techniques and theory relevant to this thesis is given in chapter 2 followed by a detailed investigation of specimen preparation techniques suitable for the preparation of cross sectional TEM specimens from oxide thin film samples in chapter 3.

In chapter 4, a detailed investigation of the microstructure of as-deposited and post-annealed STO/CFO films of thickness 25 – 200 nm by aberration corrected TEM is presented. Imaging at sub-Ångstrom spatial resolution has enabled the interface structure in STO/CFO to be analysed with a precision not previously reported in the literature. This has led to the identification of microstructural features that can be associated with the post processing conditions.

In chapter 5, electronic structure and bonding in transition metal oxides is discussed in addition to full multiple scattering theories. An investigation of fine structural variations in core loss edges present in EELS spectra acquired from cobalt and iron oxides are presented. Methods for determining the degree of inversion from core loss EELS spectra are discussed and investigated.

The results of chapter 5 are then applied to an investigation of local chemistry and electronic structure in a 50 nm post annealed STO/CFO film by STEM-EELS in chapter 6. Conclusions and ideas for future work are presented in chapter 7.

Chapter 2 – Instrumentation and Theory

2.1 Introduction

In order to fully understand the structure-property processing relationships in epitaxial thin films it is necessary to investigate the properties of the substrate/film interface. The TEM and STEM are powerful analytical tools for the study of interfaces.

The background and theory of transmission electron microscopy are introduced in the following chapter in order to provide sufficient background information for interpretation of results presented in later chapters. Particular attention is paid to high resolution electron microscopy, scanning transmission electron microscopy and EELS as these were the core analytical techniques used for the analysis of STO/CFO thin films.

2.2 Imaging with Electrons

The spatial resolution of an optical system is defined as the smallest distance at which two objects may be resolved separately. In a perfect optical system, spatial resolution is diffraction limited by the finite radii of the optical components. The resolution is diffraction limited when the first diffraction minimum of one source point coincides with the diffraction maximum of another^[49]. The theoretical angular resolution (θ_r) of a lens of diameter (d) is given by the Rayleigh criterion,

$$\sin\theta_r = \frac{1.22\lambda}{d} \quad (2.1)$$

where λ is the wavelength of the illuminating source.

The Rayleigh criterion shows that there is a fundamental limit on the resolution that can be achieved in an optical microscope that is imposed by the wavelength of light.

Following de Broglie's theorisation of wave particle duality^[50], the wave properties of the electron were confirmed independently by diffraction experiments carried out by Davisson and Germer^[51] and Thompson and Reid^[52]. From de Broglie's theorisation, it can be seen that the wavelength of electrons accelerated over a potential difference (V) decreases as the acceleration potential increases, as shown in equation 2.2,

$$\lambda = \frac{h}{\sqrt{2m_0 eV \left(1 + \frac{eV}{2m_0 c^2} \right)}} \quad (2.2)$$

where h is the Planck constant, m_0 the rest mass of the electron, e the electron charge and c the speed of light in vacuum. The equation for the relativistic

wavelength is shown as electrons accelerated over a high potentials can reach velocities that are significant fraction of the speed of light ^[53].

From equation 2.2 it was clear that the optical resolution could be overcome by using an electron microscope. Knoll and Ruska presented the first transmission electron images of various metal grid specimens in 1932. The resolution limit imposed by the wavelength of light was overcome within one year ^[53-55].

The relativistic wavelength for electrons accelerated over a potential of 300 kV is 0.02 Å, providing a theoretical sub-atomic resolution. Due to aberrations in the electron lenses used in the TEM, true atomic resolution is only achievable by aberration correction or by using high accelerating voltages. Further details are provided in section (2.8.3).

2.3 Beam Specimen Interactions

In the context of a discussion of beam specimen interactions, a thin specimen is defined as a thin electron transparent material suitable for analysis with a transmission electron beam.

Fast electrons (100 kV – 300 kV) incident on a thin specimen interact with the specimen by the Coulomb force. The coulomb interactions may be attractive, between a fast electron and an atomic nucleus, or repulsive between a fast electron and core or valence electrons within the specimen. An illustration some of the important different beam specimen interactions is shown in figure 2.1.

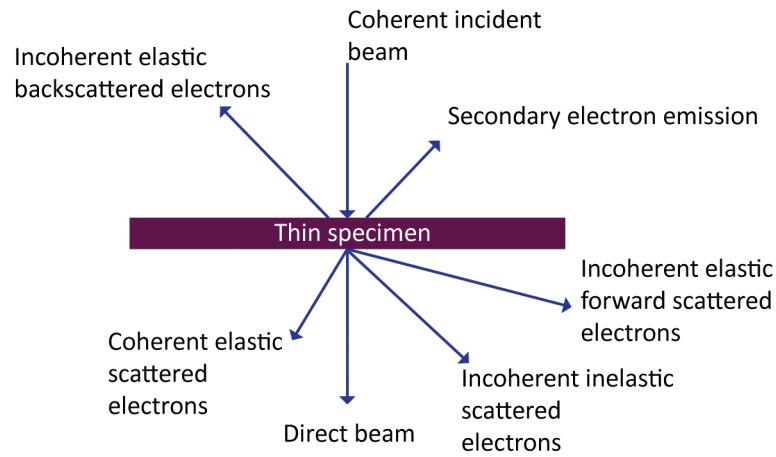


Figure 2.1– Illustration of important beam specimen interactions ^[53]

It is conventional to describe beam specimen interactions in terms of the scattering cross section and mean free path. The total scattering cross section (Q_{total}) for a specimen of thickness (t) is given by,

$$Q_{\text{total}} t = \frac{N_0 \sigma_{\text{total}} (\rho t)}{A} \quad (2.3)$$

where σ_{total} is the total scattering cross section for an isolated atom, N_0 Avogadro's number, A the atomic weight and ρ the density.

The mean free path (λ) is the average distance a fast electron travels in the thin specimen before which this scattering event occurs. The mean free path is inversely proportional to the probability (p) of a scattering event occurring, and therefore inversely proportional to the scattering cross section. Equation 2.3 can be rewritten as

$$p = \frac{t}{\lambda} = \frac{N_0 \sigma_T (\rho t)}{A} \quad (2.4)$$

The relative scattering angle depends on the nature of a scattering interaction. Scattering angles for electron-nucleus interactions are relatively high compared with scattering angles for electron-electron interactions [53]. The angular distribution of scattering is a function of the atomic scattering factor for X-rays (f_x) [56], atomic number of the scattering centre (Z) and the electron wavelength and is described by the atomic scattering factor,

$$f(\theta) = \frac{me^2}{2h^2} \left(\frac{\lambda}{\sin \theta} \right)^2 (Z - f_x) \quad (2.5)$$

where $f(\theta)$ is the atomic scattering factor, m the relativistic electron mass, and θ the scattering angle of the fast electron [53].

2.4 Elastic Scattering

Elastic scattering is defined as scattering involving no exchange of energy [56]. The probability of elastic scattering is given by the square of $f(\theta)$ [53]. The Z dependent term represents the Rutherford scattering, which is modified by f_x which accounts for scattering from the screened nuclear potential [56]. The atomic scattering amplitude decreases with θ , falling rapidly at high scattering angle [56].

The Rutherford differential cross section ($d\sigma(\theta)/d\Omega$) gives the elastic scattering cross section (σ) per unit solid angle ($d\Omega$) [53]. The screened relativistic Rutherford cross section is given by,

$$\frac{d\sigma(\theta)}{d\Omega} = \frac{\lambda^4 Z^2}{64\pi^4 a_0 \left[\sin^2\left(\frac{\theta}{2}\right) + \frac{\theta_0}{4} \right]^2} \quad (2.6)$$

where a_0 is the Bohr radius, and θ_0 is a screening parameter given by $\theta_0 = (0.117Z^{1/3})/E_0^{1/2}$ [53].

At high scattering angle, there is no phase relationship between scattered electrons. High angle elastic scattering is incoherent and scattering events can be treated independently. As the differential cross section is proportional to Z^2 , images may be formed in which the contrast is proportional to Z^2 by collecting only those electrons that are scattered to high angle. This is the basis of z -contrast image formation using annular detectors in STEM (section 2.11.1).

In crystalline specimens, the low angle scattering (10 – 20 mrad)[57] intensity is modulated by the periodic potential that is present in an ordered structure [56]. Interference effects become important due to the structural periodicity and the wave nature of the electron beam must be considered. The structure factor, $F(\theta)$, describes electron scattering from a unit cell. $F(\theta)$ is a product of the sum of the

atomic scattering factors for a unit cell, and a phase factor that accounts for phase differences between the electron waves scattered from different crystallographic planes within the cell [53].

2.5 Electron Diffraction

If the fast electron beam is treated as a plane wave, the interaction of the beam with a periodic structure causes the generation of secondary spherical wavelets at atomic scattering centres within the sample by Huygens principle [53]. The scattering intensity is modulated by interference between the secondary wavelets and unscattered plane wave as illustrated in figure 2.2 [53].

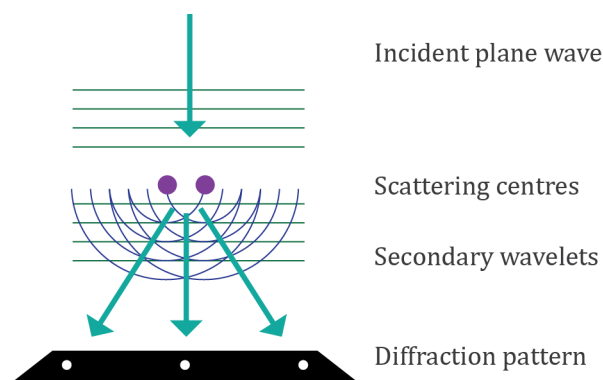


Figure 2.2 – Illustration of how the relation between the incident electron beam, secondary wavelets and the electron diffraction pattern [53].

If the interference is destructive, electron waves do not propagate through the material and the scattering intensity is zero. If the interference is constructive electron waves can propagate and the scattering intensity is non-zero. Diffraction can be explained using a simple geometrical argument in which two electron beams reflect from two atomic planes separated by a distance d as shown in figure 2.3. From figure 2.3 it is clear that $AB = d\sin\theta$ and $BC = d\sin\theta$ so that the path difference between the scattered beams is $2d\sin\theta$. Constructive

interference occurs if the path difference between the scattered beams is a whole number of wavelengths which is satisfied when,

$$n\lambda = 2d \sin \theta \quad (2.7)$$

which is known as Bragg's law ^[53]. Diffraction conditions were also formalised through wave mechanics by Laue, though the conditions derived simplify to Bragg's law and are therefore not discussed.

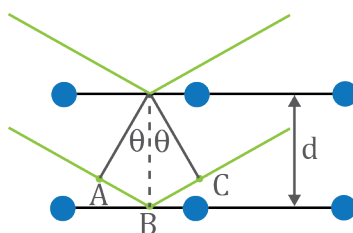


Figure 2.3 – Illustration of the path difference between two electron beams scattered from two atomic planes separated by a spacing d from ^[53]

For a particular interplanar spacing there is a characteristic scattering angle at which constructive interference occurs, known as the Bragg angle (θ_B) ^[53]. Scattered waves will only propagate in a crystal where the scattering angle is a multiple of θ_B . Unlike an image, which shows the spatial variation in scattering intensity, a diffraction pattern gives the angular distribution of the scattering intensity.

If a crystalline specimen is tilted so that a specific family of planes is normal to the electron beam, it is said to be in a zone axis orientation (ZOA). The diffraction pattern of a specimen oriented to a ZOA will consist of a symmetrical array of high intensity diffraction spots, each corresponding to a Bragg reflection for a specific crystallographic plane.

2.6 Inelastic Scattering

Inelastic scattering is scattering in which energy is transferred from the fast electron to the specimen [56]. This energy may be lost by a number of mechanisms that include the emission of secondary particles or photons. Inelastic scattering causes the emission of X-rays, secondary electrons and Auger electrons from the specimen. Inelastic scattering is also responsible for exciting plasmons in the valence electron density, and lattice vibrations (phonons) within the specimen [53,58].

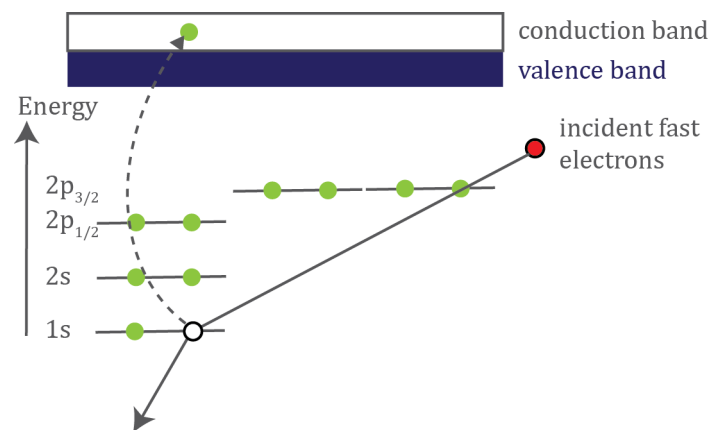


Figure 2.4 – Schematic of a core loss inelastic scattering event. The transition from a 1s level to the conduction band would contribute to a K-edge in the electron energy loss spectrum [53].

Local chemical and bonding information can be determined from the energy loss of the fast electron beam due to inelastic scattering [53,56,59]. This is the basis for electron energy loss spectroscopy (EELS) which is discussed in section 2.12.

2.7 Specimen Damage

Specimen damage occurs by atomic displacement due to high angle elastic scattering or radiolysis due to inelastic scattering ^[60]. Atomic displacement damage increases with accelerating voltage ^[60]. Radiolysis decreases with increased accelerating voltage and decreased thickness as the interaction cross section becomes smaller. There is a material dependent threshold voltage for each process. Damage can also occur due to electrostatic charging ^[53,60].

At low scattering angles the energy transfer to nuclei is low but at high angle ($\theta > 90^\circ$), energy transfer to nuclei can be sufficient to cause displacement from lattice positions to interstitials ^[60]. Displacement is known as knock on damage if the displacement occurs within the specimen and sputtering if displacement occurs at the surface causing ejection of surface atom ^[53,60].

Inelastic scattering can cause chemical bonds in the specimen to be broken. Damage by this mechanism is known as radiolysis. Radiolytic damage is thought to occur in transition metal oxides by the creation of inner shell vacancies at metal sites in the target material. This is followed by Auger decay at oxygen sites which leaves a neutral or positive oxygen atom that is repelled by the surrounding metal cations and ejected from the specimen^[60].

In an EELS fine structure investigation of transition metal oxides, Krivanek and Paterson did not damage observe specimen damage in iron or cobalt oxides ^[61,62]. EELS spectra were acquired using a dedicated STEM at accelerating voltage 100 kV, using a 2 nm probe of beam current 1 nA and acquisition times of 6-8 s per pixel ^[61,62]. In a high resolution EELS study of transition metal oxides, Mitterbauer *et al.* did not report any specimen damage even after typical exposure times of 60 – 90 s. EELS spectra were acquired using a monochromated TEM operating in diffraction mode at accelerating voltage 200 kV ^[63].

2.8 The Transmission Electron Microscope

A conventional TEM consists of an electron source followed by an array of cylindrically symmetric electromagnetic lenses and a number of electron detectors. A high vacuum (1×10^{-5} – 1×10^{-10} mbar) is maintained within the TEM column order to avoid unwanted scattering from ambient gas molecules and avoid damage to the electron source.

2.8.1. Electron Sources

A solid material can emit electrons if it is raised to high temperature (thermionic emission) or subjected to a high electric field (field emission). An electron gun consists of a thermionic or field emission source followed by electrodes that accelerate electrons, ejected from the source material, into a narrow beam of known energy proportional to the chosen accelerating voltage.

Electron emission is achieved in a thermionic gun by raising the temperature of the source by resistive heating. Ejected electrons are then accelerated over a large potential difference by an anode. A preliminary electrode known as the Wehnelt cap is placed after the source and held at small negative bias relative to the filament in order to narrow the width of the electron beam. A schematic of a thermionic gun is shown in figure 2.5.

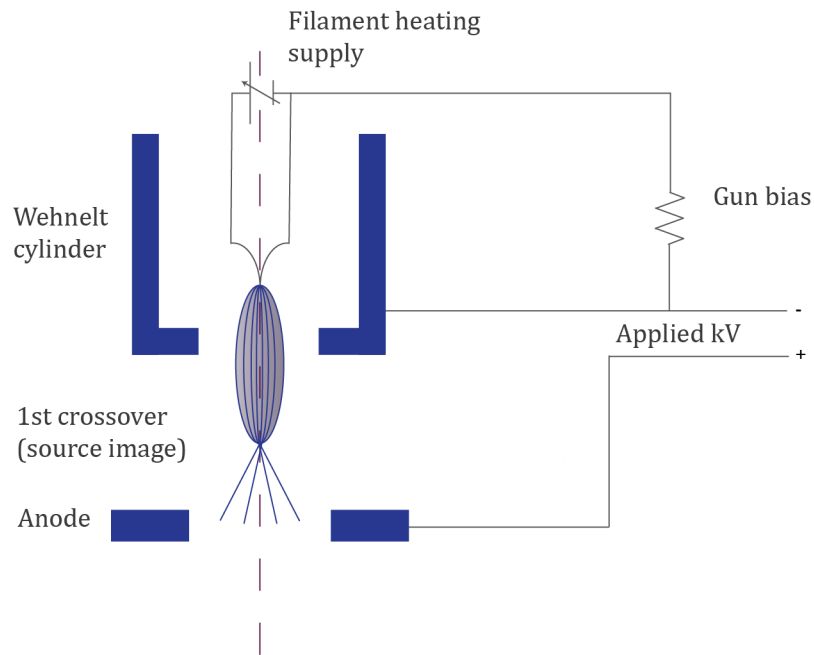


Figure 2.5 – Schematic of a thermionic electron source ^[53]

Field emission is achieved by subjecting the source material to high electric field. There is a probability that electrons may exit the surface of a solid by tunnelling through the potential barrier posed by the work function (ϕ). The resultant tunnelling current is a strong function of applied electric field ^[53,58]. A schematic of a field emission gun is shown in figure 2.6. The field emission tip consists of a single crystal of tungsten fibre drawn to a diameter of $<0.1 \mu\text{m}$. In contrast to a thermionic gun, a field emission gun has two positive electrodes. The first anode provides the extraction voltage needed to achieve electron emission and the second anode provides the accelerating voltage ^[53].

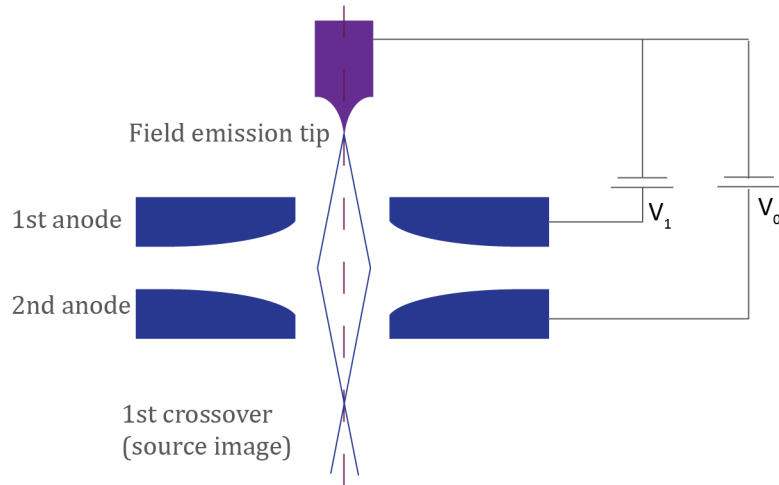


Figure 2.6 – Schematic of a field emission gun ^[53]

The important characteristics of different electron sources are summarised in table 2.1 for comparison.

Table 2.1 – Comparison of the emission characteristics of different electron sources ^[53,57,64]

	Units	Tungsten	LaB ₆	FEG	
				<i>thermal</i>	<i>cold</i>
Work function (ϕ)	eV	4.5	2.4	4.5	4.5
temperature	K	2700	1700	1800	300
Crossover	μm	50	10	0.1	0.005
Brightness	$\text{Am}^{-2}\text{sr}^{-1}$	10^9	5×10^{10}	5×10^{12}	2×10^{13}
Energy spread	eV	3	1.5	0.6	0.3
Vacuum	mbar	1×10^{-5}	1×10^{-6}	1×10^{-9}	1×10^{-10}

The brightness (current density per solid angle) of thermionic sources increases with operating temperature and for materials of low work function ^[53]. Tungsten filaments are commonly used as the source material in thermionic guns due to the high melting point (3660K) and low cost ^[53]. LaB₆ <110> single crystals provide increased brightness due to the low work function. Field emission sources are superior in terms of brightness, spatial coherence, crossover size and

energy spread and are therefore the most suitable source type for nanoanalysis. However, a much higher vacuum is required in order to keep the FEG tip free of contamination [53].

The FEI Titan is fitted with a Schottky type emitter; a thermally assisted FEG. The tip consists of a <100> Tungsten single crystal coated in Zirconia (ZrO₂). During operation the tip is heated to 1800°C, which improves electron emission and reduces contamination [53,65].

2.8.2. Electron Lenses and Aberrations

Electrons are deflected by electrostatic and electromagnetic fields so an electron beam can be focussed electrostatic and electromagnetic lenses. Electromagnetic lenses are generally superior to electrostatic lenses, as they do not suffer from high voltage breakdown. As a results, electromagnetic lenses are more widely used [53,58].

An electromagnetic lens consists of a cylindrically symmetric soft iron pole piece with a hole drilled through the centre known as the bore. A coil of copper is wrapped around the polepiece so that a magnetic field is created in the bore when current is passed through the wire; the field strength is dependent on applied current [53]. The electromagnetic lens must be water-cooled to compensate for resistive heating in the copper coils [53].

The magnetic field is axially symmetric but inhomogeneous in the beam direction. Electrons of charge (*e*) passing through an electromagnetic field experience a force (**F**) given by,

$$\mathbf{F} = -e(\mathbf{v} \times \mathbf{B}) \quad (2.8)$$

where **E** and **B** are the electric and magnetic field strengths respectively [53,58].

The electric field component is zero. The magnetic field has axial and radial components. An electron passing through the lens feels a force from each component and follows a helical path through the lens where the axial (z) displacement is given by,

$$z = v_{\text{axial}} t \quad (2.9)$$

where v_{axial} is the axial velocity travelled in time (t). The radial displacement is given by,

$$r = \frac{mv_{\text{radial}}}{eB} \quad (2.10)$$

where m is the electron mass, e the electron charge and v_{radial} the radial velocity.

A parallel beam entering a perfect lens is caused to reconverge at a point known as the crossover or focal point. The focal length is the distance between the lens and the focal point. In the case of electron lenses, the focal point is more commonly referred to as the crossover point ^[53]. A stronger lens has a shorter focal length and a crossover that is closer to the lens. Parallel rays entering a perfect lens converge at the crossover.

Due to imperfections in real lenses, electrons travelling along axial paths far from the optic axis are not brought to focus at the same point as electrons following axial paths close to the optic axis ^[53], illustrated in figure 2.7a. An axial ray travelling far from the optic axis is focused more strongly than a ray close to the optic axis, which leads to image distortion referred to as spherical aberration (C_s). The information limit (d) in a TEM is limited by spherical aberration to,

$$d = 0.6(C_3\lambda^3)^{1/4} \quad (2.11)$$

where C_3 is the 3rd order spherical aberration coefficient ^[53,66].

Electron lenses also suffer from chromatic aberration. Electrons of different energy are brought to a focus at different points ^[53]. Sources of chromatic aberration (C_c) include energy spread in the electron source and a post specimen energy spread due to inelastic scattering ^[53]. A ray diagram illustrating the effect of C_c is shown in figure 2.7b.

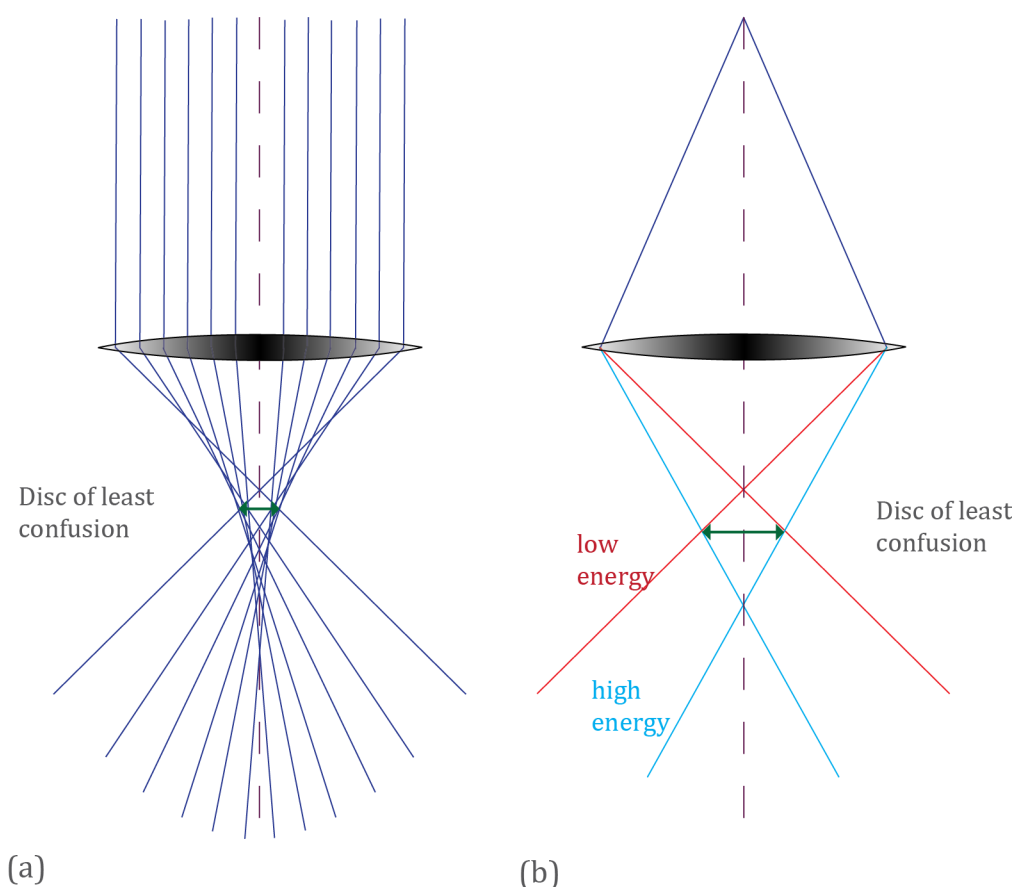


Figure 2.7 – Illustration of the effects of: (a) spherical aberration and (b) chromatic aberration in an electron lens. ^[53,58]

Coma, which is a non-axial aberration, leads to further image distortion. Rays emanating from source points that are not on the optic axis travel at angle to the optic axis and are not focussed at the same point in an image ^[53]. Coma has a radial component which is isotropic and an azimuthal component that is anisotropic ^[66]. All rotationally symmetric lenses have a coma free plane ^[66].

2.8.3. Aberration Correction

Rotationally symmetric electron lenses have large positive aberration coefficients that are inherent to their rotational symmetry [67]. Scherzer showed that these aberrations could be corrected using certain combinations of multipole lenses [68]. By aberration correction, the resolution limit of a TEM is decreased beyond the limit normally imposed by the rotationally symmetric lens design.

Haider *et al.* report two configurations of electron multipole lenses that allow spatial resolution limits of $< 1 \text{ \AA}$ [66]. In the first, a conventional objective lens is used for image formation in addition to five multipole lenses. In the second design, two hexapole lenses and four weak transfer lenses compensate the C_s of a conventional objective lens [66]. Though a hexapole corrector cannot compensate C_c , the constraints on field stability to maintain a hexapole field ($\sim 10 \text{ p.p.m}$) are less than for a quadrupole field ($\sim 0.1 \text{ p.p.m}$), so the hexapole design is favoured [66]. Shown in figure 2.8 is a schematic of a double hexapole C_s corrector.

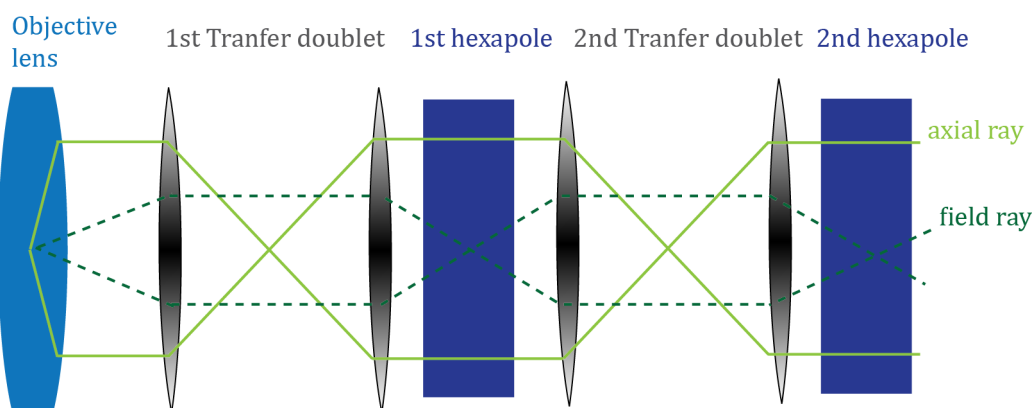


Figure 2.8 – Schematic of the double hexapole C_s corrector showing objective lens, two hexapoles and four transfer lenses [66].

Primary aberrations in the 1st hexapole, which are non-rotationally symmetric, are corrected by the 2nd hexapole. The most significant aberration in the double hexapole configuration is then a 3rd order spherical aberration that is rotationally symmetric and opposite in sign to that of a rotationally symmetric

lens [66,69]. The magnitude of the 3rd order spherical aberration is proportional to the square of the hexapole field strength. By applying a suitable field strength to the hexapoles, it is possible to compensate the positive C_s of the objective lens with the negative C_s of the double hexapole configuration [66,69].

Radial coma is eliminated by making the coma free plane of the C_s corrector coincident with the coma free plane of the objective lens, which is done by adjusting the strength of the 1st transfer doublet [69]. Azimuthal coma can be reduced by applying a field over the 1st transfer doublet that is opposite in sign to the objective lens, but cannot be completely cancelled [66,69].

Alignment of the double hexapole corrector is performed using the Zemlin tableau method [70].

If C_s is zero, the information limit is defined by C_c and the energy spread (ΔE) [53].

$$d_{C_s=0} = \sqrt{\left(\frac{\Delta E}{E}\right) \lambda C_c} \quad (2.12)$$

2.8.4. Image Formation

Preliminary analysis of a specimen is generally carried out using a viewing screen. The screen is coated with doped ZnS crystals that emit green light ($\lambda \approx 550$ nm) when irradiated with electrons. The light intensity visible on the screen is proportional to the scattered electron intensity so that an image of the specimen is formed [53].

The FEI Titan contains two charge-coupled device (CCD) cameras, the Gatan multiscan CCD and Gatan Imaging Filter (GIF) CCD. The multiscan CCD is used for TEM imaging and diffraction analysis. The GIF CCD is used for EELS analysis and energy-filtered transmission electron microscopy (EFTEM). A CCD is a metal oxide semiconductor device consisting of isolated quantum wells (pixels) that store a charge proportional to the electron intensity falling on the CCD [53]. The

charge from each pixel is read out in serial, in rows to amplifiers. The amplifiers are connected to suitable electronics and a desktop computer. Data can be read and manipulated by appropriate software.

The GIF CCD and Gatan CCD are 2048 x 2048 detectors. The GIF CCD is divided into four quadrants, which decreases readout time. Binning may also decrease readout time. Binning is achieved by moving more than one row at a time into the readout array. The readout array is moved by more than one column, which introduces an averaging effect (figure 2.9). The effective number of pixels decreases but the summing effect increases read out speed and the signal to noise ratio. X and y binning must be the same when imaging but can take different values when collecting EELS spectra.

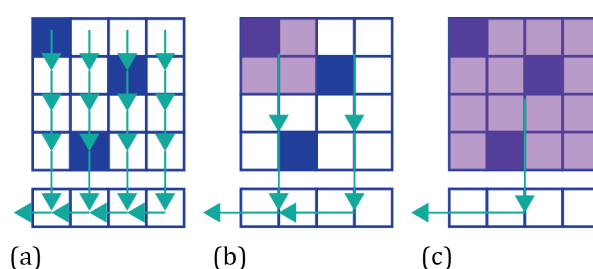


Figure 2.9 – CCD readout at binning (a) 1, (b) 2 and (c) 4 Adapted from ^[53]

2.8.5. EELS Acquisition

EELS spectra are recorded on the GIF CCD using the Gatan Imaging Filter (GIF) Tridiem 865 parallel electron energy-loss spectrometer operating in spectroscopy mode. A schematic of the GIF 865 is provided in figure 2.10.

Electrons enter the spectrometer through the entrance aperture and enter an electrically isolated drift tube housed in a 90° magnetic prism ^[56]. Electrons of different energies follow paths of different curvature due to the magnetic field, which causes a dispersion in the x direction as shown in figure 2.10 ^[56]. The prism has a focussing effect and causes the dispersed electron signal to form a line profile at the detector (CCD), which is the raw EELS spectrum ^[56].

An external voltage may be applied to the drift tube, which increases the electron velocity and offsets the EELS spectrum on the detector. Post prism quadrupole lenses can alter the magnification in the dispersion plane ^[56]. Aberrations from the magnetic prism are corrected by the quadrupole and sextupole lenses ^[56].

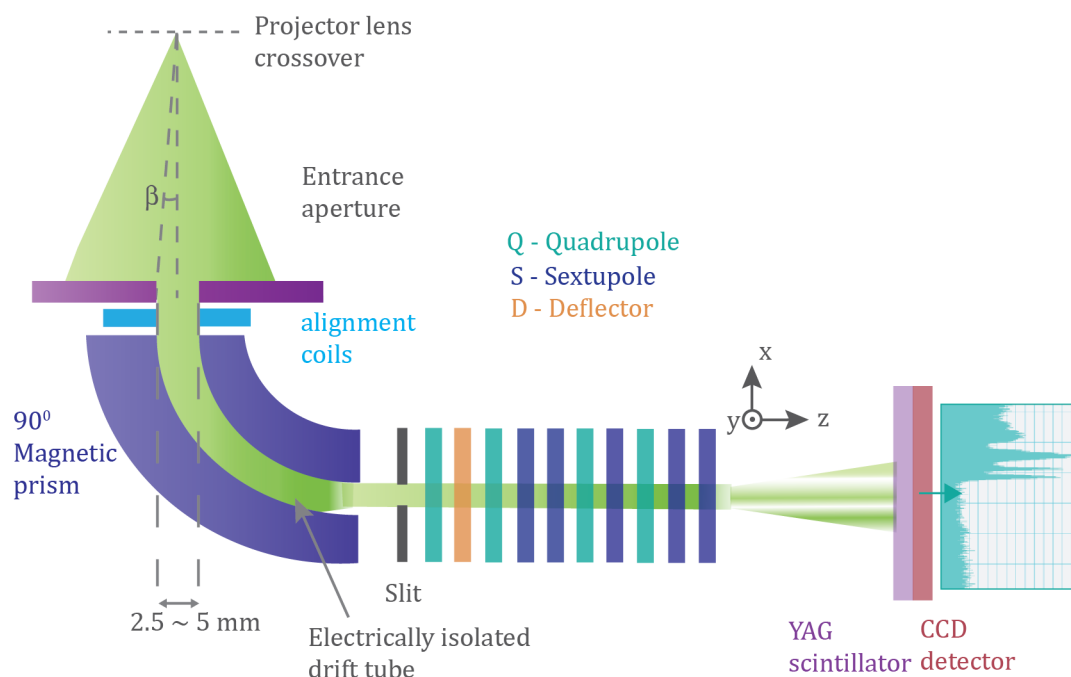


Figure 2.10 – Schematic of the electron optics in the Gatan Imaging filter optics EELS spectrometer ^[56].

2.8.6.FEI Titan 80-300

The FEI Titan is fitted with an electron monochromator, double hexapole aberration corrector (CEOS, GmbH) and a three-condenser lens system. A schematic of the FEI Titan column is shown in figure 2.11. An overview of the electron optics in the FEI Titan is given in the following sections.

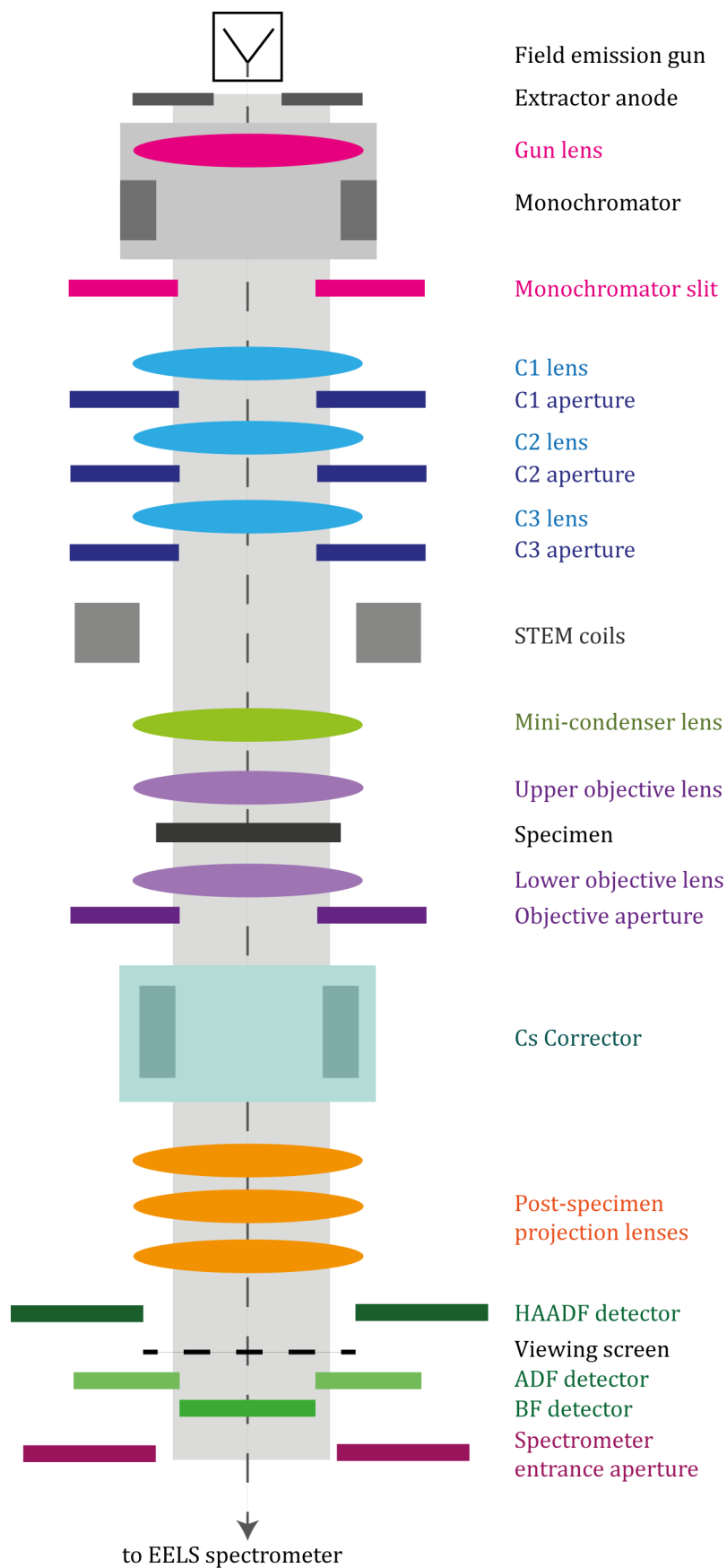


Figure 2.11 – Schematic of the FEI Titan column ^[71].

2.8.6.1. Monochromation

Electron monochromation is achieved in the FEI Titan with a Wien filter immediately below the gun lens. A schematic of a Wien filter is shown in figure 2.12.

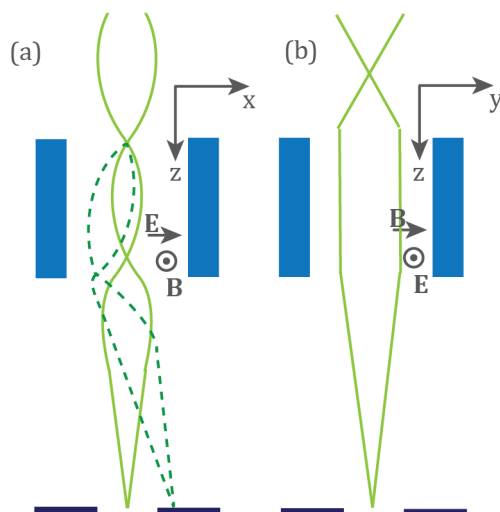


Figure 2.12 – Illustration of electron paths in the Wien filter in: (a) the dispersive direction and (b) non-dispersive direction ^[59].

The Wien filter has an electromagnetic field in the y-direction and an electrostatic field in the x-direction as shown in figure 2.12. The field polarities are arranged so that the magnetic and electrostatic forces oppose ^[59]. Electrons of the same energy travelling parallel to the optic axis are not deflected as the forces felt by the electrons from the electrostatic and electromagnetic fields cancel. Electrons of different energies or following non-axial paths are deflected, following helical paths. This gives rise to energy dispersion in the x direction as shown in figure 2.13 ^[72]. By using an energy selecting slit to select part of the beam for imaging and analysis, the effective energy spread of the source is reduced which has the effect of improving energy resolution.

The monochromator acts as a lens. The lens strength is approximately proportional to an instrument specific parameter known as the monochromator excitation ^[73]. Shown in figure 2.13 is an illustration of the energy dispersion of

the electron beam at different excitation values. Increasing the excitation increases the energy dispersion. This has the effect of decreasing the effective energy spread and improving energy resolution, but also generally decreases the beam current that can be used to form a beam or probe for analysis.

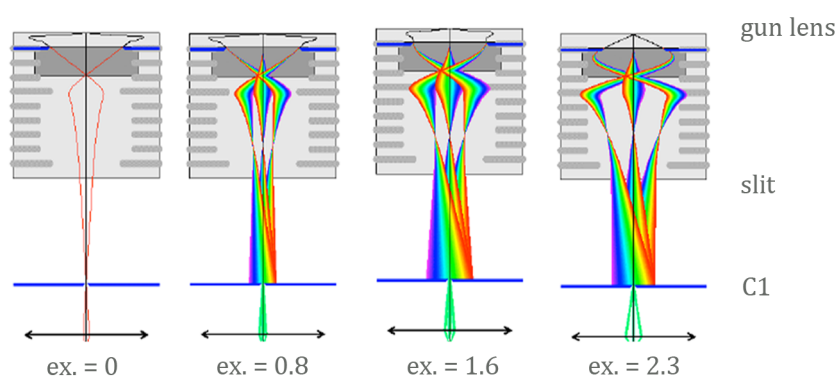


Figure 2.13 – Schematic showing the increase in energy dispersion with monochromator excitation [73].

The monochromator can be operated in accelerating or decelerating modes. In accelerating mode, the monochromator potential is less than the gun lens potential but in decelerating mode the monochromator potential is greater than the gun lens potential. Reducing the gun lens potential reduces the effect of gun lens aberrations, which enables higher energy resolutions to be achieved. While the energy resolution is lower in decelerating mode, the beam current is a $\sim 5\times$ higher [74].

The FEI Titan can be operated in filtered (monochromated) or unfiltered (non-monochromated) modes. Unfiltered mode corresponds to a monochromator excitation of zero. Filtered mode corresponds to a non-zero monochromator excitation and therefore involves analysis with an energy-filtered beam.

2.8.6.2. Pre-specimen Lenses

The pre-specimen electron optical system in the FEI Titan consists of one electrostatic lens and five electromagnetic lenses. These are the gun lens (electrostatic), 1st condenser lens (C1), second condenser lens (C2), third condenser lens (C3), minicondenser lens (MC) and the upper objective lens. A schematic of the pre-specimen lens arrangement is given in figure 2.14.

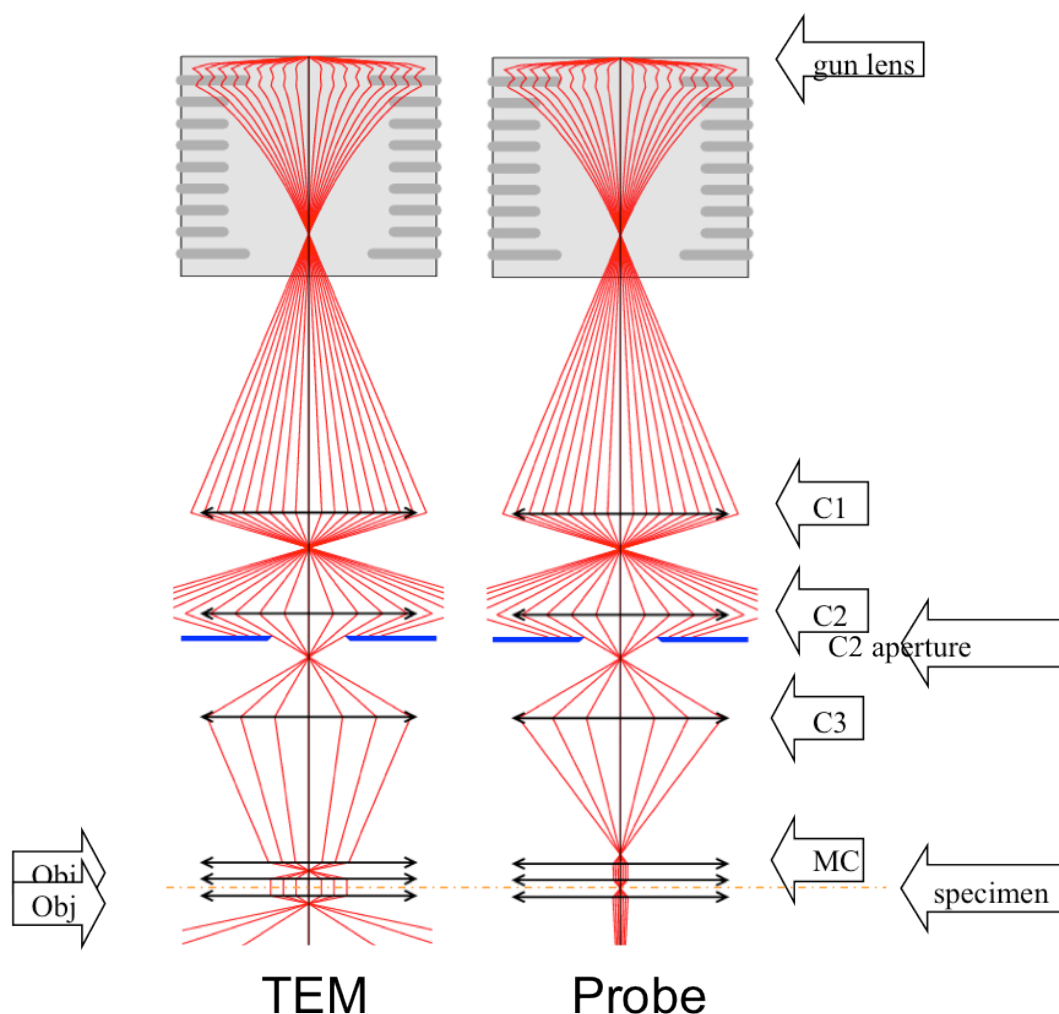


Figure 2.14 – Schematic of the 3-Condenser lens system in the FEI Titan [74].

The lenses in the TEM column are arranged such that image plane of a particular lens is the object plane of the following lens. The first lens in the FEI Titan is the gun lens, which is located below the FEG. Increasing the gun lens strength increases demagnification of the source and decreases beam current [74]. The gun lens image forms the object for the first condenser lens.

In a conventional 2-condenser lens system, the 1st condenser lens forms an image of the electron source and defines beam current [53]. The 2nd condenser lens determines the size of the area of illumination in TEM [53]. As the area of illumination decreases, the beam convergence increases so that the illumination is not parallel in a two-condenser system.

The FEI Titan has a three-condenser system. In the three-condenser system C1 and C2 form a zoom system and C2 and C3 form a second zoom system. The object and image planes of the zoom system are fixed but the object and image planes of the lenses can vary within the system.

The strength of the C1-C2 zoom system affects beam current and controls the parameter referred to as spot number [74]. In TEM, the C2-C3 zoom defines the illumination area. The zoom system provides true parallel illumination [74]. In STEM (probe), the second zoom system (C2-C3) defines convergence zoom and the convergence angle (α) [74]. The C2 aperture acts as a beam-defining aperture in both TEM and STEM modes.

When the monochromator is excited, an intermediate image of the source is formed at the monochromator slit as shown in figure 2.14 [74]. In unfiltered mode the source image is demagnified by the 1st condenser lens but in filtered mode the source image is too large ($\sim 1 \mu\text{m}$) to be focussed into a sub nanometre probe by the 1st condenser alone [74]. To form a sub nanometre probe, C2 provides additional demagnification of the source image. C2 and C3 do not act as a zoom system in this case and the C3 aperture becomes the beam defining aperture [74].

The objective lens in the FEI Titan consists of the upper objective lens polepiece, which is above the specimen, and the lower objective lens polepiece, which is below. The specimen is immersed in the field of the objective lens. If the minicondenser lens is switched on then the magnetic field of the minicondenser compensates the magnetic field of the upper objective lens, forming parallel

illumination (TEM) as shown in figure 2.15. The upper objective lens forms a probe (STEM) at the specimen when the minicondenser is unexcited [74].

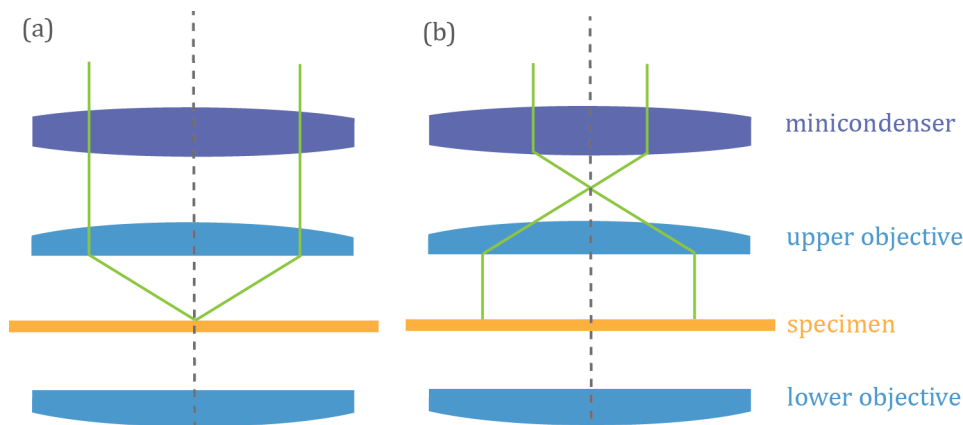


Figure 2.15 – Illustration of the minicondenser lens excitation in (a) STEM mode and (b) TEM mode [65,74].

2.8.6.3. Post Specimen Lenses

Electrons forward scattered from the exit surface of the TEM specimen are focused by the lower objective lens to form an image and diffraction pattern at the 1st image and back focal planes respectively as shown in figure 2.16.

The image plane of the intermediate lens is coincident with the object plane of the fixed strength projector lens system. The projector system is used to project the image or diffraction pattern on to the viewing screen or CCD. The microscope can be switched between diffraction and imaging modes by adjusting the intermediate lens strength, which determines whether an image or diffraction pattern is formed at the screen and CCD.

If the strength of the intermediate lens is such that that the image plane of the objective lens falls on the object plane of the intermediate lens, an image is formed. An objective aperture can be inserted at the back focal plane to improve mass thickness or diffraction contrast (section 2.9). If the strength of the intermediate lens is such that the back focal plane falls on the object plane of the

intermediate lens a DP is formed. A diffraction aperture can be inserted at the image plane to select regions of interest for diffraction analysis.

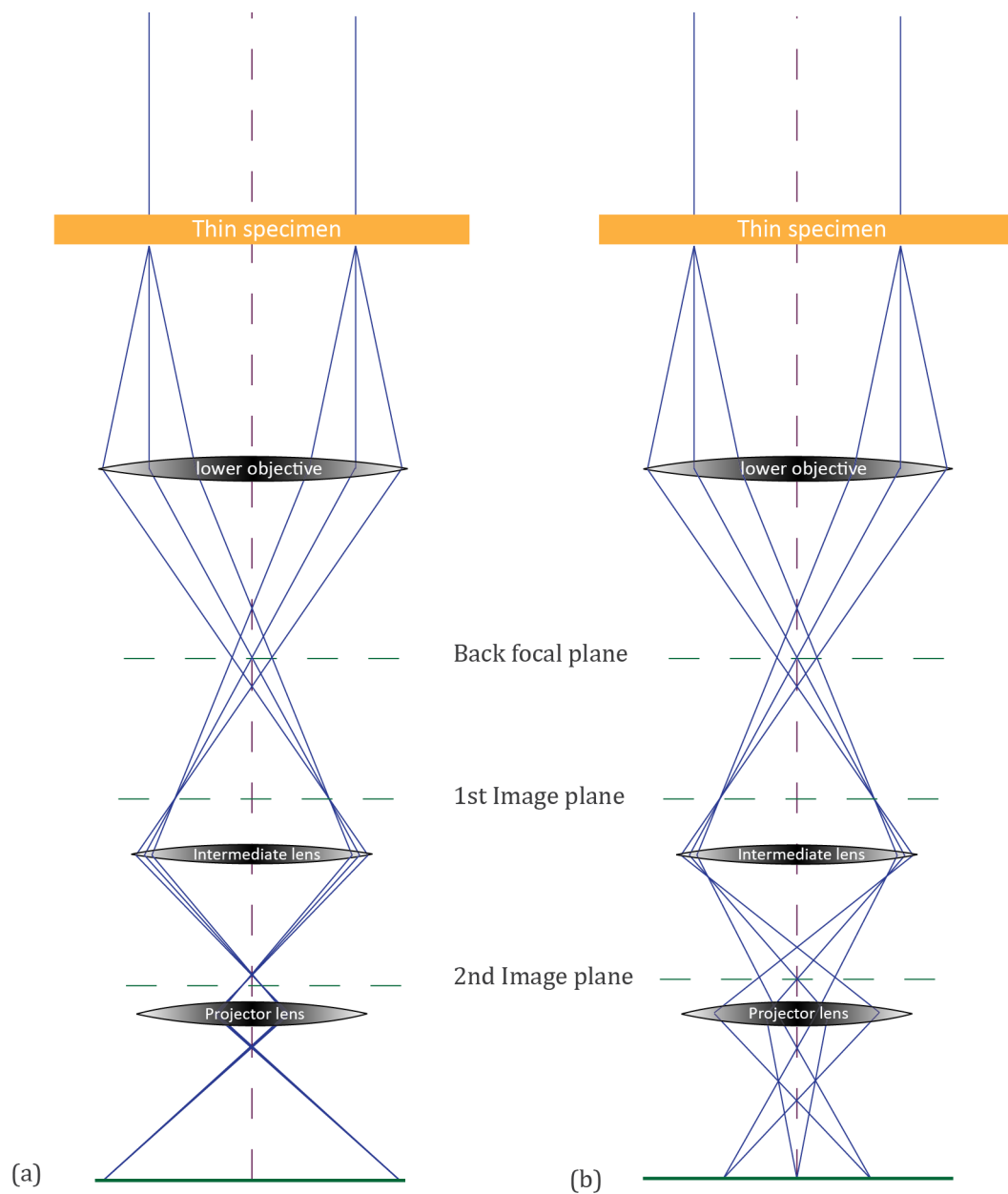


Figure 2.16 – Ray diagrams in the TEM for (a) Imaging mode and (b) Diffraction mode

2.9 TEM Image Contrast

Contrast is defined as the relative intensity change between adjacent features in an image and allows the features to be seen. If a specimen scatters incident electrons inhomogeneously, then image contrast is present in TEM images, which is proportional to the spatial distribution of the scattering intensity. As there are a number of different electron scattering mechanisms, there are a number of mechanisms for contrast formation in TEM images [53].

If forward scattered electrons are collected by the lower objective lens, they contribute positively to the image intensity. In order for scattered electrons to be collected by the lower objective lens, the scattering angle must be less than the lens acceptance angle. An objective aperture located at the back focal plane is typically used to limit the acceptance angle, which enhances contrast at low magnification.

Bragg scattering does not occur in non-periodic structures so contrast is predominantly formed from mass-thickness variation in non-crystalline specimens [53]. The probability of scattering is proportional to specimen density and thickness (equation 2.4) so specimen regions of high density or high thickness will be strongly scattering. These regions cause electrons to scatter outside of the objective lens acceptance and appear dark in the TEM image.

For crystalline specimens, it is conventional to orient the specimen to a ZOA so that a region of interest will be in the Bragg condition and diffraction contrast is enhanced. If the objective aperture is centred on the undiffracted beam, strongly scattering features appear dark on a bright background, known as bright field imaging. If the objective aperture is centred on a diffracted beam, strongly scattering features appear bright on a dark background, known as dark field imaging. It is conventional to tilt the incident beam so that the diffracted beam is on the optic axis to reduce the effect of aberrations. Both diffraction contrast and mass-thickness contrast are forms of amplitude contrast.

2.10 High Resolution Transmission Electron Microscopy

If the interaction of an electron wave with a thin specimen causes a change in phase but no change in amplitude, the specimen is said to behave as a weak phase object [53,75]. By forming an image of a periodic structure with the transmitted electron beam and at least one other beam, an interference pattern is observed in the image. Image contrast due to this interference is known as phase contrast and its analysis generally referred to as high resolution transmission electron microscopy (HRTEM).

When passing through a specimen of thickness z and potential $\phi(x,y,z)$, an electron of wavelength $\lambda = h/\sqrt{2meV_0}$ is subject to a phase change of,

$$\frac{\pi}{\lambda V_0} \int \phi(x,y,z) dz = \frac{\pi}{\lambda V_0} \phi(x,y) \quad (2.13)$$

where $\phi(x,y,z)$ is the specimen potential projected in the beam direction.

The specimen transmission function, or exit plane wavefunction, describes the incident electron wave after modification by the periodic potential and is given by,

$$q(x,y) = e^{-i\sigma\phi(x,y) - \mu(x,y)} \quad (2.14)$$

where $\mu(x,y)$ is an absorption function [75]. If a specimen is thin and the weak phase object approximation (WPOA) is valid, $q(x,y) \ll 1$ and $\mu(x,y)$ may be ignored. $q(x,y)$ is then simplified by a Taylor expansion to,

$$q(x,y) = 1 - i\sigma\phi(x,y) \quad (2.15)$$

The contrast transfer function ($T(\mathbf{u})$) describes how the phase of the exit wavefunction is modulated by the electron optics of the TEM [53] and is given by,

$$T(\mathbf{u}) = A(\mathbf{u})E(\mathbf{u})e^{i\chi(\mathbf{u})} \quad (2.16)$$

where $A(\mathbf{u})$ is the aperture function, $E(\mathbf{u})$ a damping envelope function and $\mathbf{u}$ the spatial frequency ($1/d$). $\chi(\mathbf{u})$ is a phase distortion function, which is a function of defocus (Δf) and C_s [53,76]. The defocus is defined as a change in focus from Gaussian focus (f_0) [77].

$$\chi(\mathbf{u}) = \pi \Delta f \lambda u^2 + \frac{\pi}{2} C_s \lambda^3 u^4 \quad (2.17)$$

From the contrast transfer function and specimen transmission function, the wavefunction ($\psi(x,y)$) may be calculated for the image plane [53,75]. The image intensity is then determined from $|\psi(x,y)|^2$ and to a first-order approximation is given by,

$$I(x,y) = 1 - 2\sigma\phi(x,y) \quad (2.18)$$

From equation 2.18 it is clear that the image intensity is proportional to the specimen potential $\phi(x,y,z)$. The phase contrast represents a projection of the atomic potentials in a periodic specimen [53,75].

Under phase contrast conditions, the point resolution of the TEM is defined as the inverse of the maximum spatial frequency at which electron waves contribute to the image with contrast of the same sign [77]. In an uncorrected TEM, the point resolution is maximised under the Scherzer condition [53]. As $\chi(\mathbf{u})$ is a function of Δf and C_s , the Scherzer defocus is instrument specific. For the Imperial College FEI Titan, the Scherzer defocus was calculated as $\Delta f = 59.5$ nm

with the C_s corrector switched off, using the JEMS software package. Shown in figure 2.17 is the $T(\mathbf{u})$ for the Imperial college FEI Titan at Scherzer defocus.

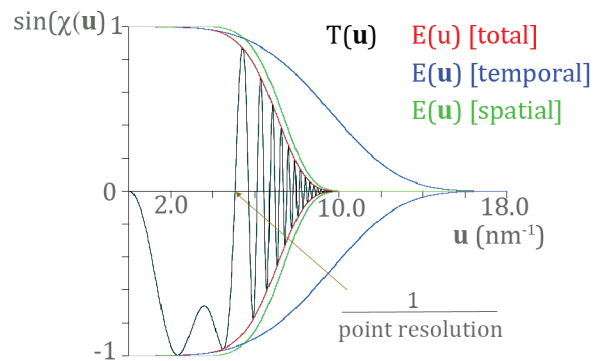


Figure 2.17 –Contrast transfer function for the Imperial College FEI Titan without C_s correction at Scherzer defocus ($\Delta f = 59.5$ nm, $C_s = 1.3$ mm) as calculated with JEMS.

From figure 2.17 it is clear that $T(\mathbf{u})$ is an oscillatory function with a complicated dependence on $\mathbf{u}$. For spatial frequency bands where $\sin(\chi(\mathbf{u}))$ is negative, the contrast observed is positive, with atomic columns appearing dark on a light background [53,76]. Where $\sin(\chi(\mathbf{u}))$ is positive, contrast is negative and atomic columns appear light on a dark background [53,76]. For spatial frequencies where $\sin(\chi(\mathbf{u}))$ is zero, no information is transferred from the specimen to the image [76].

From figure 2.17 it is clear the point resolution of the FEI Titan can be approximated to $\sim d = 2$ Å, without image correction. At spatial frequencies of $\mathbf{u} > 5$ nm⁻¹ significant contrast reversals would be observed in images, limiting the interpretation of higher spatial frequency information [76]. The envelope functions can be seen to have a damping effect that increases with $\mathbf{u}$, though in the absence of image correction the damping envelopes do not limit the point resolution.

Shown in figure 2.18 is the contrast transfer for the FEI Titan calculated for $\Delta f = +6.2$ nm and $C_s = -13$ μm using JEMS.

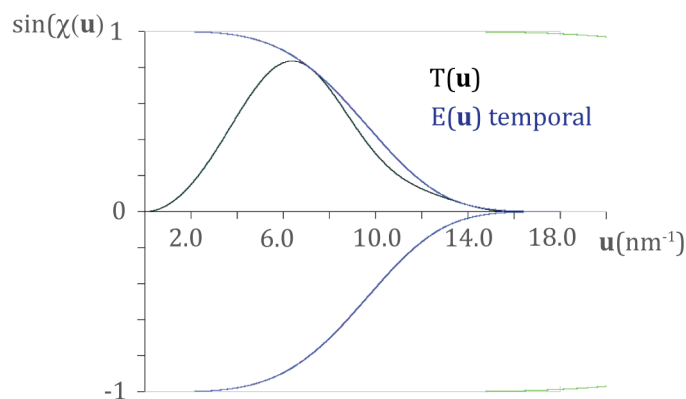


Figure 2.18 – Contrast transfer function for the Imperial College FEI Titan at $\Delta f = 6.2$ nm and $C_s = -13$ μm , as calculated with JEMS.

It is apparent that the point resolution can be significantly increased by C_s correction ($\sim d = 0.7$ Å) and is limited by $E(u)$ rather than the effect of contrast reversal. By correcting C_s to a small negative value as shown in figure 2.18, a negative C_s imaging (NCSI) can be achieved where phase contrast is negative contrast up to the information limit, making HRTEM images much easier to interpret [78,79].

Contrast delocalization effects are typically present in HRTEM images as a result of the point-spread function of the TEM [77]. Source points are resolved as discs in an image which leads an overlap of spatial information in a HRTEM image, which is particularly detrimental to the analysis of an interface [77]. Delocalization effects are effectively removed by C_s correction, which enables the structure of interfaces to be studied with greater confidence with a C_s corrected TEM [77].

2.11 Scanning Transmission Electron microscopy

In a scanning electron microscope (STEM), a convergent probe is formed from a demagnified image of the electron source [57]. For the spatial resolution to be high, a large demagnification (M) is needed to form a probe of small radius (r_s). The angular divergence of the convergent beam increases with demagnification [57]. In a perfect system, probe size could be decreased by using very large convergence angles [53]. As the effect of aberrations increases with convergence, a beam defining aperture is used to limit α , reducing the effect of aberrations in the probe forming lenses [57]. The use of an aperture reduces probe broadening, which increases the resolution, but reduces the fraction of the beam current contributing to the convergent probe. An increase in spatial resolution is generally associated with a decrease in probe brightness leading to a compromise between the experimental resolution and signal to noise ratio (SNR) [57]. The beam-defining aperture in the FEI Titan is the C2 aperture when operating in unfiltered mode and the C3 aperture when operating in filtered mode. A convergent probe is formed with the minicondenser lens as previously described in section 2.8.6.2.

Forward scattered electrons fall onto an array of detectors of fixed geometry and the scattering intensity is integrated over the area of each detector to determine the detector signal for a particular probe position [57,80,81]. The probe is scanned over a region of interest so that STEM images are formed in serial. Increasing the dwell time per pixel increases the total scattering intensity collected, which improves the SNR noise ratio. Due to specimen drift, this is at the expense of spatial resolution.

The FEI Titan contains bright field (BF), annular dark field (ADF) and high angle annular dark field STEM detectors as shown in figure 2.18. The fraction of the scattering intensity falling on each detector depends on the inner collection angle (θ_{inner}) and outer collection angle (θ_{outer}) of a particular detector.

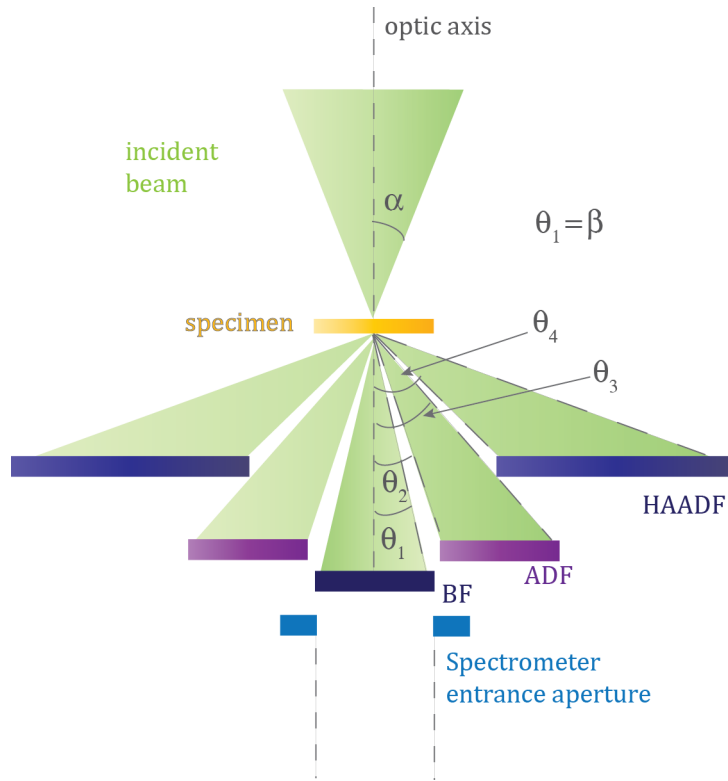


Figure 2.19 – Schematic of STEM detector geometry in the FEI Titan.

From figure 2.19 it is clear that the outer collection angle of the BF detector (θ_1) is defined by β . The inner and outer collection angles for the ADF detector are θ_2 and θ_3 respectively. The inner and outer collections for the HAADF detector are θ_3 and θ_4 respectively. θ_{inner} and θ_{outer} vary as a function of camera length (L). Inner and outer collection angles relevant used in this thesis are given in table 2.2.

Table 2.2 – Inner and outer collection angles for STEM detectors at camera lengths 38 mm and 160 mm in the Imperial College FEI Titan.

β	L (mm)	Detector	θ_{inner} (mrad)	θ_{outer} (mrad)
	38	BF ¹	-	41
		ADF	41	227
		HAADF	65.7	317.8
	160	BF	-	10
		ADF	10	55
		HAADF	49	238

2.11.1. Contrast

Image contrast in STEM images depends on the angular relationship between the STEM detector used for image formation and the scattered electron intensity. In the case of crystalline specimens, the first order ($n = 1$) diffraction angle is typically 10 - 20 mrad so that coherent Bragg scattering is significant at low scattering angle [57].

The convergent electron diffraction pattern consists of a series of overlapping discs of width defined by 2α , corresponding to the Bragg peaks allowed in a crystalline specimen [53,80]. Phase contrast is observed in a STEM image where the detector collects overlapping discs [82] and the detector area is small relative to the Bragg angle [57]. From figure 2.20 it is clear that there is significant overlap for BF detector so BF images are formed coherently and can show phase contrast [57].

¹ BF and ADF inner and outer collection angles stated are stated for simultaneous insertion of the detectors.

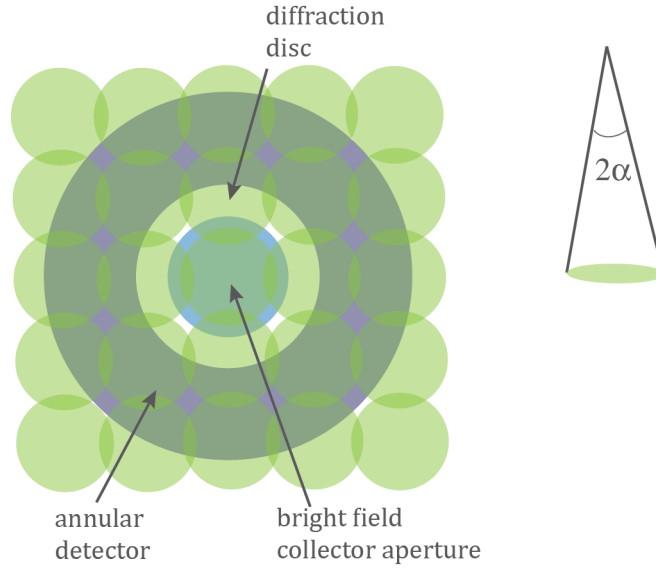


Figure 2.20 – Schematic of convergent electron diffraction pattern for a simple cubic crystal and its relation to the STEM detector geometry [57].

As an annular detector has a large area (figure 2.18), integrating the scattering intensity over the detector area averages out coherence effects between diffraction discs [57,83]. As the scattering angle increases, thermally diffuse scattering increases at the expense of Bragg scattering [82]. Thermally diffuse scattering reduces coherent scattering in the same atomic column [84]. Using an annular detector with suitably high inner detection angle ($\theta_{\text{inner}} > \sim 30 \text{ mrad}$) [85] enables images to be formed incoherently.

As a result of thermal diffuse scattering at high angle, atoms in a specimen may be treated as independent scatterers which allows the atomic scattering factors to be replaced by atomic cross sections [83]. At high scattering angles, the scattering cross section is approximately proportional to Z^2 [53]. A specimen is therefore treated in terms of an object function which is formed from the variation in scattering cross section, which is peaked at atomic sites [83]. For a thin specimen, the image intensity $I(\mathbf{R})$ is a convolution of the object function $O(\mathbf{R})$ and the probe intensity profile $P^2(\mathbf{R})$.

$$I(\mathbf{R}) = O(\mathbf{R}) \otimes P^2(\mathbf{R}) \quad (2.19)$$

To first approximation, the resolution is defined by probe size ^[83], which is limited by aberrations in the probe forming lenses ^[84]. If the probe diameter is less than the interatomic spacing for a crystalline specimen in zone-axis orientation, the atomic structure may be resolved ^[84,86], which is the basis for HRSTEM imaging.

2.12 Electron Energy-Loss Spectroscopy

Electrons that have been scattered inelastically carry information about the bonding environment and electronic structure in a solid [56,59]. Electron energy loss spectroscopy (EELS) allows this information to be extracted from the electron energy loss spectrum, which is a plot of the variation in electron scattering intensity with energy-lost by the transmitted electron [56].

2.12.1. The Electron Energy-Loss Spectrum

Shown in figure 2.21 is an example EELS spectrum for $\alpha\text{Fe}_2\text{O}_3$ adapted from the EELS atlas [87]. Key features are highlighted.

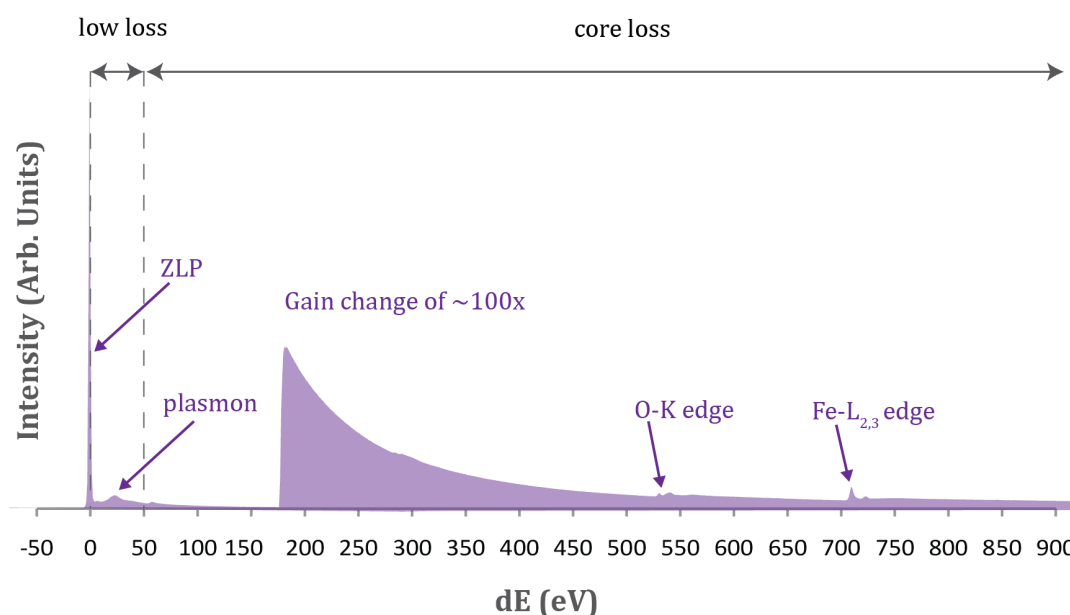


Figure 2.21 – EELS spectrum for $\alpha\text{-Fe}_2\text{O}_3$ adapted from the EELS atlas. The zero loss peak (ZLP), plasmon peak, oxygen-K edge and iron-L_{2,3} edge are highlighted [87].

The highest intensity feature in the spectrum is the zero loss peak (ZLP) at an energy loss of 0 eV, which contains the unscattered and elastic scattering intensities. To a first approximation, the full-width half-maximum (FWHM) of the ZLP peak is defined by the energy spread of the electron source which typically defines the energy resolution [56].

Phonon scattering occurs over a small energy loss range (10-100 meV) typically less than the energy resolution, so is generally ignored ^[59]. The energy-loss range of 5-50 eV is referred to as the low-loss region ^[59]. The strongest feature in the low loss region is the plasmon peak at around 30 eV. This is the result of an oscillation in the valence electron density of a solid, known as a Plasmon excitation. Plasmon peaks may be observed in thick specimens after other scattering events at multiples of the Plasmon energy, ^[56,59]. The valence electron density in a specimen defines the plasmon energy and the plasmon resonance defines the width of the plasmon peak ^[56]. Interband transitions, which are the transition of valence electrons to unoccupied states, may also be present in the low loss region of the EELS spectrum ^[56].

At higher energy-loss, the scattered intensity decreases smoothly as a high order inverse power law of energy-loss. Superimposed onto this background are sharp increases in intensity that correspond to the ionization thresholds for specific inner shell atomic excitations. These are known as ionization edges as the intensity drops off slowly with increased energy-loss after the edge onset ^[56,59].

An ionization edge results from the excitation of localized inner shell electrons to unoccupied states immediately above the Fermi energy ^[56]. A core loss edge is characteristic of an atomic species as the electron binding energy of the excited electron is characteristic of the atomic electron configuration ^[56]. The integrated signal of a core loss edge is proportional to the number of atoms in a specimen ^[56]. This enables elemental quantification (section 2.12.4) in addition to elemental identification. A summary of the initial and final states for core loss edges relevant to this thesis are given in table 2.3. The edge type defines the initial state. At low scattering angles, inelastic scattering obeys the dipole approximation which is discussed in section 2.12.2.

Table 2.3 – Summary of the initial states and final states for K and L core loss edges in the EELS spectrum.

Edge	Initial state	Final state (dipole allowed)
K	1s	p
L ₂	2p _{1/2}	s, d
L ₃	2p _{3/2}	s, d

2.12.1. The Double Differential Cross Section

An electron scattered inelastically undergoes a momentum change of $\mathbf{q} = \mathbf{k}_0 + \mathbf{k}_f$, where $\mathbf{k}_0$ and $\mathbf{k}_f$ are the initial and final wave vectors respectively of a fast incident electron [56]. A schematic diagram illustrating the relation between the momentum transfer of the fast electron ($\mathbf{q}$), $\mathbf{k}_0$ and $\mathbf{k}_f$ is shown in figure 2.22.

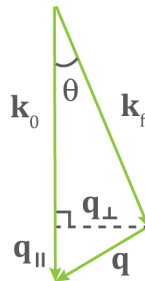


Figure 2.22 – Schematic of an inelastic scattering process showing the initial and final wavevectors, and momentum transfer $\mathbf{q}$ [56].

As the energy of the fast electron is high, then $\mathbf{q}$ is small relative to $\mathbf{k}_0$ so the momentum change depends on $\mathbf{k}_0$, the scattering semi angle (θ), and θ_E which is a characteristic scattering angle for a particular inelastic scattering process [56].

$$q^2 = k_0^2 (\theta + \theta_E^2) \quad (2.20)$$

The characteristic scattering angle for energy-loss E is given by

$$\theta_E = \frac{E}{\gamma m_0 v^2} \quad (2.21)$$

where m_0 is the electron rest mass and v the velocity of the fast electron. γ is a relativistic factor given by $\gamma = (1 - v^2/c^2)^{-1/2}$ [56,88].

The EELS signal is described by the double differential cross section, which is given by

$$\frac{d^2\sigma}{dE d\Omega} \quad (2.22)$$

where σ is the total inelastic scattering cross section. $d^2\sigma/dE d\Omega$ defines the inelastic scattering intensity over energy loss range E_0 to $(E_0 + dE)$ and solid angle $d\Omega$ [56].

The electronic configuration of a solid can be described in terms of a set of wavefunctions ($\psi(\mathbf{r})$) that are determined from the solution of the many body Schrodinger equation for the potential in the solid [88]. If the energy of incident fast electrons is assumed to be high relative to the energy of the excited states, the Born approximation may be applied so that electron transitions are to final states of fixed geometry. The total wavefunction for the solid is then given as the product of the plane wave states of the fast electrons ($e^{i\mathbf{k}\cdot\mathbf{r}}$) and atomic states of the system [56,88].

Fermi's golden rule describes the transition rate of ejected electrons from an initial state wavefunction ($\psi_i(\mathbf{r})$) to final state wavefunction ($\psi_f(\mathbf{r})$) which is proportional to the probability of a transition and therefore proportional to the double differential cross section [56,88].

$$\frac{d^2\sigma}{dE d\Omega} \propto \frac{4\gamma^2}{a_0^2 q^4} \left| \int \psi_i \exp(i\mathbf{q}\cdot\mathbf{r}) \psi_f^* d^3\mathbf{r} \right|^2 \rho(E) \quad (2.23)$$

Where a_0 is the Bohr radius and $\rho(E)$ is the density of states (DOS), and assuming electrons other than the excited electron are not affected by the excitation process (one electron approximation) [59,88].

2.12.2. Near-Edge Fine Structure

For a core loss ionization edge, the initial state is the ground state configuration. The final state of an electron is an excited state in which the inner shell electron is promoted to a higher unoccupied state, leaving a core hole in the inner shell [88]. As the possible final states are those which are unoccupied in the ground state, the variation in scattering intensity above the ionization threshold of a core loss edge is proportional to the ground state unoccupied density of states, modified by presence of a core hole [56,59,88]. The variation in the scattering intensity in the first 10-15 eV above an ionization edge is known as the energy loss near-edge fine structure (ELNES) [56,59]. [53]

The $e^{i\mathbf{q}\cdot\mathbf{r}}$ term in equation 2.23 can be expanded as shown in equation 2.24.

$$e^{i\mathbf{q}\cdot\mathbf{r}} = 1 + i\mathbf{q}\cdot\mathbf{r} - \frac{1}{2!}(\mathbf{q}\cdot\mathbf{r})^2 - \frac{1}{3!}i(\mathbf{q}\cdot\mathbf{r})^3 + \dots + \frac{1}{n!}(i\mathbf{q}\cdot\mathbf{r})^n \quad (2.24)$$

For low scattering angles $\mathbf{q}$ is small and the non-linear terms may be ignored, which is known as the dipole approximation [56,88]. Under the dipole approximation equation 2.23 may be simplified to a form shown in equation 2.25

$$\frac{d^2\sigma}{dE d\Omega} \propto \frac{4\gamma^2}{a_0^2 q^4} \left| \int \psi_i(\mathbf{q}\cdot\mathbf{r}) \psi_f^* d^3\mathbf{r} \right|^2 \rho(E) \quad (2.25)$$

The $\left| \int \psi_i(\mathbf{q}\cdot\mathbf{r}) \psi_f^* d^3\mathbf{r} \right|^2$ term, known as the transition-matrix term, must be non-zero for the scattering intensity to be non-zero. Under the dipole approximation the transition matrix is only non-zero if the difference between the angular momentum quantum number (l) of the initial and final state is 1, formally known

as the dipole selection rule ($\Delta l = \pm 1$) [56,88]. A list of dipole allowed ionization edges is given in table 2.3.

The basic edge shape is defined by the matrix term which decreases slowly with energy-loss as the degree of overlap between ψ_i and ψ_f decreases. The $\rho(E)$ term is superimposed on to the basic edge [88]. As the matrix term varies slowly with energy loss, the ELNES is typically defined by the $\rho(E)$ term in equation 2.25. The DOS defines the number of electron energy states within a specific energy range in a solid. The intensity in the ELNES over a given energy loss range reflects the unoccupied DOS. High intensity is observed in the ELNES if the number of unoccupied states in the DOS at a particular energy is large [88].

For dipole allowed transitions, the $\rho(E)$ term in equation 2.25 is more accurately defined as a partial DOS or symmetry-projected DOS, corresponding to the density of final states allowed under the dipole selection rule (table 2.3) [88]. For the matrix element to be significant, there must be some overlap between ψ_i and ψ_f . As a result, some of the spatial component of ψ_f must be localized to the atom site undergoing excitation, which means the $\rho(E)$ term contributing to the ELNES is a site and symmetry projected DOS [88].

2.12.3. Thickness Measurements

If inelastic scattering events are treated independently, the probability (P_n) of n collisions may be determined from Poisson statistics as

$$p_n = \frac{1}{n!} m^n e^{-m} \quad (2.26)$$

where m is the mean number of collisions [59].

The mean number of collisions can be approximated as the ratio of sample thickness and the inelastic mean free path (λ). By substituting $m = t/\lambda$ in equation 2.26, an expression for specimen thickness (t) is found that is a function of λ , the total intensity (I_t) and the zero-loss (I_0) intensity for a low loss EELS

spectrum. The relative thickness (t/λ) is typically determined from low loss EELS spectra by applying equation 2.27 in the log-ratio technique.

$$t = \lambda \ln \left(\frac{I_t}{I_0} \right) \quad (2.27)$$

Egerton reports an acceptable thickness range for application of equation 2.27 as $0.1 < t/\lambda < 5$ [72]. A reasonable thickness for TEM specimens suitable for EELS is $0.3 < t/\lambda < 0.5$ [56].

The log-ratio technique may also be used to determine the absolute thickness if E_0 , α and β are known. A value for λ is parameterized from β and the incident energy and mean energy loss. The mean energy loss is calculated from an effective atomic number, which may be estimated from the mean atomic number [59].

Egerton reports an accuracy of $\pm 20\%$ for the log-ratio absolute thickness method in contrast to $\pm 10\%$ for the log-ratio relative method [59].

2.12.4. Quantification

From the ionization edges it is possible to perform elemental quantification from inelastic partial cross sections that are calculated as a function the experimentally determined values for α , β , the energy window (Δ) and initial energy of the fast electrons (E_0). The EELS quantification procedure is summarised and discussed in the following section.

It is first necessary to extract the ionization signals of the core loss edges of interest from the decreasing background. At high energy loss the log of the background intensity in the EELS spectrum decreases approximately with the log of energy loss. This background intensity is generally modelled using a power law function of the form $I = AE^{-r}$ [56,59]. Shown in figure 2.23 is an example background intensity model (red) used to extract the background intensity from

a cobalt- $L_{2,3}$ spectrum (green) in the Gatan Digital Micrograph software. The fitting parameters A and r are determined from the model fit in the fitting window and the background model is projected forwards and backwards in energy loss. A more accurate fit is generally observed if for a large window width, in the absence of preceding ionization edges or artefacts.

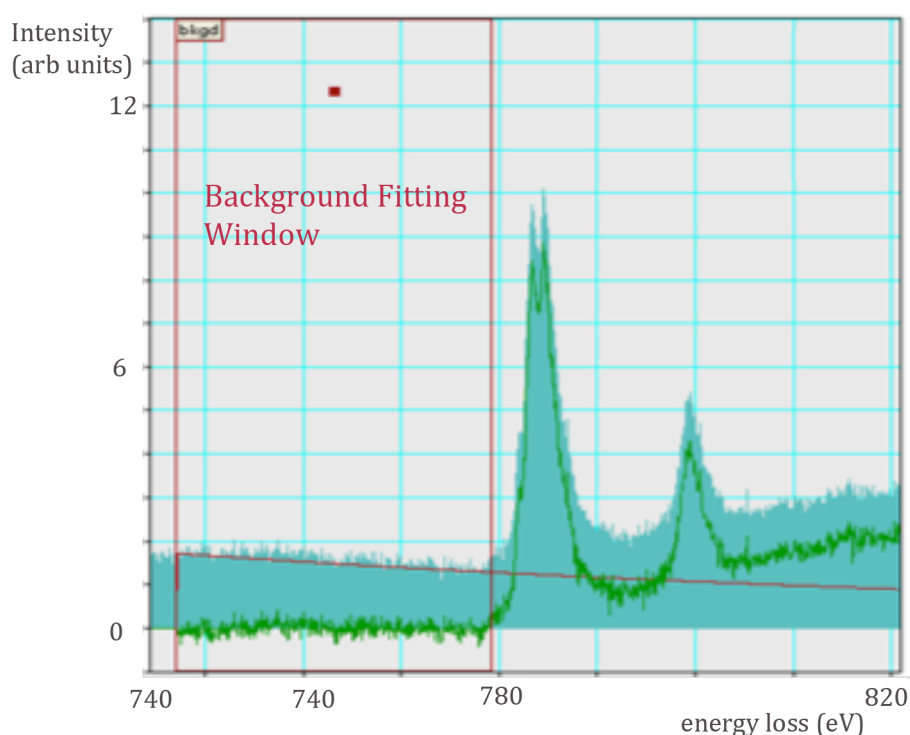


Figure 2.23 – Cobalt $L_{2,3}$ -spectrum acquired from CoO. The background intensity model shown is a power law model of the form AE^{-r} .

To meaningfully compare quantification results for different regions of a specimen, core loss EELS spectra must be normalised against thickness to retrieve the single scattering distribution^[56]. The single scattering distribution is recovered by removing multiple scattering contributions in the core loss by a deconvolution with the low region of the EELS spectrum. This can be performed by Fourier log deconvolution if the low loss region is present in the same spectrum as the ionization edges. If the loss region is not present, a fourier ratio deconvolution can be performed using a low loss spectrum collected from the same position as the core loss spectrum under the same experimental conditions

$(\alpha, \beta, \Delta, E_0)$ [56]. For specimens of $t/\lambda > 0.3 - 0.5$, meaningful quantification cannot be performed without determining the single scattering distribution [56]. Following extraction of the ionization edges and determination of the single scattering distribution, partial cross sections are calculated for the ionization edges of interest.

In order to calculate a partial cross section, a model is required for atomic inelastic scattering. As the binding energy of inner shell electrons is large, inner shell excitations may be characterised using one electron models [59]. The generalized oscillator strength (GOS) describes the response of an atom to a fast incident electron [59]. The simplest method for determining the GOS is based around the solution of the Schrodinger equation for the hydrogen atom. The electrostatic term is modified to take into account the nuclear charge and electron screening potential for elements of $Z > 1$ [59]. The GOS can be more accurately determined by models in which the many body Schrodinger equation is solved iteratively using self-consistent potentials, as in the Hartree-Fock model. Partial cross sections for EELS quantification are typically determined using a Hartree-Slater model which is a simplified Hartree-Fock procedure, assuming spherical symmetry in atomic potentials [59]. A comprehensive discussion about the GOS and various models for inner shell excitation may be found in the literature [56,59].

The EELS analysis routine in digital micrograph determines a differential energy cross section $d\sigma/dE$ for a particular ionization edge which is then integrated over a user defined energy window to give the partial cross section. The routine may use hydrogenic or Hartree-Slater models for the wavefunctions [89]. The Hartree-Slater models in digital micrograph are based on the generalized oscillator tabulated by Rez [89,90]. An example of a Hartree-Slater model of the differential energy cross section for the iron- $L_{2,3}$ edge is shown in figure 2.24.

After signal extraction and calculation of the partial cross section relative atomic concentrations are determined as

$$\frac{n_A}{n_B} = \frac{\sigma_A(\underline{\alpha}, \underline{\beta}, \underline{\Delta}, \underline{E_0})}{\sigma_B(\underline{\alpha}, \underline{\beta}, \underline{\Delta}, \underline{E_0})} \cdot \frac{I_B(\underline{\alpha}, \underline{\beta}, \underline{\Delta}, \underline{E_0})}{I_A(\underline{\alpha}, \underline{\beta}, \underline{\Delta}, \underline{E_0})} \quad (2.28)$$

where n_A/n_B is the relative atomic concentration ratio of elements A and B of partial cross sections σ_A and σ_B for integrated signal intensity I_A and I_B [56]. An example signal integration window for the iron- $L_{2,3}$ edge is shown in figure 1.21.

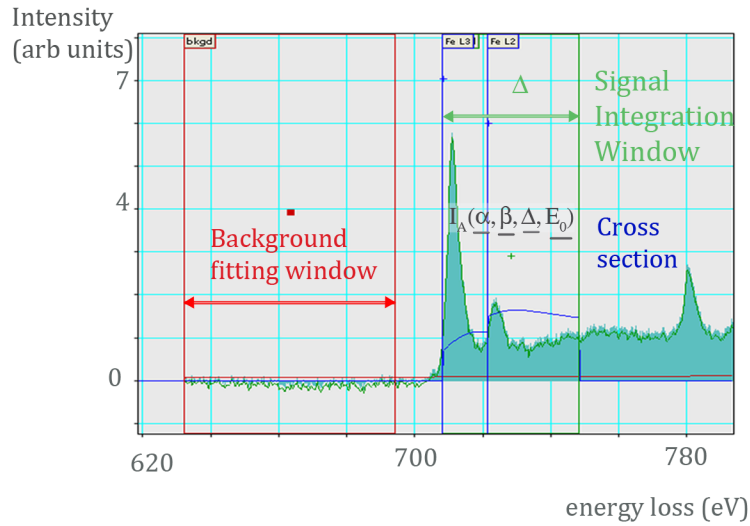


Figure 2.24 – Example iron- $L_{2,3}$ spectrum in which the background intensity has been removed using a power law model of the form AE^{-r} . Normalization against thickness was performed using a Fourier ratio deconvolution. The cross section and signal integration windows are shown.

2.13 Energy Filtered Transmission Electron Microscopy

An energy-filtered transmission electron microscopy (EFTEM) image is an image that is formed with electrons of specific energy loss ^[56]. Scattered electrons are allowed to pass through an electron spectrometer. An energy filtering slit is inserted into the beam path after the drift tube in the spectrometer (figure 2.10) and used to select electrons of specific energy loss and form the EFTM image at the spectrometer CCD instead of a spectrum ^[91].

A zero-loss image is an image formed with electrons that have been scattered elastically and have not lost any energy. If a zero-loss image and an unfiltered image are acquired from the same region of a specimen under the same conditions, the relative specimen thickness at each pixel can be determined by application of equation 2.27.

An EFTEM thickness map is calculated from zero-loss and unfiltered images. The intensity distribution in the thickness map corresponds to variations in relative thickness across a region of interest.

2.14 TEM Specimen Preparation Techniques

In order to analyse a material in the TEM, a specimen must be made that is electron transparent and representative of the bulk material. In order to analyse the substrate/film interface of a thin film material, a cross sectional TEM (XTEM) is made so that the interface is parallel to the electron beam when in the microscope.

Two common techniques for the preparation of XTEM specimens of oxide thin films are focussed ion-beam (FIB) milling and argon ion milling. In both techniques ion beams are used to thin a specimen to electron transparency by sputtering. The theory of sputtering and XTEM specimen preparation by FIB and argon milling is introduced in the following sections. An investigation of the effect of preparation parameters on specimen quality is presented in chapter 3.

2.14.1. Sputtering

A high-energy ion incident on a solid collides with a surface atom causing a transfer of momentum. This momentum transfer causes a cascade of further subsurface elastic collisions. Surface atoms are ejected where the overall momentum transfer for a surface atom is sufficient to overcome its surface binding energy ^[92]. The removal of material by this process is known as sputtering.

In addition to causing the ejection of surface atoms, the incident ion beam also creates a layer of damage in the form of an amorphous layer at the sputtering surface. The damage layer is caused by the sputtering process and ion implantation ^[93]. The thickness of the amorphous damage layer is proportional to the penetration depth of the sputtering ions, which is a function of beam energy and angle of incidence ^[93,94].

2.14.1. Dual Beam Focussed Ion Beam Microscopy

In the focused ion beam (FIB) microscope, the ion source consists of tungsten needle maintained at high positive potential attached to a heated Ga reservoir. Liquid Ga readily wets the tungsten tip and Ga ion beam is formed by field extraction. The ion beam is accelerated and focused by electrostatic lenses. Beam positioning is maintained by electrostatic quadrupoles and octopoles [93,95]. The ion beam is rastered over the surface of a specimen to form images or perform etching. The FIB chamber is kept under vacuum during operation at a typical chamber pressure of around 1×10^{-6} mbar.

Secondary electrons are generated due to the interaction of the Ga ions with specimen. The secondary electrons are used to form an image, which is referred to as the ion image as it is formed using the ion beam. Care must be taken to minimise exposure time when imaging with the ion source, as sputtering occurs whenever the specimen is exposed to the ion beam. A dual beam FIB system includes an electron source as well as an ion source. This allows a specimen to be imaged non-destructively, enabling thinner TEM specimens to be made in dual-beam microscope. Focal points for the e-beam and Ga-beam are coincident allowing both sources to be used without repositioning the specimen. A schematic of a dual beam FIB is given in figure 2.25. The coincident focal points of the ion and gallium beams, the FIB lamellae surface

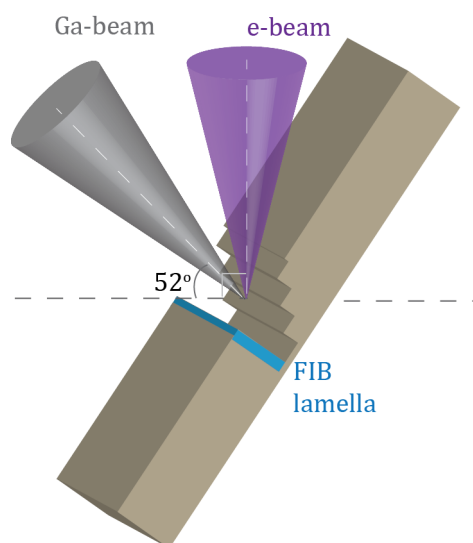


Figure 2.25 – Schematic of dual beam showing the coincident focal points of the electron and ion beams, the FIB trench and the FIB lamella surface.

Before a specimen enters the FIB, it is gold coated to increase conductivity. A specimen must be conductive so that there is good contrast in the ion and electron images and to prevent charging, which is a source of drift. After gold coating, the specimen is loaded into the FIB microscope and the FIB chamber pumped to vacuum. TEM specimens are then prepared by a method known as in-situ liftout method (INLO) [93].

The first stage of the INLO procedure is to define a region of interest of the specimen and coat with a platinum layer. The platinum layer acts to protect the specimen from sputtering by the ion beam. A platinum layer is deposited using the electron beam followed by a second platinum layer deposited using the ion beam. Regular cross sections are then milled either side of a region of interest referred to as the FIB lamellae which is typically $\sim 1\ \mu\text{m}$ in width. Cleaning cross sections are then milled to produce a FIB lamellae with parallel sides.

Both the regular cross sections and cleaning cross section milling patterns create a wedge shaped trench as seen in figure 3.19. As the regular cross section is milled from the bulk specimen a large beam current and q value (figure 2.26) is used [65]. At high beam current the beam is broad and the trench surface is stepped as seen in figure 2.25.

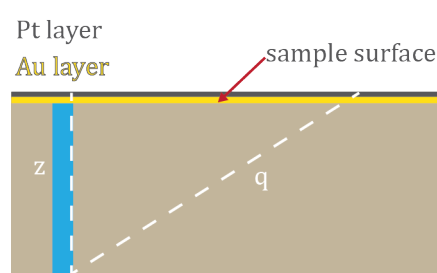


Figure 2.26 – Schematic showing cross section of a bulk FIB specimen. Platinum and gold layers are highlighted in addition to the FIB lamella (blue) and FIB “swimming pool” trench [65].

The intensity distribution of the ion beam is of a Gaussian form so the FIB lamella milled by rough cross sectioning is wedge shaped [65]. In order to mill a lamella with parallel sides a tilt angle is introduced, and the beam current decreased so that less material is removed by sputtering. A schematic illustrating the different lamella produced with and without the cleaning cross section are shown in figure 2.27.

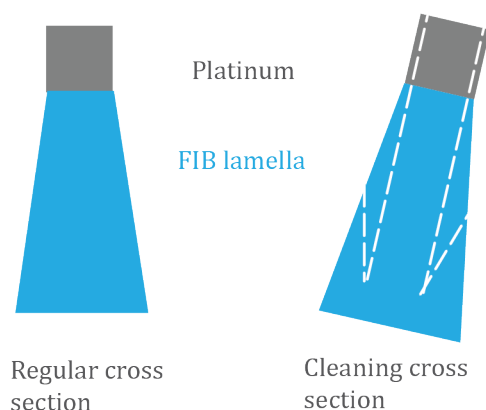


Figure 2.27 – Schematic showing cross section and regular cross section milling stages [65].

Once the regular lamella surfaces have been prepared by cleaning cross sectioning, the lamella is welded to an Omniprobe microprobe with platinum. The lamella is then detached from the bulk specimen and welded to an Omniprobe TEM grid and thinned to electron transparency by further ion milling at progressively decreasing beam current. Final cleaning is typically performed using a low kV beam to remove amorphous layers associated with sputtering damage [93].

2.14.2. Mechanical Polishing and Argon Ion Milling

In conventional ion milling, an argon beam incident on a mechanically pre-thinned specimen sputters material from a specimen until it becomes perforated. The pre-thinned specimens are circular as shown in figure 2.29 and are typically rotating during the thinning process.

Thin films were typically supplied as 0.5 mm x 0.5 mm squares as shown in figure 2.28a. In order to reorient the specimen so that the interface would be parallel to the electron beam in the TEM, it was necessary to embed the thin film as previously described by Scott *et al.* [96]. Thin film specimens were cut into strips of width ~1 mm with a low speed diamond saw (Buehler, Isomet) as shown in figure 2.28b. The strips were then cleaned in acetone, isopropanol and water for ten minutes in an ultrasonic bath. Strips were fixed together with Epotek 353ND epoxy (figure 2.28c) and cured at 100°C~130°C for 30 minutes. The fixed strips were embedded into a slotted molybdenum rod with Epotek 353ND under the same conditions. Upon curing, a molybdenum/film ensemble was embedded into brass tubing by the same technique. This process is illustrated schematically in figure 2.28d.

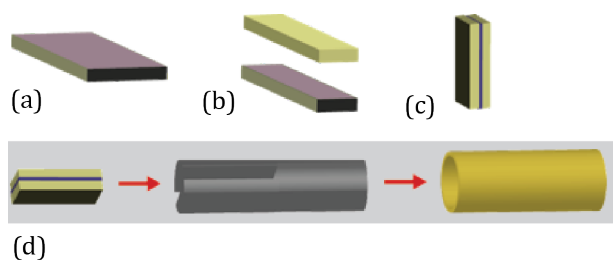


Figure 2.28 – Schematic of pre cross-section preparation steps

An embedded film was then sectioned into bulk cross sections of thickness ~500 μm using a diamond saw. A schematic showing the section dimensions is given in figure 2.29.

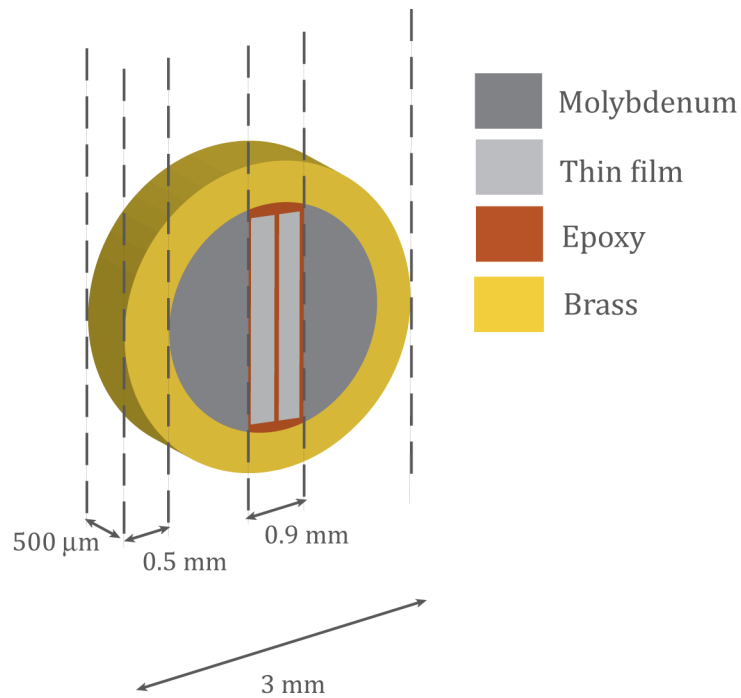


Figure 2.29 – Schematic of the conventionally prepared XTEM specimen before dimple grinding and argon milling.

The surfaces of a bulk section were polished with 1200 SiC paper using a disc grinder (Gatan). The section thickness was reduced to 70 ~ 100 μm before polishing with a lapping wheel using diamond suspension of decreasing particle diameter of 6, 3 and 1 μm . Shallow dimples were applied to each surface using a dimple grinder (Gatan) such that final central thickness was 20~30 μm . Final cleaning was carried out in boiling water, hot acetone and isopropanol. Final thinning was performed by argon milling in a PIPS (Gatan). Typical beam angles of $\theta = 3\text{-}10^\circ$, were used and beam energies of 0.2 - 5 keV. The effects of low energy and low temperature milling are discussed in detail in chapter 3.

2.15 X-Ray Powder Diffraction

X-ray diffraction (XRD) is analogous to electron diffraction, which was discussed in section 2.5. XRD analysis is typically performed on powder specimens to determine phase purity [95]. A powder specimen consists of many particles oriented randomly. For every possible set of crystal planes, one or more of the crystals will be in the Bragg condition. If a powder specimen is scanned through a large range of 2θ angles relative to a static X-Ray beam, all possible diffraction angles are represented in the scan. At certain values of 2θ , high intensity peaks are observed in the XRD pattern, corresponding to Bragg angles for particular planes [95]. The XRD pattern is characteristic of a material, which enables the phase purity to be determined by comparing to tables of standard powder diffraction patterns

A simplified schematic of an XRD chamber is shown in figure 2.30. An XRD pattern is acquired by defining the initial and final 2θ angle step size and dwell time per step. All XRD patterns were acquired using a high resolution X-ray diffractometer (Philips, X'Pert Pro) with a Cu K_α source in line focus mode. The diffractometer used had an X-ray mirror, a Ge monochromator and X'celerator detector. XRD powder diffraction patterns were typically acquired between an initial 2θ of 15° and final 2θ of 90° . The step size was 0.012° and the effective acquisition time 100s per step.

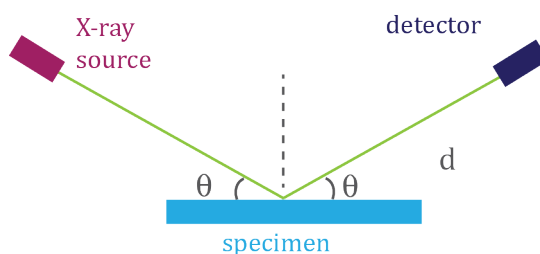


Figure 2.30 –Simplified schematic of the relative orientation of the X-ray source, specimen and detector in a typical X-Ray diffractometer [15].

Chapter 3 - TEM Specimen Preparation Techniques for Oxide Thin Film Materials

3.1 Introduction

Functional oxide thin films are typically grown to film thickness of ≤ 100 nm. The analysis of nanosized regions of interest by TEM is generally carried out using high magnification techniques such as HRTEM and HRSTEM. In order to acquire meaningful images using these techniques, the specimen thickness must be significantly lower than that which is acceptable for conventional imaging. Analysis by STEM-EELS requires ultra-thin specimens, ideally having negligible thickness variation.

The dual beam-FIB and argon ion milling specimen techniques are widely accepted as suitable for the preparation of thin XTEM specimens. Barna *et al.* previously produced TEM specimens from bulk Si and GaAs and report a reduction in damage layer thickness with low energy argon milling [97,98]. The total area of the electron transparent region for argon ion milled specimens is typically large ($\sim 0.1 \mu\text{m}^2$) but argon ion milling can be unsuitable for the study of thin film interfaces as it lacks site specificity; areas of interest are removed easily by the ion beam. Dual beam FIB milling can be used to produce TEM specimens from specific sites of interest though FIB specimens are generally poorer quality than argon milled specimens [99].

A systematic investigation of argon milling parameters has been performed focusing on the effect of low energy milling at room and low temperatures. The effect of varying specimen orientation was investigated in addition to milling energy. This has enabled XTEM specimens to be prepared from oxide thin films of thickness ≤ 200 nm by conventional argon ion milling with a degree of control and reproducibility. XTEM specimens were also prepared by dual beam FIB and compared to argon ion milled specimens. Additional thinning of FIB prepared

specimens was carried out by low energy argon ion milling as previously demonstrated by Scott *et al.* [99]. XTEM specimens were compared by TEM/STEM imaging, and relative thickness mapping by EELS, using an FEI Titan at 300 kV.

Significant spatial drift of ~ 20 nm/minute was observed when imaging insulating specimens by HRTEM. An investigation of the effect of carbon coating these specimens was carried out by HRTEM. Following this investigation, the effect of H_2/O_2 plasma cleaning on thin carbon layers investigated by EFTEM thickness mapping.

3.2 Experimental Technique

XTEM specimens of STO/CFO and $LaAlO_3/CoFe_2O_4$ (LAO/CFO) thin films of film thickness 25 – 200 nm were prepared by conventional argon milling (section 2.14.2), and INLO (section 2.14.1) in a dual beam FIB system. A summary of XTEM specimens relevant to this chapter are given in table 3.1. Thin film thickness (h) is defined as the thickness of a thin film in the growth direction; specimen thickness (t) is defined as the thickness of the TEM specimen in the beam direction in TEM.

Table 3.1 – Summary of the preparation routes for TEM specimens forming basis of this chapter

Sample	Sample ID	Substrate	h (nm)	Preparation	
				INLO	Argon
1	CFS 716.3	STO	50		✓
2	CFS 9226.1	STO	25		✓
3	CFS 723.4	STO	200		✓
4	CFS 50f1	STO	50	✓	✓
5	CFL 25f	LAO	25	✓	✓
6	CFS 50f2	STO	50	✓	✓

The FIB milled specimens were prepared using an FEI 600 Nova Nanolab at the University of Loughborough. Samples were gold coated using a k550 sputter coater (Emitech, UK) for 2 minutes at 25 mA, followed by electron (3.0 kV, 1.1 nA) and ion (30 kV, 20 nA) beam platinum deposition in the Nanolab system. Regular cross-sections and cleaning cross sections were milled at 30 kV and beam currents of 20 nA, and 7 nA respectively.

Lamellae were attached to an Omniprobe™ needle, lifted out and attached to an Omnigrid™ TEM grid with a 30 kV 30 pA ion beam. Final polishing was carried out at 30 kV using sequentially reduced beam currents of: 1 nA, 0.5 nA, 0.3 nA and 0.1 nA. Final cleaning was performed at 5 kV and beam current 70 pA.

The parameters for conventional XTEM specimen preparation were previously given in section 2.14.2. XTEM specimens prepared by argon ion milling were found to suffer from severe hydrocarbon contamination when imaging in STEM. The contamination rate was not reduced by H₂/O₂ plasma cleaning (section 3.7) before analysis.

Specimen 1 and specimen 2 were plasma cleaned using a Gatan Solarus model 950 plasma cleaner (Gatan, UK) before the argon milling stage of preparation to prevent contamination when performing STEM analyses. As plasma cleaning is known to cause specimen heating, cleaning was performed before argon milling with a 50% rest period, to allow the cleaning period to be increased (30 minutes) whilst also while minimising damage. Specimens were cleaned free standing so that periphery contamination that would usually be masked by a TEM holder was exposed to the plasma. The pre argon milling plasma cleaning parameters used are given in table 3.2. Cleaning was performed once for each specimen surface.

Table 3.2 – Plasma cleaning parameters for plasma cleaning performed before argon milling.

Parameter	
Time	30 minutes
duty cycle	50%
flow (Ar/O ₂)	33 sccm
Forward RF	50 W
Forward RF range	5 W
Max. reflected RF range	5 W

After plasma cleaning, argon ion milling was carried out using a Gatan 691 precision ion polishing system (PIPS). Specimens were rotated at 3 - 4 RPM with double sector modulation during all argon milling steps. Double sided thinning was performed with 5 kV argon beams incident 8° to the specimen surfaces until perforation; the ion beam was aligned perpendicular to the substrate/film interface in order to reduce preferential milling ^[96]. Upon perforation, the angle of incidence of the argon beams was reduced to 3 - 4° and specimens were rotated so that the substrate/film interface was parallel to the ion beam. Double sided thinning was then carried out sequentially reduced energies of 1 kV, 0.5 kV and 0.2 kV for 40 minutes. Low temperature milling was carried out at liquid nitrogen temperature (T=97K).

Carbon layers of thickness 5 – 10 nm were deposited on the exit surface of argon ion milled specimens using an Auto 306 carbon coater (Edwards, UK) or K975x Turbo Evaporator (Quorum, UK) where necessary to reduce drift that occurs due to charging. Carbon layer thickness and layer degradation due to H₂/O₂ plasma cleaning were characterized by EFTEM thickness mapping using the FEI Titan.

All XTEM specimens were plasma cleaned before TEM analysis using a H₂/O₂ plasma in the Solarus system. The plasma cleaning parameters used are given in table 3.3. R.F. values are as previously stated in table 3.2.

Table 3.3 – Typical plasma cleaning parameters used for plasma cleaning before TEM imaging and analysis.

Parameter	
Time	120s
duty cycle	25%
flow (O ₂)	6.4 sccm
flow (H ₂)	27.5 sccm

3.3 Dual Beam FIB

The target specimen thickness after polishing at 30 kV and 0.1 nA by INLO, was 100 nm. Ishitani *et al.* report amorphous damage layers of thickness 25 nm and 5 nm at Ga beam energies of 30 kV and 5 kV respectively [94]. A FIB specimen of thickness 100 nm would therefore consist of approximately 40 nm of representative material and 60 nm of amorphous damage. STO/CFO and LAO/CFO FIB milled specimens were polished at 5 kV in order to remove the expected damage layer [93].

Shown in figure 3.1c and 3.1d are HAADF-STEM images of specimen 4, a 50 nm STO/CFO specimen prepared by INLO. From figure 3.1c the substrate and film are clearly visible, as are the deposited gold and platinum layers. Also shown in figure 3.1d, is a survey region over which a low loss spectrum was acquired by STEM-EELS. From this spectrum image, a relative thickness map was calculated by the log-ratio method (equation 2.27) for each spectrum image pixel, which has been overlaid in order to highlight relative thickness changes in the region.

From the thickness map shown in figure 3.1d, it can be seen that the relative specimen thickness in the region of interest highlighted in figure 3.1d was found to lie in the approximate range $0.4 < t/\lambda < 0.8$. The mean relative specimen thickness was found to be $t/\lambda = 0.55$. The mean λ for this region is close to the target value for EELS analysis ($0.3 < t/\lambda < 0.5$) but the thickness variation is too high for meaningful quantification of the Ti, Co, Fe and O composition, or analysis of the fine structure in the O-K, Fe-L_{2,3} and Co-L_{2,3} edges.

Mitome *et al.* report a value of ~100 nm for the electron inelastic mean free path for 300 kV electrons in STO [100]. If λ is assumed to be of the same order for STO and CFO, the absolute thickness for spectrum image region shown in figure 3.1d would be in the approximate range $40 \text{ nm} > t > 80 \text{ nm}$ and the mean absolute thickness $t = 55 \text{ nm}$.

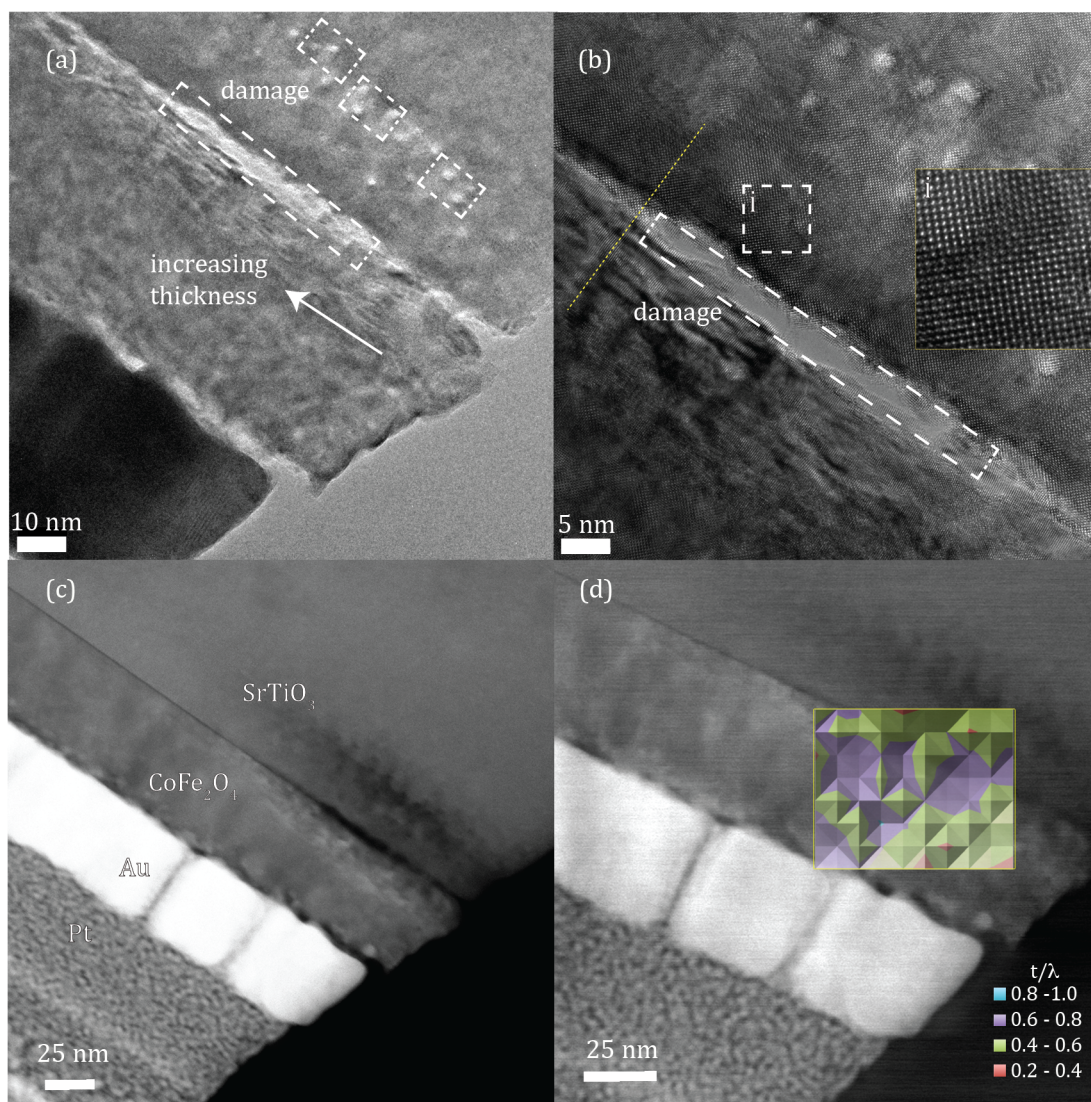


Figure 3.1 Images of specimen 4, a 50 nm STO/CFO specimen prepared INLO using a dual beam FIB. (a) TEM image showing electron beam damage, (b) HRTEM image showing beam damage at the STO/CFO interface and inset showing the STO lattice, (c) STEM-HAADF image showing gold and platinum deposition layers, and (d) STEM-HAADF image with relative thickness map calculated from a low loss EELS spectrum image overlaid.

Shown in figure 3.1a and figure 3.1b are TEM images of specimen 4. From the inset (i) shown in figure 3.1b it is clear that the STO lattice is well resolved which would suggest the specimen is thin, in agreement with the estimated absolute thickness determined from the low loss thickness map. The high quality of the

lattice image shown in inset (i) would also suggest that an the amorphous damage layer does not contribute significantly to the total thickness, indicating successful removal of the amorphous material by low kV cleanup at 5 kV.

Shown in figure 3.1a and figure 3.1b are damage regions that were observed after intermittent electron beam exposure of approximately two hours in TEM. Damage was not localized to the area of illumination and was thought to be a result of charging ^[60]. This effect was not observed in other FIB or argon milled specimens.

Shown in figure 3.2a and 3.2b are TEM images of specimen 6, which is a 50 nm STO/CFO specimen, prepared by INLO. As specimen 4 and 6 are similar and were prepared under the same INLO conditions, it is reasonable to expect similar contrast in substrate lattice images acquired under similar conditions.

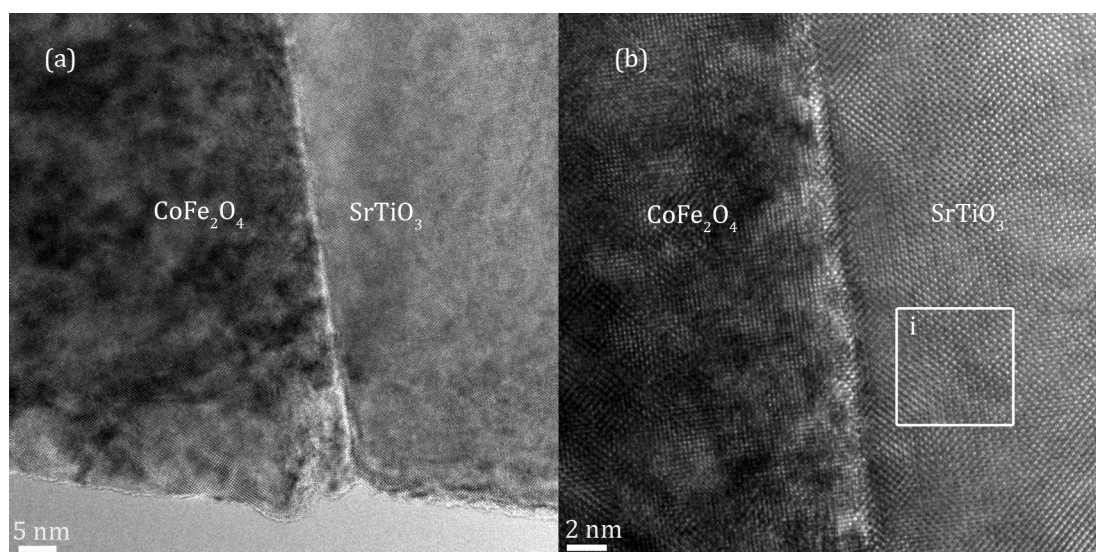


Figure 3.2 TEM images of specimen 6, a 50 nm STO/CFO specimen prepared by INLO using a dual beam FIB. (a) TEM image showing the thinnest region of film and substrate, and (b) HRTEM image showing mottled contrast and phase contrast variation due to amorphous damage and thickness variation.

Comparing inset (i) shown in figure 3.1b to inset (i) shown in figure 3.2b, it is clear that the contrast is worse in the STO lattice image acquired from specimen 6 than seen in the STO lattice image for specimen 4. If specimen 6 were thicker it would behave less like a weak phase object, resulting in poorer phase contrast. The poor contrast could also be explained by the presence of a thicker amorphous layer on specimen 6. The mottled appearance of the STO lattice image shown in figure 3.2b is characteristic of amorphous damage by ion milling reported by Scott *et al.* [99,101]. Consequently it is likely that specimen 6 is thicker or more damaged than specimen 4. This would suggest some unreliability in the INLO technique using the Helios system, given that specimen 4 and specimen 6 were prepared under identical conditions.

Shown in figure 3.3a is a composite TEM image of specimen 5, which is a 25 nm LAO/CFO specimen, prepared by INLO. The composite image shown was generated using the photomerge function in Adobe Photoshop CS5.

Comparing figure 3.3a with figure 3.2a, it would appear that specimen 5 is lower in thickness than specimen 6. The diffraction contrast observed between the LAO substrate and CFO film in figure 3.3a is less than observed between the STO substrate and CFO film in figure 3.2a, which is a good indication of reduced thickness. Diffraction contrast in figures 3.1a and 3.3a is too similar for a meaningful qualitative comparison of the thicknesses of specimen 4 and specimen 5.

Given that the thickness of the LAO/CFO specimen is expected to be low, a good lattice image for this specimen would also be expected. From figures 3.3b and 3.3c it is clear that the LAO lattice is not resolved at all. Speckled contrast can be observed in the substrate region in both figure 3.3b and 3.3, which is characteristic of an amorphous region. As specimen 5 is thin and the lattice is not resolved, it is likely that the damage layer of specimen 5 represents a significant fraction of the total specimen thickness. In a TEM/STEM study of STO/LAO multilayers, Montoya *et al.* previously found LAO to be more susceptible to milling damage than STO [101] which would support this hypothesis.

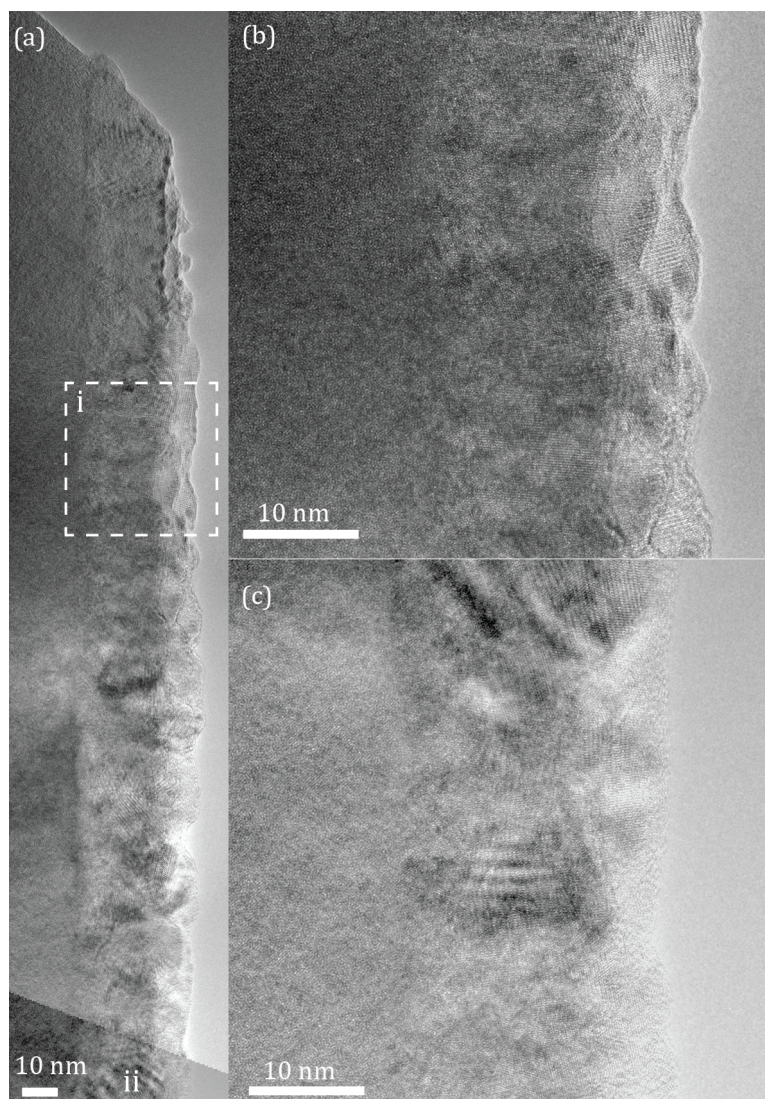


Figure 3.3 Images of specimen 5, a 25 nm LAO/CFO specimen prepared by INLO. (a) Composite TEM image showing a large thin region and delamination of the Pt and Au coating. The composite was generated using the photomerge tool in Adobe photoshop CS5. (b-c) Selected regions at higher magnification showing amorphous damage to the LAO substrate and CFO layer.

3.4 Argon Ion Beam Milling

Argon ion milling was carried out until perforation at 5 kV and 8°. Damage layers ranging from 5 nm to 0 nm are reported for beam energies between 3 kV and 0.25 kV for GaAs and Si respectively [97,98]. Double sided argon ion milling at 6 kV to 1.5 kV was found to produce good quality lattice images of Al/Spinel interfaces by Strecker *et al.* at 1.5 kV [102].

Single sided thinning was previously found to introduce bending effects close to the central hole due to the inhomogeneous nucleation of defects and introduction of heat [102]. A high density of defects and defect agglomerates were observed when thinning from one side, but were absent when specimens were double thinned under otherwise identical conditions [102]. All conventionally milled specimens in this project were prepared by double sided thinning.

XTEM specimens of specimen 1 and specimen 2 were prepared by argon ion milling as described in chapter 2 and section 3.2. Milling was performed at room temperature ($T = 300\text{ K}$) for CFS 716a.3 and liquid nitrogen temperature ($T = 97\text{ K}$) for CFS 9226.1 after perforation. TEM/STEM imaging was performed after each milling stage in order to determine the extent of beam damage for different beam energies at different temperatures.

3.4.1. Room Temperature Milling

Shown in figures 3.4a-d is a region of specimen 1, which is a 50 nm STO/CFO specimen prepared by argon milling. Figures 3.4a-d show specimen 1 after perforation, which was achieved by milling with 5 kV argon beams incident 8° to the specimen and perpendicular to the substrate/film interface.

The same regions is shown in figures 3.4e-h, after low energy milling for 40 minutes at 1 kV followed by 40 minutes at 0.5 kV. Milling was performed with argon beams incident 3° to the specimen and parallel to the substrate film/interface. Both figure 3.4a and 3.4e are composite images. The contrast and brightness of figure 3.4e were balanced using the photomerge function in Adobe Photoshop CS5. The photomerge function failed to produce satisfactory results for figure 3.4a, hence unbalanced images are displayed.

When preparing thin film specimens by argon ion milling, there is compromise between the target TEM specimen thickness and the thin film thickness that will remain after preparation. In order to produce the thinnest TEM specimens it is usually necessary to sputter material from the top surface of the thin film. For films of thickness less than 200 nm the thickness lost can represent a significant fraction of the total thin film thickness.

The conventional preparation technique reported by Scott *et al.* [96] was found to produce large electron transparent regions if milling was stopped immediately after perforation. However, regions where the entire thin film was intact were too thick for lattice imaging and core loss EELS. Low energy milling at glancing angle parallel to the substrate/film interface was found to reduce specimen thickness in a highly controlled fashion resulting in negligible removal of material from the top surface of the thin film.

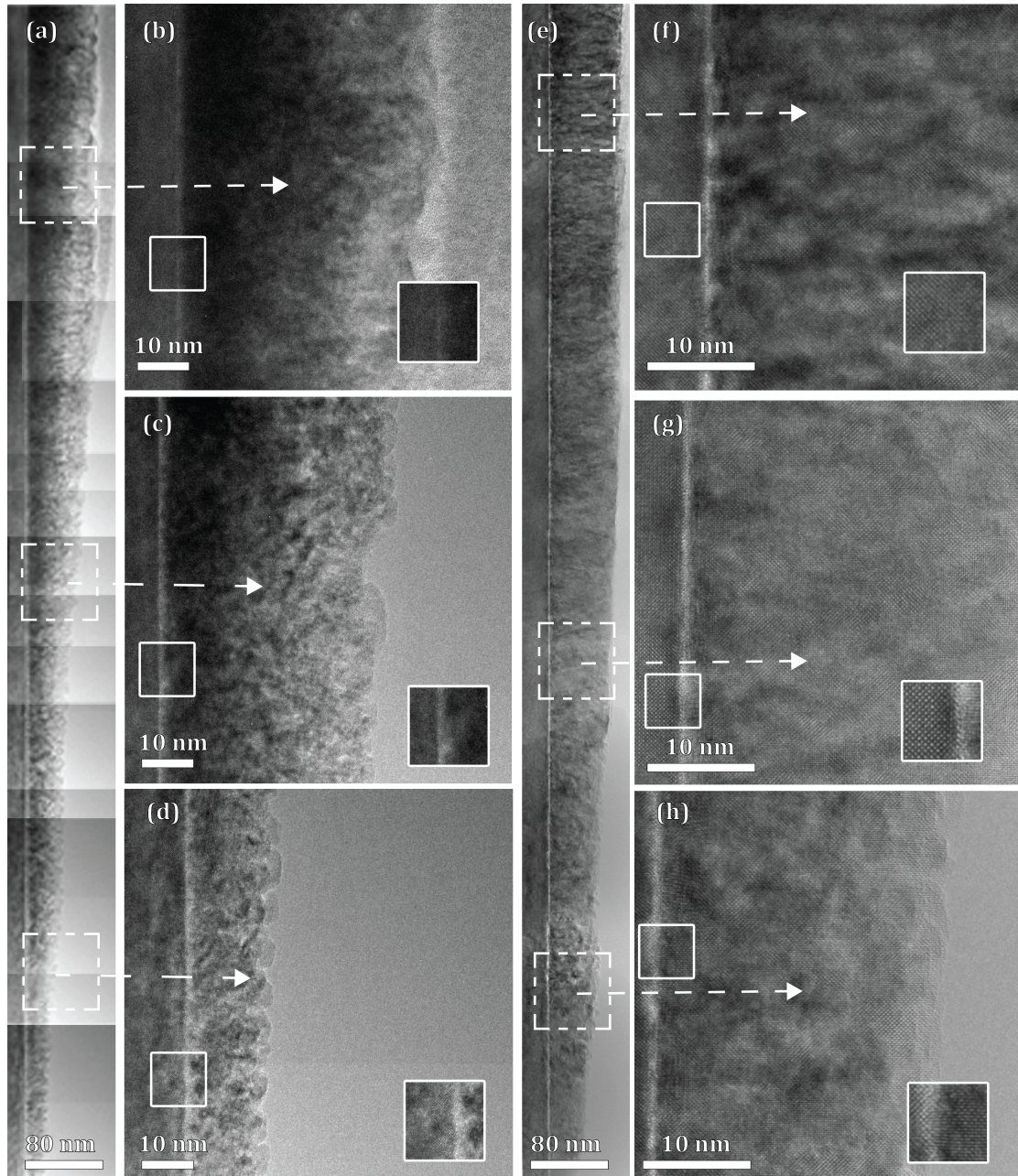


Figure 3.4 TEM images of a region specimen 1, a 50 nm STO/CFO specimen prepared by argon milling at 5 kV (a-d), and after 1 kV and 0.5 kV at room temperature. Images (b-d) show higher magnification regions of interest taken from image (a). Images (f-h) show higher magnification regions of interest taken from image (e). The substrate and film lattices are only well resolved after low energy milling. Insets shown to the right of images b-d and f-h correspond to the smaller highlighted regions close to the interface in each image.

No significant changes to film topography were observed after low energy milling. At high magnification in figures 3.4b-d and 3.4f-h, the lattice is only well resolved after low energy milling. Lattice imaging at the substrate/film interface was possible over a region of $\sim 1\ \mu\text{m}$ after milling at 0.5 kV.

For insulating specimens, electrically conducting epoxy can be used to provide charge drainage, counteracting charge drift and damage in the TEM. It is desirable that some epoxy be retained after the final milling stages. In addition, analysis of film topography is justifiable if the epoxy is retained. Shown in figure 3.5a and 3.5b are HAADF STEM images acquired from different regions of the specimen 1 after 5 kV argon milling and 0.5 kV argon milling respectively. It is apparent from figures 3.5a and 3.5b that an epoxy layer is retained for the argon milling conditions used to prepare specimen 1. The region over which epoxy was retained is marked in figure 3.5a and 3.5b. The region over which HRTEM imaging was possible after low energy milling is also marked in figure 3.5b.

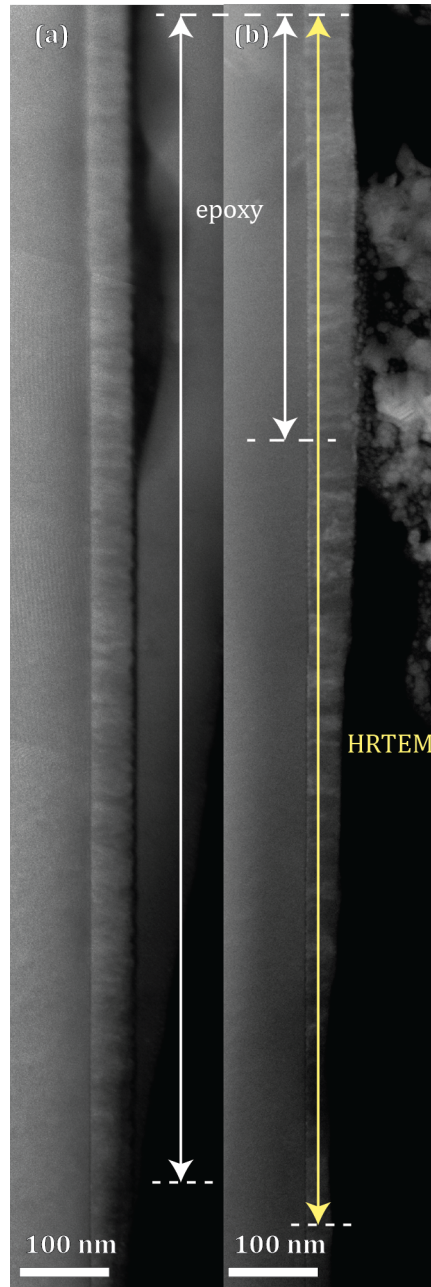


Figure 3.5 STEM HAADF images of two different regions of specimen 1 after (a) 5 kV milling, and (b) 1kV and 0.5 kV milling. Epoxy regions and the region of interest suitable for HRTEM imaging are highlighted.

3.4.1. Low Temperature Milling

HRTEM images of specimen 1 milled at room temperature with beam energies 1 kV and 0.5 kV are shown in figures 3.6a and 3.6b. HRTEM images of specimen 2, which is a 25 nm STO/CF0 specimen prepared by argon milling at liquid nitrogen temperature are shown in figures 3.6c-e. Images for at 1 kV, 0.5 kV and 0.2 kV milling are shown in figures 3.6c, 3.6d and 3.6e respectively.

From figures 3.6a and 3.6b it is clear that the STO lattice is poorly resolved after 1 kV milling at room temperature but well resolved after room temperature milling at 0.5 kV. Conversely, from figure 3.6c, it is clear that the STO lattice is well resolved after 1 kV milling at liquid nitrogen temperature. Contrast variations in the STO lattice image for 0.5 kV low temperature milling are less apparent than in the STO lattice image for room temperature 0.5 kV milling, suggesting a reduction in specimen thickness variation with low temperature low energy milling. From figure 3.6e it is clear that milling at 0.2 kV at liquid nitrogen temperature produced a specimen that was both very thin and highly uniform suggesting these were the optimum final milling conditions.

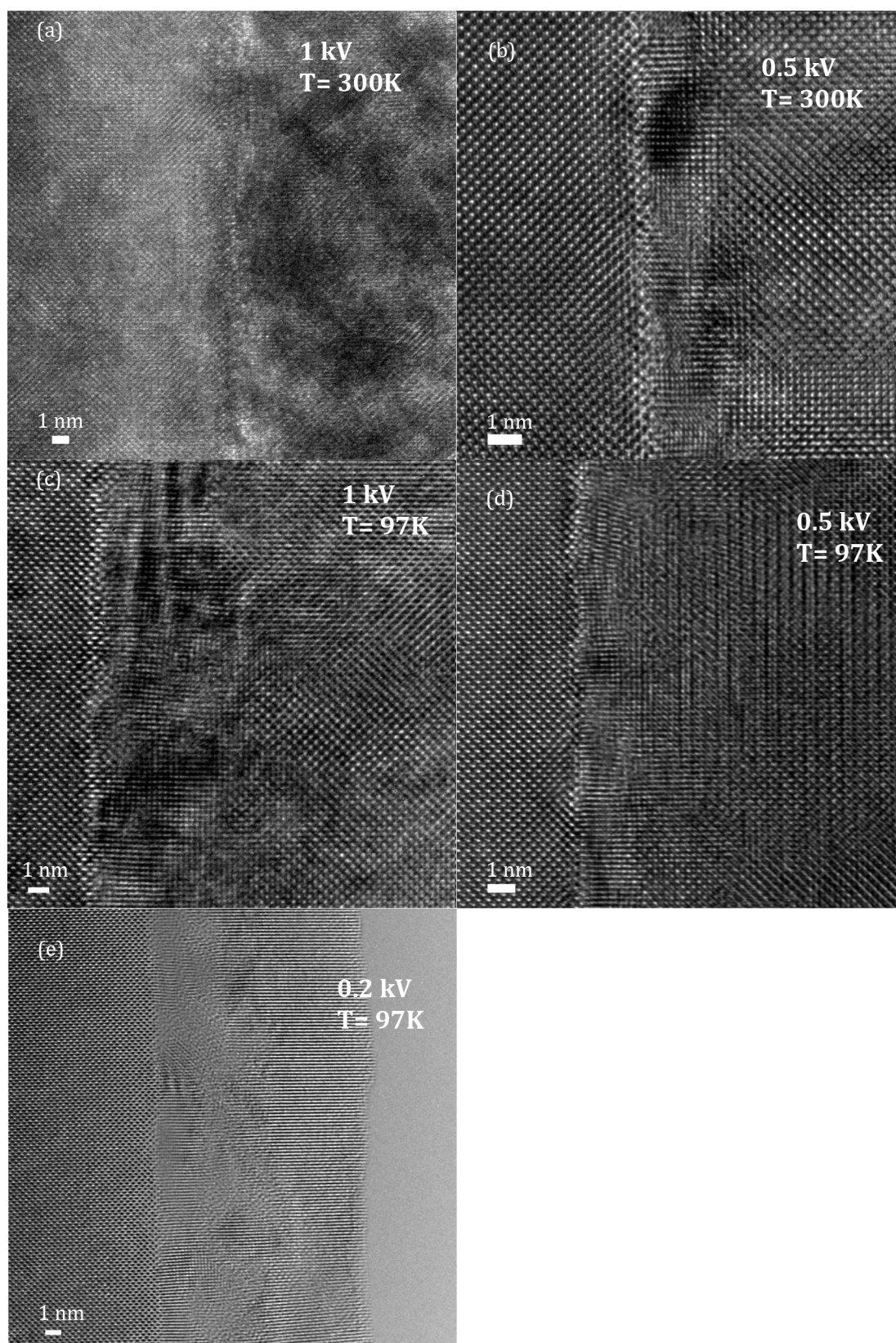


Figure 3.6 HRTEM images of specimen 1 prepared by argon milling at 300K (a) 1 kV, (b) 0.5 kV and specimen 2 at 97K, (c) 1kV, (d) 0.5 kV and (e) 0.2kV 97K.

HRSTEM images of specimen 1 and specimen 2 are shown in figure 3.7a-d. From figures 3.7a-d, improvements in the quality of the STO lattice images acquired at low temperature are less apparent, though some improvement was observed at 1 kV, in agreement with the HRTEM results. From figure 3.7 it is also clear that some surface mottling is still present after milling at 0.5 kV low temperature and energy 0.5 kV.

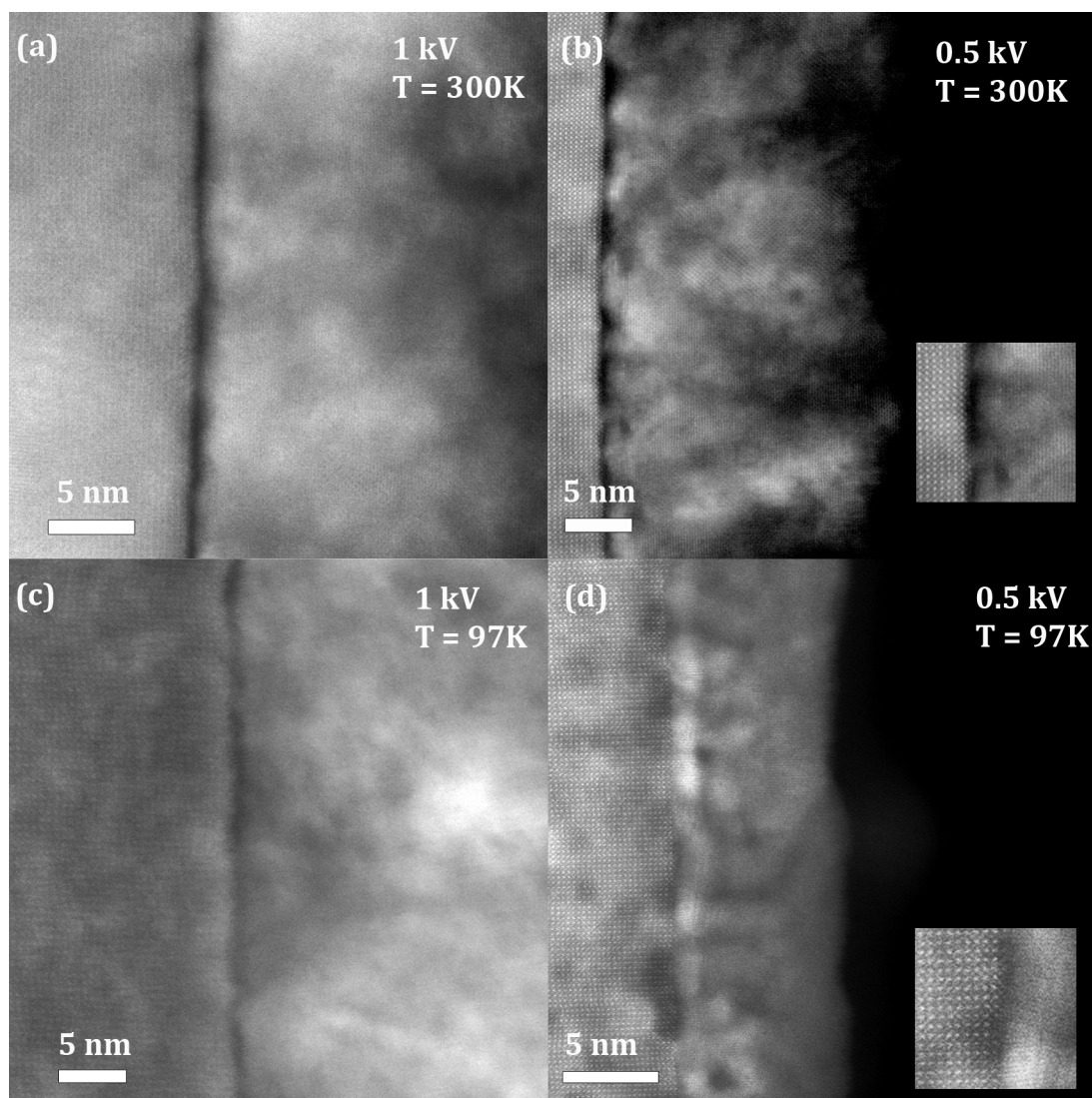


Figure 3.7 HRSTEM images of specimen 1 after argon milling at 300 K and energy: (a) 1 kV, (c) 0.5 kV, and specimen 2 after argon milling at 97 K at (a) 1 kV, and (b) 0.5 kV.

3.5 Dual Beam FIB Milling and Low Energy Argon Milling

Post INLO argon ion milling was carried out on specimen 4 (STO/CFO) and specimen 6 (STO/CFO) using a PIPS (Gatan, UK). Milling was performed with beam(s) incident 3° to the FIB section surface and 1 kV. Double sided thinning was performed for 40 minutes on specimen 4. Single sided thinning was performed on specimen 6 with no rotation; the sample was oriented toward the beam to reduce the chance of copper redeposition from the Omnidrig.

Huang previously showed that argon milling at 5 kV for a 30s improved the surface quality of a FIB specimen prepared from a piezoelectric device ^[103]. Scott et al. also found improvements to the surface quality of Si, GaAs and steels after FIB specimens were argon ion milled at 2 kV and 0.5 kV ^[99].

TEM and STEM images of specimen 6 after single sided argon ion milling at 1 kV are shown in figure 3.8a-d. Comparing figure 3.8b to figure 3.2b, it is clear that post INLO argon milling at 1 kV has significantly improved the quality of the STO lattice image. This clearly indicates that the 1 kV static argon milling step was successful in reducing specimen thickness or the relative damage layer thickness.. Mottling was still observed after 1 kV argon milling, in agreement with images acquired from specimen 1 after similar argon ion milling conditions. Conversely, the STO lattice image observed for specimen 6 showed improved contrast in comparison to that STO lattice image of specimen 1 after argon milling specimens at room temperature at 1 kV (figure 3.7a).

Shown in figure 3.9 are thickness profiles calculated from low loss EELS spectrum images. The thickness profiles shown in figure 3.9 correspond to the survey regions shown in the ADF STEM image shown in figure 3.8d acquired from specimen 6. From figure 3.9, it is clear that the thickness change over the area of interest shown for specimen 6 is large ranging from a minimum of around $t/\lambda = 0.3$ to a maximum of around $t/\lambda = 1.0$. The large thickness

variation produced by single sided low energy argon milling indicates this method is unsuitable for producing regions of interest suitable for analysis by EELS.

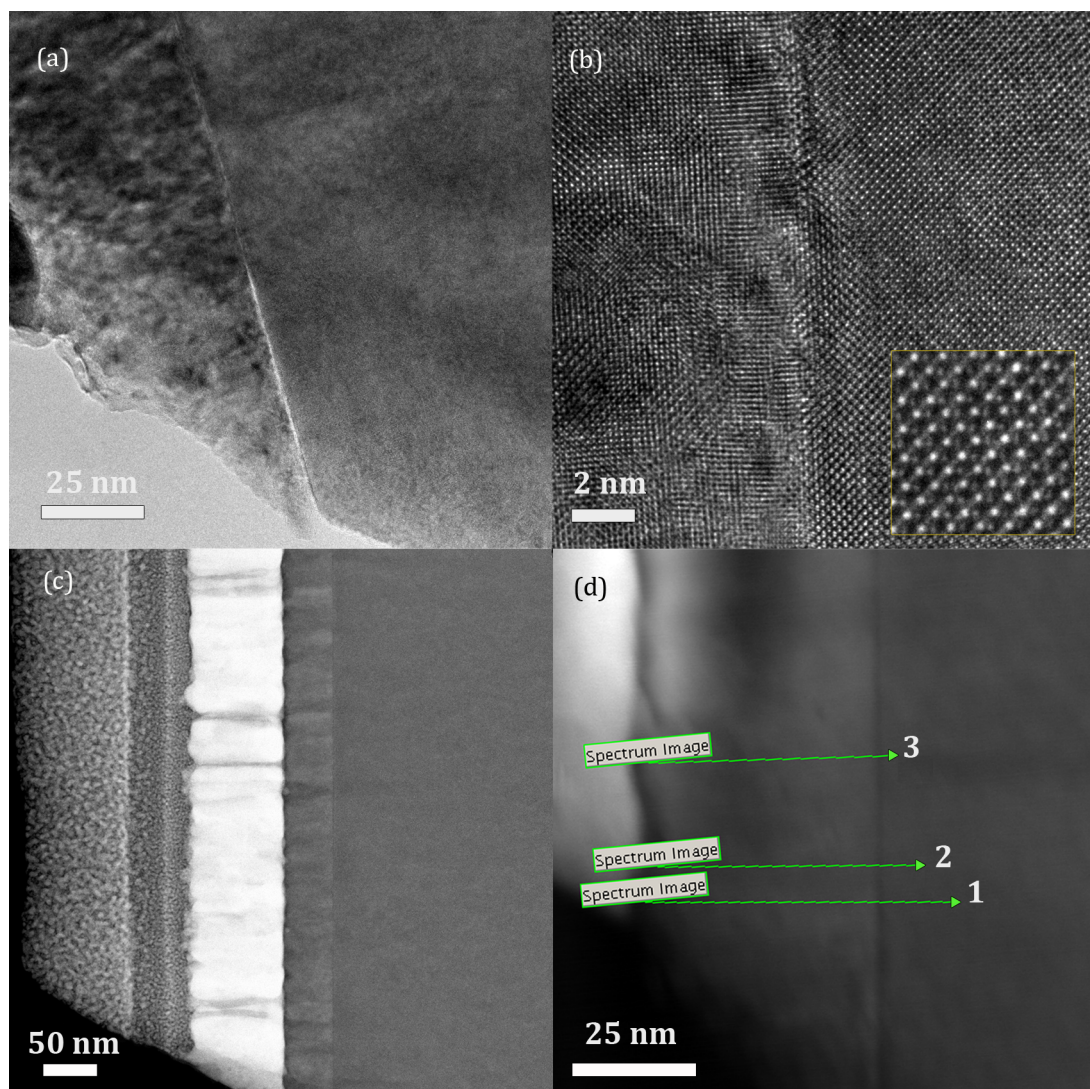


Figure 3.8 Images of specimen 6, a 50 nm STO/CFO specimen prepared by INLO and single sided argon ion milling at 1 kV for 20 minutes using a single ion gun and no rotation. (a) TEM image, (b) HRTEM images, (c) HAADF-STEM image, and (d) ADF STEM image with spectrum image survey regions marked.

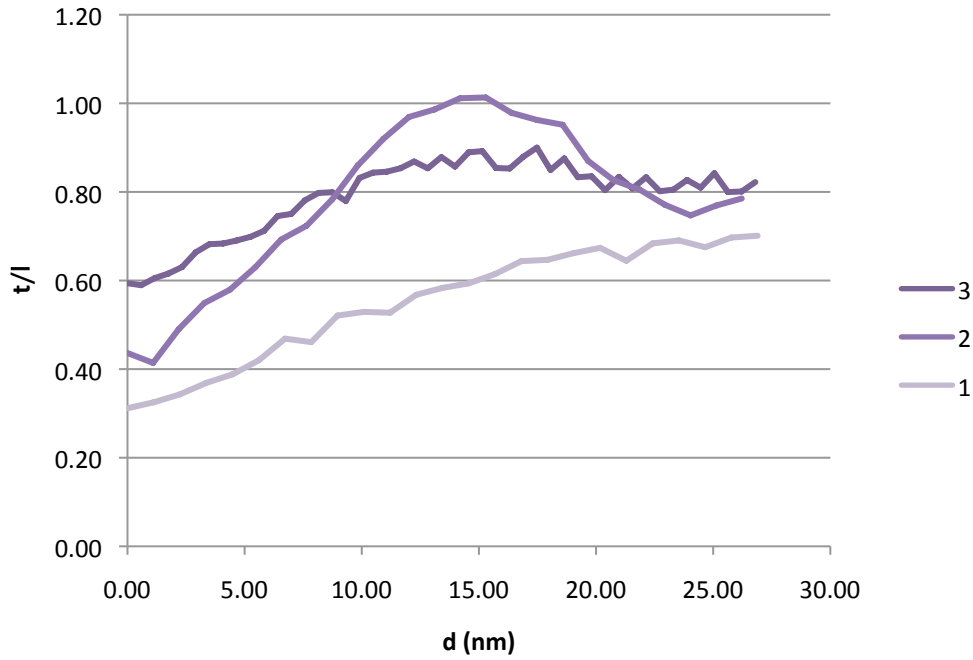


Figure 3.9 Relative thickness profiles for specimen 6 calculated from low-loss EELS spectrum images. Regions 1-3 correspond to regions 1-3 shown in figure 3.8d.

Images of specimen 4, an STO/CFO specimen prepared by INLO and double-sided argon milling at 1 kV are shown in figure 3.10a-d. Comparing figure 3.1a and 3.1b to figure 3.10a and 3.10 d, it is clear that post INLO argon milling did not significantly improve the contrast in the STO lattice image, suggesting the surface quality and specimen thickness are similar before and after argon milling in this case.

Shown in figure 3.10d is a spectrum image survey region over which a thickness map calculated from low loss EELS spectra is overlaid. Significant changes in the average relative specimen thickness and variation in relative thickness before and after argon milling were not observed. Scott *et al.* previously produced a $2 \mu\text{m}^2$ region from a silicon sample prepared by FIB, in thickness range $0.3 < t/\lambda < 0.4$ by post-FIB argon milling at 0.5 kV with a Gentlemill (Technoorg, Hungary). This was not achieved by argon milling performed on specimen 4 or specimen 6 using a PIPS (Gatan, UK). It is expected the unpredictable argon milling observed is a result of specimen positioning. FIB lamellae could not be

resolved by eye giving a high degree of uncertainty in positioning Omnigrid™ specimens in the PIPS so that the argon beam(s) were incident on the FIB lamellae.

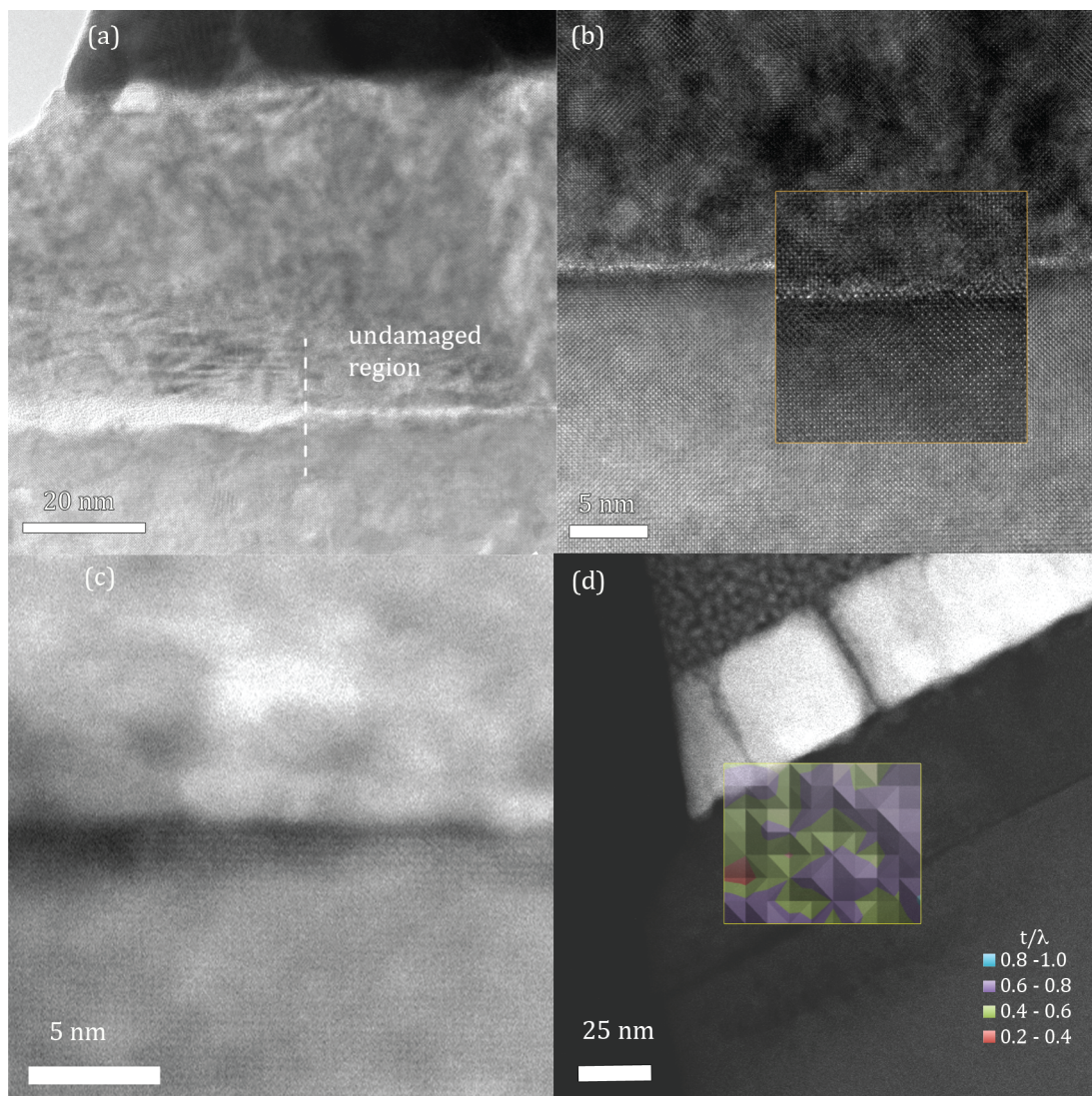


Figure 3.10 Images of specimen 4 after 1 kV double-sided argon milling. (a) TEM image showing electron beam damage, (b) HRTEM image showing STO lattice image in the undamaged region, (c) HRSTEM-HAADF image showing the STO lattice and (d) STEM-HAADF image with relative thickness map calculated from a low loss EELS spectrum image overlaid.

3.6 Carbon Coating

Insulating specimens suffer from charge build up effects due to irradiation by the electron beam in the TEM. This can cause damage ^[60] and is a source of drift. A charged region of specimen and electrons in the electron beam repel; this can induce a beam deflection or cause the TEM specimen to move unpredictably at high magnification.

Sequences of sixty high resolution images of specimen 3, a 200 nm STO/CFO specimen prepared by argon milling, were recorded in TEM at 2s intervals. Image series were recorded before carbon deposition, then after a 10 nm carbon layer was deposited by evaporation on to the exit surface of the TEM specimen using the Auto 306 carbon coater (Edwards, UK).

Figure 3.11 shows images of uncoated specimen 3 taken at 0s, 20s, 40s, 60s, 80s and 100s. An easily identifiable feature is marked. In each image, the current and previous positions of this feature are marked. Figure 3.12 shows the equivalent results for specimen 3 coated with 10 nm of amorphous carbon.

Spatial drift was observed for both specimens though the characteristics of the drift observed for coated and uncoated specimens differed. The displacement of the marked feature for the uncoated specimen is in all cases, much greater in magnitude than any displacement recorded for the coated specimen for any 20s time interval. The total displacement was sufficiently large after 100s that the feature moved completely out of the field of view.

For the coated specimen, the displacement direction of the marked feature did not change over the series to a 1st approximation. Drift of this nature is characteristic of stability issues associated with the operating environment of the TEM, and can almost always be reduced by leaving a specimen to settle. For the uncoated specimen, the displacement direction between marked positions of was found to be unpredictable. Improvements were not observed with time and drift of this nature was only reduced after carbon coating.

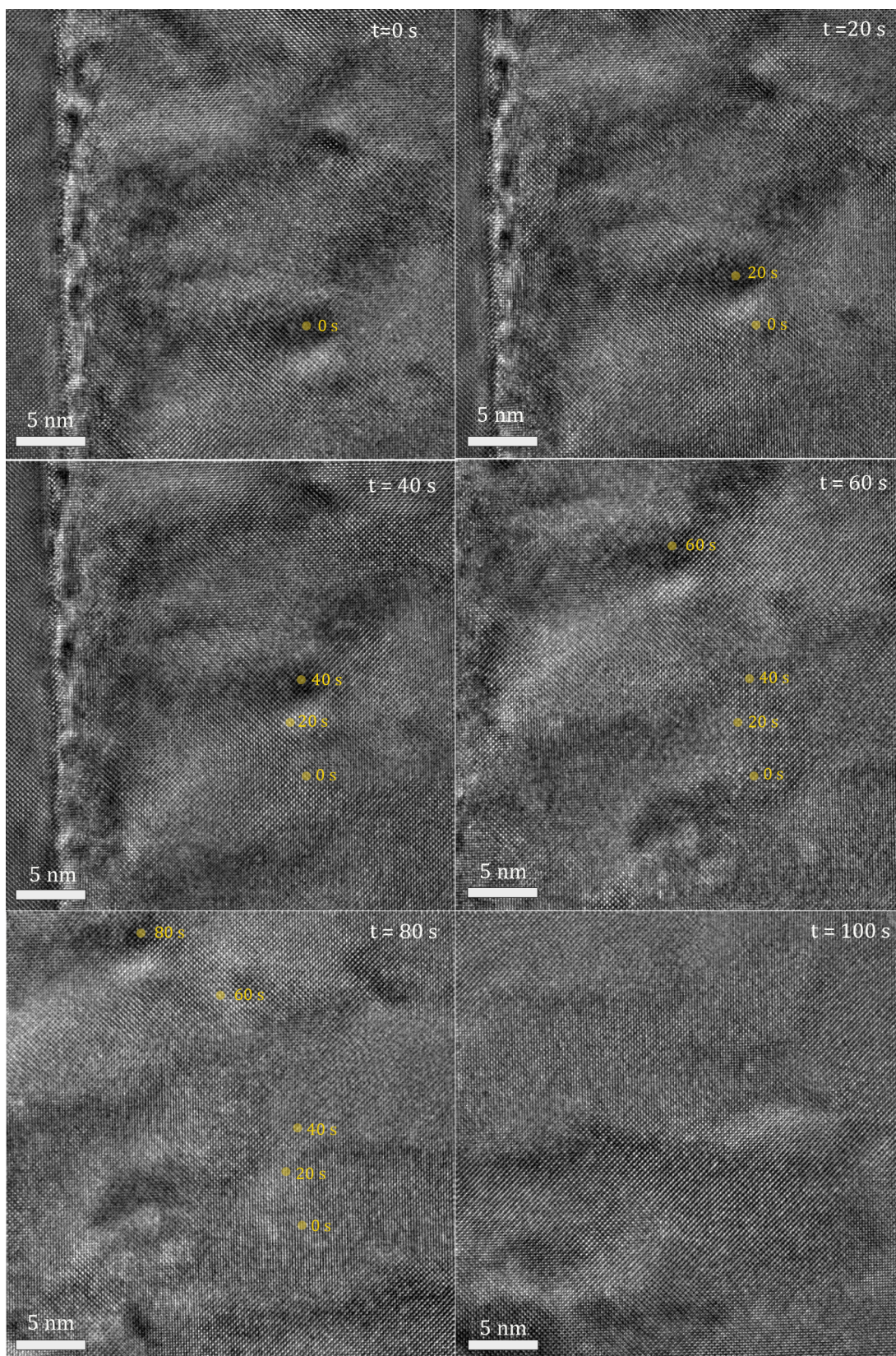


Figure 3.11 HRTEM images of specimen 3 with no carbon coating, taken over 100s.

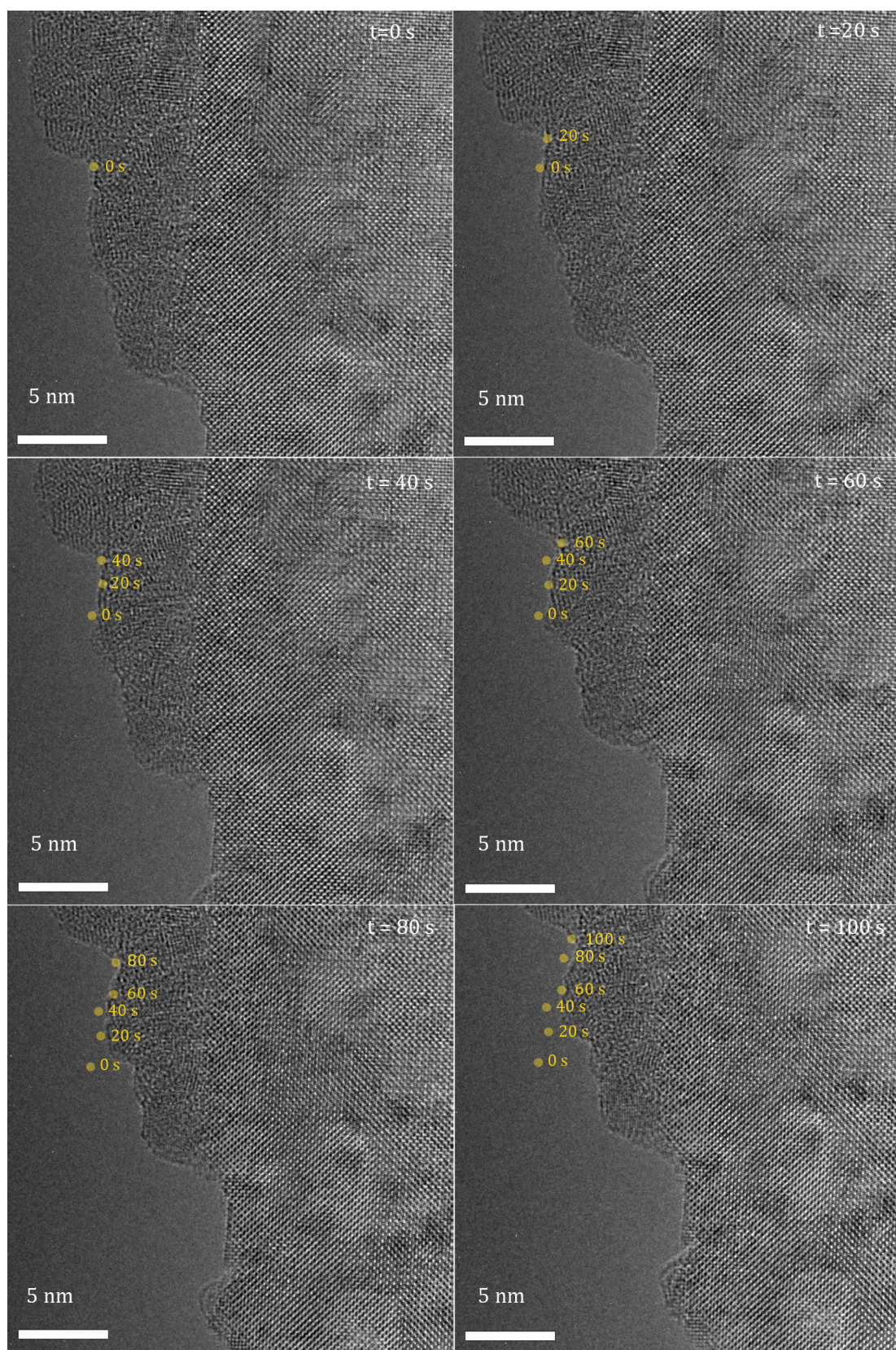


Figure 3.12 HRTEM images of specimen 3 with a 10 nm carbon layer deposited on the exit surface, taken over 100s.

3.7 Plasma Cleaning

Hydrocarbon contaminants are present on the surface of all TEM specimens; the level of contamination depends strongly on the preparation method and specimen handling history ^[104]. When in the TEM, mobile hydrocarbon contaminants migrate to the beam position and form carbonaceous pillars detrimental to imaging and analysis. The rate of contamination increases as the beam current density increases in TEM/STEM, and as the area over which the beam is scanned in STEM decreases ^[104].

Contamination can be removed from a TEM specimen by plasma cleaning. Contaminants are removed by sputtering and chemical reaction; an oxygen plasma removes hydrocarbon contamination by oxidation into CO, CO₂, and H₂O, which are readily extracted through by a vacuum system ^[104,105]. Additional sputtering of prepared TEM specimens is undesirable in most cases. The Solarus plasma cleaner (Gatan, UK) utilizes a hydrogen-oxygen mixed plasma that is reported to cause minimal sputtering ^[106]. H₂/O₂ plasma cleaning was performed on specimens before all TEM/STEM experiments using the Solarus.

The plasma cleaning parameters used are given in table 3.3. Without plasma cleaning, the rate of contamination for all specimens was too high for HRSTEM or EELS analysis. For argon milled specimens, the contamination rate was only successfully reduced to an acceptable level by introducing an Ar/O₂ plasma cleaning step before argon ion milling (3.2), in addition to the H₂/O₂ plasma cleaning step before TEM/STEM.

Plasma cleaning was performed on commercially available carbon films (Agar, UK) in order to determine the suitability of the H₂/O₂ cleaning recipe for specimens coated with carbon. Plasma cleaning was carried out with the flow rates given in table 3.3 and R.F values given in section 3.2. Cleaning steps of 30 s were applied at a duty cycle of 100%.

Thickness maps were collected by EFTEM from 6 different regions of the carbon film, evenly spread over the specimen, for accumulative cleaning times of 0 s, 30 s and 60 s. For accumulative cleaning time = 90 s, thickness maps were collected from four different regions. Three repeats were made for each region measurements taken for each area. The mean relative thickness was calculated from all thickness maps collected for a given cleaning step.

λ for 300 kV electrons in amorphous carbon was found to be 177 nm by comparing relative and absolute thicknesses determined from the log-ratio technique for thickness measurement by EELS. Relative thickness and absolute thickness were determined using the “calculate relative thickness” or “calculate absolute thickness” functions in Digital Micrograph.

Thickness measurements were performed on low loss EELS spectra acquired from a commercially available carbon film (Agar, UK) under the same conditions. Relative thicknesses determined by EFTEM were converted to absolute thicknesses by substituting $\lambda = 177$ nm into equation 2.27.

Figure 3.13 shows TEM images of a carbon film taken throughout accumulative plasma cleaning of 0 – 90 s. From figure 3.13 it is clear that there are no significant microstructural changes to the carbon film with successive plasma cleaning of 30s. The variation of mean absolute thickness with accumulative plasma cleaning time is shown figure 3.14. A thickness decrease of 10 nm was observed after 30 s of cleaning though further accumulative cleaning of 60 s resulted in a much smaller decrease of 3 nm, supporting reports that the Solarus H₂/O₂ plasma cleaning recipe causes minimal sputtering ^[106]. The large initial decrease in thickness is expected to represent the removal of surface contamination from the carbon film.

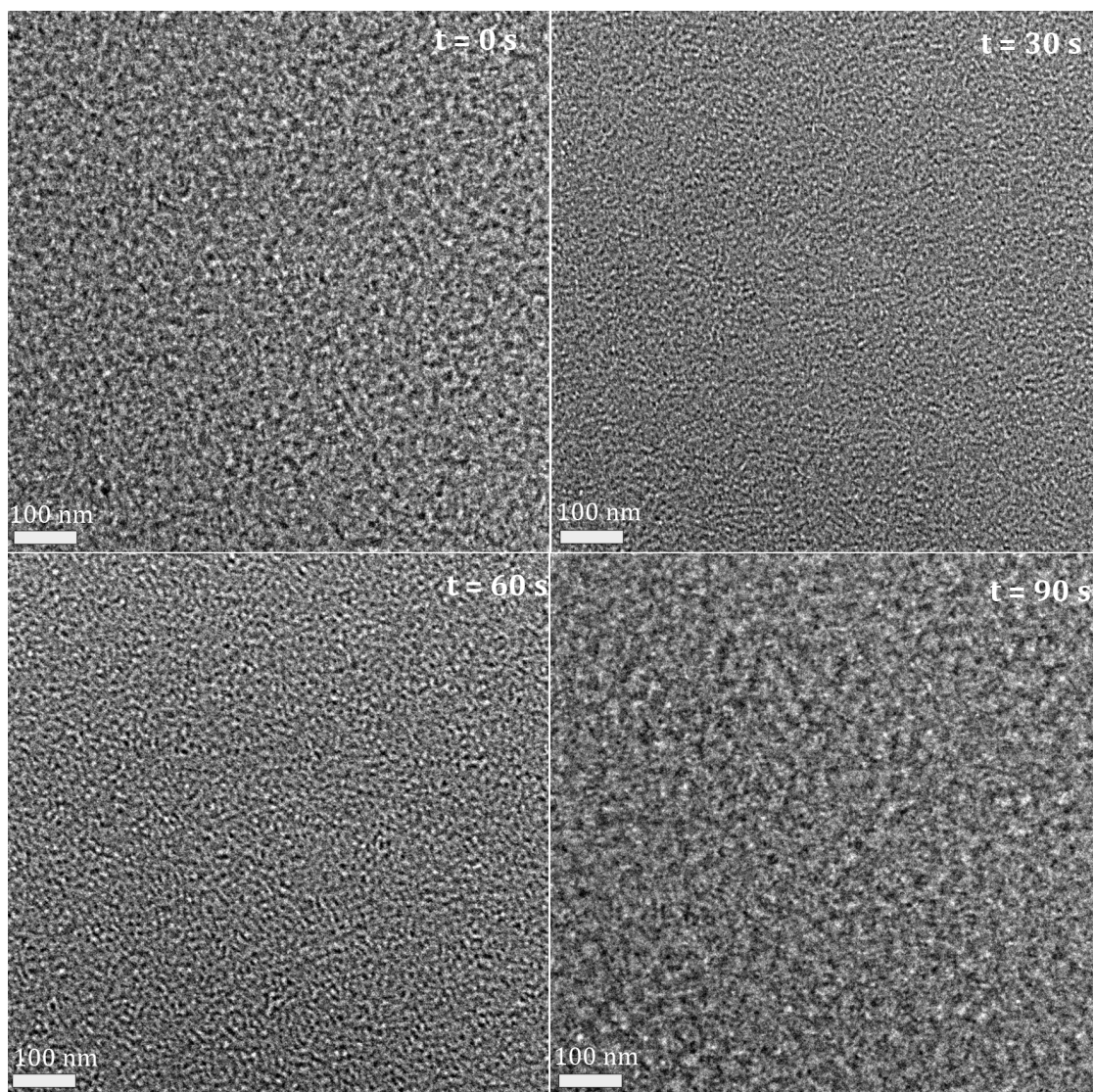


Figure 3.13 Carbon films after accumulative H_2/O_2 plasma cleaning times of: (a) 0s, (b) 30s, (c) 60s and (d) 90s.

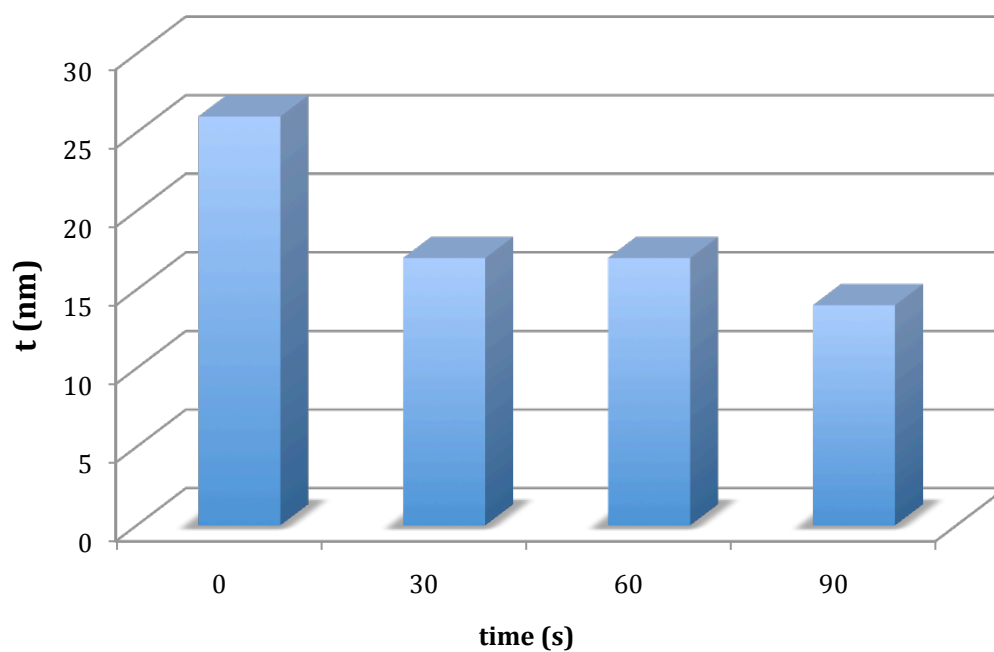


Figure 3.14 Absolute thickness of a carbon film as determined by EFTEM thickness mapping after accumulative H_2/O_2 plasma cleaning of: (a) 0s, (b) 30s, (c) 60s, and (d) 90s.

3.8 Conclusions

Dual beam FIB milling and argon ion milling were both found to produce electron transparent areas suitable for HRTEM analysis. Areas of interest were typically $\sim 0.01 \mu\text{m}^2$ for FIB milled specimens and $\sim 0.1 \mu\text{m}^2$ for argon milled specimens. The dual beam FIB method was highly reproducible though surface roughness and overall thickness of FIB milled specimens meant specimens were typically unsuitable for HRSTEM or core loss EELS even after low energy cleaning. A high degree of reproducibility was also found for the argon milling method if conventional high energy ion milling perpendicular to the substrate/film interface was followed by low energy milling parallel to the interface.

Low energy argon milling was found to produce regions of interest with less amorphous damage than FIB or conventionally prepared specimens; XTEM specimens produced were typically suitable for HRSTEM and core loss EELS. Low temperature milling at 1 kV was found to cause less amorphous damage than 1 kV room temperature milling. However, no benefit was observed for 0.5 kV low temperature milling over 0.5 kV room temperature milling. Final cleaning at 0.2 kV and low temperature was found to produce thin and highly uniform areas of interest though the combined effects of low temperature low energy milling could not be separated.

The thickness of FIB milled specimens too thick for HRTEM/HRSTEM was successfully reduced by single sided argon ion milling at 1 kV without rotation using a PIPS. However, the post milling thickness gradient was too high for core loss spectroscopy. Double sided thinning FIB specimens in the PIPS gave no improvements; a result of difficulties in aligning the argon ion beams on the FIB lamellae.

Drift due to charging was successfully reduced by depositing thin carbon layers on the exit surface of STO/CFO XTEM specimens. Hydrocarbon contamination

levels were successfully minimised by the introduction of a 30 minute Ar/O₂ plasma cleaning step before argon milling, in addition to 2 minute H₂/O₂ cleaning step preceding TEM/STEM analysis. Plasma cleaning for 90 s with H₂/O₂ was found to cause minimal-damage to commercially amorphous carbon films indicating carbon films deposited on TEM specimens would remain after plasma cleaning in a hydrogen oxygen plasma.

Chapter 4 – Microstructure of SrTiO₃/CoFe₂O₄ Thin Films

4.1 Introduction

The microstructure of an epitaxial thin film can depend strongly on the substrate material and surface crystallography, as well as the lattice mismatch and thin film growth and post processing conditions. As thin films are often thinner than 100 nm, the structure of the substrate/film interface often plays a significant role in defining the functional properties of a thin film due to the importance of surface effects at the nanoscale.

Epitaxial CFO thin films were previously grown on MgO [36,45,46], MgAl₂O₄ - (MAO)^[26] and CoCr₂O₄ (CCO) buffered MAO [26] and a strong dependence of film structure on deposition conditions and film thickness is widely reported [45,107]. Epitaxial growth of CFO on STO (001) has been demonstrated by pulsed laser deposition (PLD)^[3] and laser molecular beam epitaxy (LMBE)^[34] in spite of a high lattice mismatch. Xie *et al.* confirmed an epitaxial growth relationship by TEM for STO/CFO grown by MBE. Xie *et al.* also report a semicoherent interface in STO/CFO with structural defects present every ~ 4 nm though detailed analysis of these defects was not present and the interface structure of STO/CFO was not well resolved [35].

Here, an investigation of the microstructure of the perovskite/spinel interface in as-deposited (AD) and oxygen post-annealed (OA) STO/CFO thin films of film thickness 25 - 200 nm is presented.

4.2 Experimental Technique

CFO thin films were grown by PLD on (001) STO by Axelsson *et al.* [3]. A description of the deposition parameters used was given in section 1.4.1 [3]. STO/CFO XTEM specimens were prepared by room temperature low energy argon milling as described in previous chapters. A summary of specimens relevant to this chapter are given in table 4.1.

Table 4.1 – XTEM specimens relevant for the microstructural investigation.

Post Processing	h (nm)	Specimen	Specimen ID
As-deposited	25 nm	1	CFS 721.3
		2	CFS 721.4
Oxygen post-annealed ²	25 nm	3	CFS 714b.1
	50 nm	4	CFS 716a.3
	200 nm	5	CFS 723.4
		6	CFS 723.5

HRTEM imaging was carried out using an FEI Titan operating at 300 kV and using a double hexapole C_s corrector (CEOS, GMbh) for aberration correction. All imaging was carried out at with the specimens at [010] ZAO. For all images shown in this chapter, the electron beam direction is defined as [010] which is parallel to the interface plane. The CFO growth direction, which is the direction normal to the substrate/film interface plane is defined as [001] and referred to as out-of plane. The direction parallel to substrate/film interface and normal to the beam direction is defined as [100] and referred to as the in plane direction. This notation was adopted to match definitions previously reported by Axelsson *et al.* [3].

² Identical deposition and post-annealing conditions were used for all films, as previously given in section 1.4.1.

Optimum focal conditions for TEM imaging are given at an instrument dependent fixed objective lens current ^[53]. The defocus value at this lens current is defined as $d = 0$ (figure 4.1b). The plane at which a specimen is in focus under these conditions is the eucentric plane; a specimen coincident with the eucentric plane is at eucentric height. Overfocus is defined as strengthening of the objective lens so that the focal point is above the eucentric plane (figure 4.1a); underfocus is as a weakening of the objective lens such that the focal point is below the eucentric plane ($d < 0$). Specimen height is defined as z .

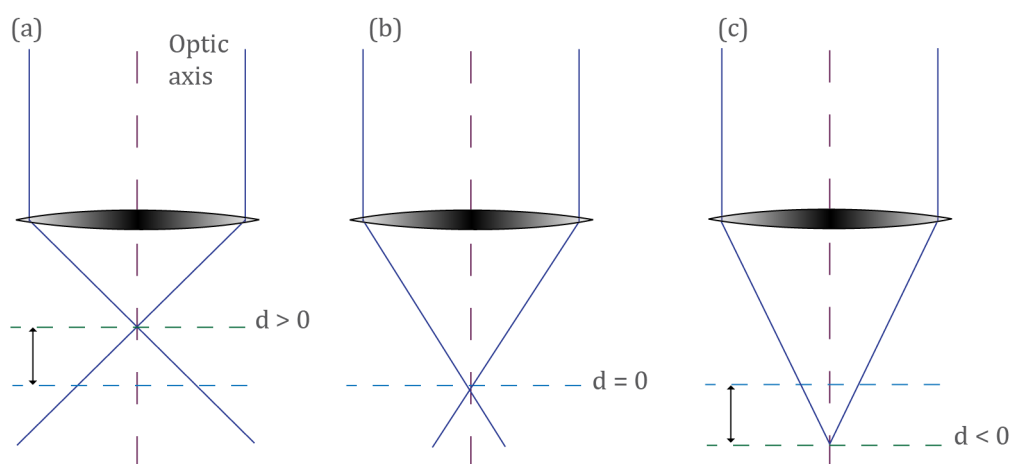


Figure 4.1 – Schematic showing simplified ray diagrams for the objective lens at: (a) overfocus, (b) eucentric focus, and (c) underfocus.

Alignment of the image corrector was typically carried out using commercially available carbon films (Agar, UK) at $z \sim -300$ nm. Alignment was performed by the Zemlin tableau method ^[70] to outer tilt angles of 18 – 24 mrad, at magnification 185K and again at magnification 380K – 790K.

Specimens were brought to focus by setting $d = 0$ and moving the specimen to eucentric height. Fine focal adjustments were carried out at high magnifications, by varying the defocus by up to ± 200 nm.

4.3 Misfit Accommodation Mechanisms

The in-plane Burgers vector was determined for CFO films at varying distance from the substrate/film interface, for specimens listed in table 4.1. Lattice and defect strain were calculated using a self-consistent approach in order to quantify mechanisms for the relaxation of strain at different regions in the films. Full experimental details are provided in sections 4.3.1 and 4.3.2.

The microstructure of an epitaxial thin film depends on the nature of the interface between the substrate and film phases. The properties of the interface depend on the thin film thickness and lattice mismatch. An interface is said to be coherent if there is a perfect lattice match between the two phases [33,108,109]. The in-plane lattice strain (ϵ) for a phase of spacing a_1 grown on a phase of spacing a_2 is given by

$$\epsilon = \frac{a_1 - a_2}{a_2} \quad (4.1)$$

If the interface is coherent, the strain is accommodated by the elastic deformation of the lattice of the thin film phase (spacing a_1) [33]. For a thin film of thickness h , the elastic strain energy (E_{elastic}) per unit area of interface is given by,

$$E_{\text{elastic}} = \frac{1}{2} E h \epsilon^2 \quad (4.2)$$

where E is an elastic modulus of that depends on the crystal orientation of the interface [33].

Elastic strain energy increases with film thickness. Below a critical thickness (h_c) the addition of misfit dislocations causes the total energy of the thin film phase to increase. Above the critical thickness, addition of misfit dislocations will decrease the total energy of the film [110]. A semicoherent interface is then formed consisting of coherent regions separated by misfit dislocations [33,108,109].

The lattice mismatch is partly accommodated by the misfit dislocations and elastic deformation of the thin film phase.

In order to determine h_c for a particular thin film, both the elastic modulus E and strain energy E_{elastic} must be found which is non trivial. By way of example for CFO films, Xie *et al.* [35] previously report a coherent interface for the (001) MgO/CoFe₂O₄ ($\epsilon = +0.3\%$) system and a semicoherent interface for (001) SrTiO₃/CoFe₂O₄ ($\epsilon = -7.4\%$). An illustration of a semi-coherent interface is shown in figure 4.2.

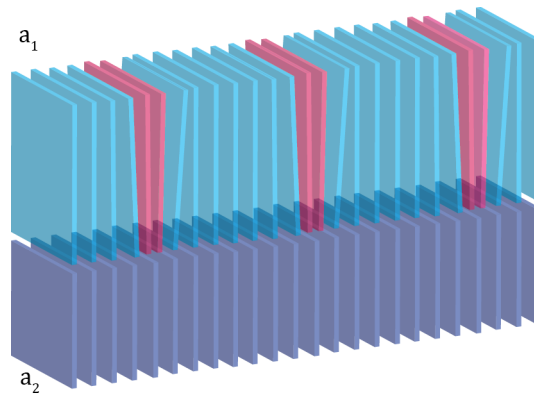


Figure 4.2 – Semicoherent interface between phases of lattice spacing a_1 and a_2 . Misfit dislocations are highlighted in red [33].

The strain energy associated with a misfit dislocation may be divided into two components. One component is stored in the dislocation core and the second component stored outside of the core elastically [111]. The energy associated with the core is typically small compared to the elastic energy. A thin film containing dislocations will be heavily distorted around the dislocation cores though the long range strain fields tend to cancel so that the energy per dislocation is reduced [111].

The spacing (s) of mismatch dislocations that will completely accommodate the lattice mismatch over a region of n planes is given by

$$s = (n + 1)a_1 = na_2 \quad (4.3)$$

Rearranging and substituting for ϵ in equation 4.2, gives an expression for s .

$$s = \frac{a_1 a_2}{a_2 - a_1} \quad (4.4)$$

As previously discussed in section 1.4.3, CFO is able to grow epitaxially on STO (001) due to a close match between the oxygen sublattices of the two phases in spite of a high lattice mismatch of -7.4% [3,32]. Defining a_1 as the (400) CFO spacing and a_2 as the (100) STO half spacing, to first approximation, the lattice mismatch would be satisfied by a semicoherent STO/CFO lattice containing misfit dislocations of Burgers vector $\mathbf{b} = a_o/4[100]$ CFO spaced by 2.8 nm. Misfit dislocations of $\mathbf{b} = a_o/4 [010]$ would also be expected as the interface is planar and therefore has a mismatch in two directions.

4.3.1. Elastic Relaxation

Shown in figure 4.3a-c are HRTEM images acquired from a 25 nm AD STO/CFO XTEM specimen (specimen 2). A selected area diffraction pattern acquired from a 200 nm OA STO/CFO XTEM specimen (specimen 5) is shown in figure 4.3d.

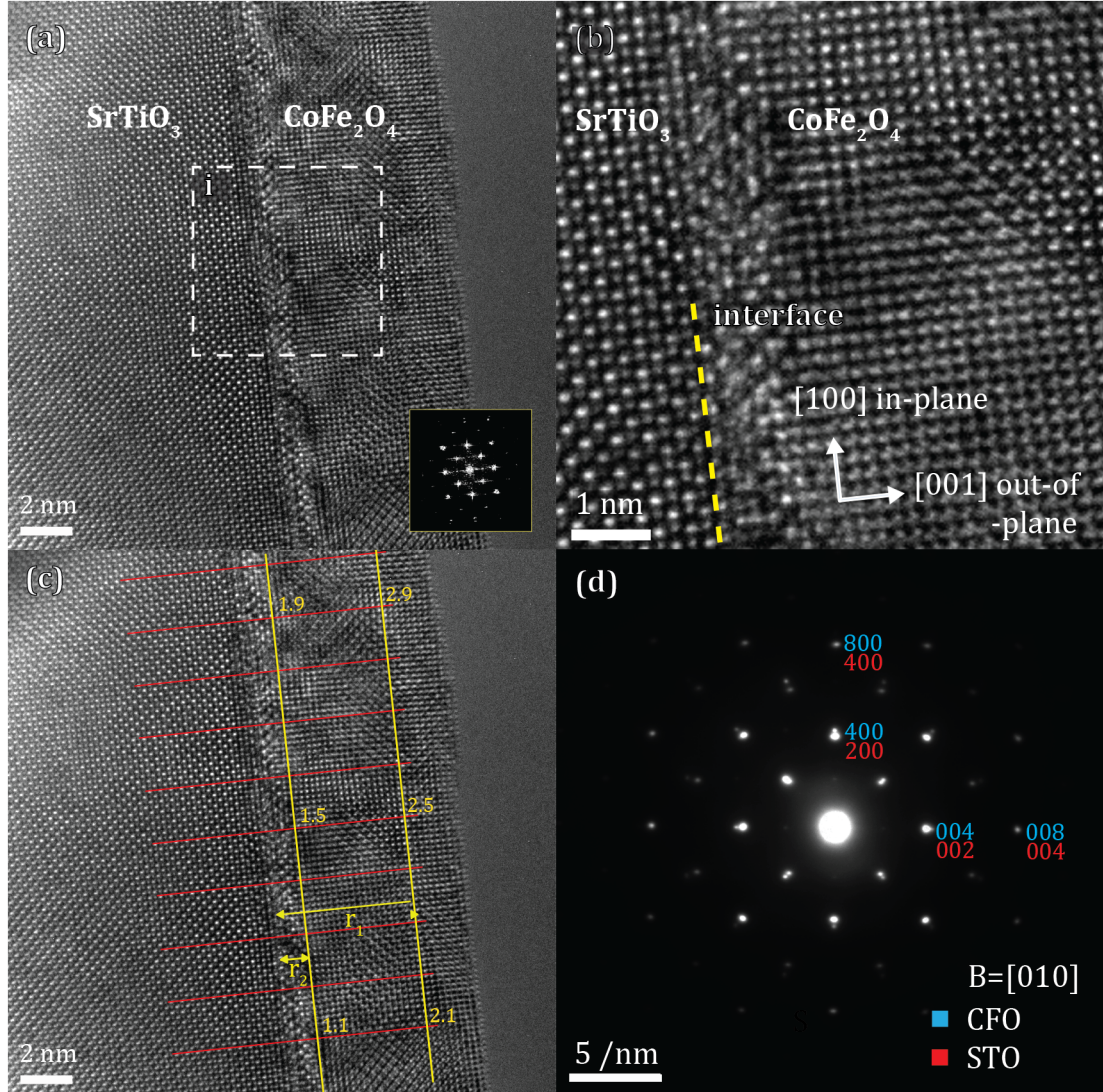


Figure 4.3 – HRTEM images ($C_s = -0.45 \mu\text{m}$, $d = 198 \text{ nm}$) of a 25 nm AD STO/CFO thin film (specimen 2) showing: (a) the sharp substrate/film interface and high crystallinity of substrate and film, (b) Crystallinity in substrate and film with distortion at the interface, and (c) regions of interest along which the in-plane and out of plane lattice parameters were measured. (d) Diffraction pattern acquired from a 200 nm OA STO/CFO thin film clearly showing substrate/film epitaxy.

From figure 4.3a and 4.3d it is clear that CFO films grown on STO are highly crystalline with an overall orientation relationship of in agreement with Axelsson *et al.* [3,32] and the wider literature, of $(001)_{\text{STO}} // (001)_{\text{CFO}}$ [34,35]. It is clear from figure 4.3b that some structural distortion is present in the CFO layer in the near interface region, with approximately 5 $(004)_{\text{CFO}}$ layers disrupted before the CFO is seen to form a coherent structure.

In order to investigate mechanisms for the accommodation of misfit in STO/CFO, the elastic relaxation and relaxation by defect nucleation were quantified. Elastic strain and defect strain (section 4.3.2) were measured over regions of interest at progressively increasing distance from the substrate/interface to correlate changes in the strain relief mechanism with distance from the interface.

Shown in figure 4.3c are example regions of interest over which in-plane (yellow) and out of plane (red) $\langle 400 \rangle$ spacings were measured. In plane measurements were taken at various perpendicular distances defined as r , as shown in figure 4.3 and table 4.2. Regions of interest were marked with overlays of 5 – 10 STO (100) spacings following a numbering system based on the overlay grid as shown in figure 4.2c, to reduce the experimental error. Up to ten CFO (400) spacings were measured at a time using the histogram tool in digital micrograph. The integration width was adjusted over the measured region to maximize the signal to noise ratio. The error (Δc) was taken to be 1 pixel width per peak such that the total error per measurement was

$$\Delta c = \sqrt{\Delta a^2 + \Delta b^2} \quad (4.5)$$

Figure 4.4 shows images illustrating this method. The integration area is shown in figure 4.4a as a dashed rectangle. An example histogram is shown in figure 4.4b.

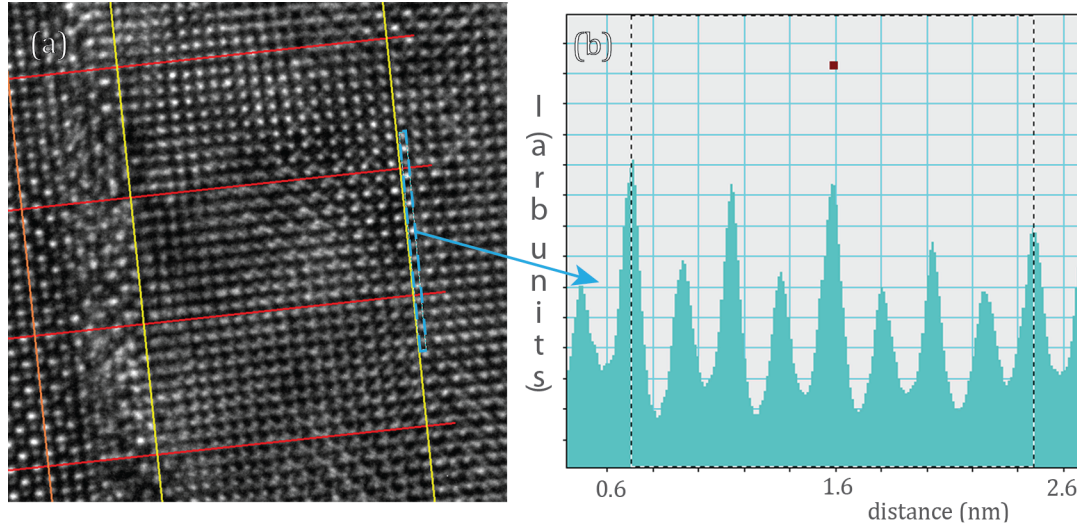


Figure 4.4 – HRTEM image of a 25 nm AD STO/CFO thin film (specimen 2) showing: (a) integration region (blue) and (b) histogram showing the image intensity profile along over the integration clearly showing CFO lattice spacings.

Approximately 90 STO (100) spacings were measured in plane and 60 spacings out of plane for each film, away from the interface. A scaling factor (κ) was calculated based on the ratio between the average measured and bulk STO (100) spacings using equation 4.6. Scaling factors applied were typically $\kappa \sim 0.95$.

$$\kappa = \frac{a_{\text{substrate}}}{a_{\text{bulk}}} \quad (4.6)$$

The substrate was assumed to be strain free; variations in the STO lattice parameter were taken to be a result of magnification calibration errors in the TEM. The scaling factor (k) was used to re-scale all CFO spacing measured before calculating lattice strain ($\epsilon_{\text{lattice}}$) using equation 4.7.

$$\epsilon_{\text{lattice}} = \frac{a_{\text{film}} - a_{\text{bulk}}}{a_{\text{bulk}}} \quad (4.7)$$

Where a_{film} and a_{bulk} are the thin film and bulk CFO <400> spacings respectively.

Compressive and tensile strains are defined by negative and positive values of $\epsilon_{\text{lattice}}$ respectively. Experimental errors were combined using standard error formulae in order to determine the uncertainty in the elastic strains calculated. Results are summarized in table 4.2. X-ray diffraction data acquired by Axelsson *et al.* [32] is shown for comparison.

Table 4.2 – In-plane and out of plane lattice strain calculated for STO/CFO specimens in comparison to x-ray diffraction data previously acquired by Axelsson et al. [32].

Specimen		r (nm)	HRTEM: $\epsilon_{\text{lattice}}$ (%)		XRD: $\epsilon_{\text{lattice}}$ (%)	
Description			In plane	Out of plane	In plane	Out of plane
1	25 nm AD	1	-0.25 ± 0.02	0.60 ± 0.1	-	-0.34 [32]
		6	0.27 ± 0.01	0.75 ± 0.01	-	-0.34 [32]
		10	-0.68 ± 0.01	-	-	-0.34 [32]
2	25 nm AD	1	-0.94 ± 0.02	0.29 ± 0.02	-	-0.34 [32]
		5	-2.54 ± 0.05	-0.09 ± 0.003	-	-0.34 [32]
4	50 nm OA	0	-4.64 ± 0.07	-31.00 ± 3	-0.43 [32]	-0.37 [32]
		6	-1.39 ± 0.02	2.00 ± 0.06	-0.43 [32]	-0.37 [32]
		8	-0.77 ± 0.07	-	-0.43 [32]	-0.37 [32]
5	200 nm OA ³	1	-2.23 ± 0.01	-	-	-
		3	-0.35 ± 0.01	-	-	-
		10	1.08 ± 0.01	-	-	-
6	200 nm OA	1	1.98 ± 0.05	2.84 ± 0.01	-	-
		3	1.73 ± 0.03	3.05 ± 0.01	-	-
		10	0.42 ± 0.01	-	-	-

³ The region of interest investigated for specimen 5 was too small for accurate determination of the out of plane lattice strain. Out of plane data is therefore not shown for specimen 5.

Analysis of HRTEM images has shown that in 25 nm as-deposited films, there is a small compressive in-plane lattice strain at the interface. At a distance of around 5 nm from the substrate interface conflicting results were found, with tensile strain observed in specimen 1 and compressive strain observed in specimen 2. In general, the out of plane strain for as-deposited 25 nm specimens was found to be small and tensile. The magnitude of the in-plane and out of plane lattice strain was small in as-deposited films, accounting for only (3-30)% of the mismatch strain suggesting the misfit is not accommodated elastically in as-deposited STO/CFO.

In contrast to the as-deposited films, a more significant in-plane lattice strain was observed for most of the OA specimens at the interface. In the case of specimen 4, $\epsilon_{\text{lattice}}$ was found to account for 62% of the mismatch strain, suggesting the misfit accommodation in this specimen at the interface was mostly by elastic relaxation. It is also clear from specimen 4 that the magnitude of the $\epsilon_{\text{lattice}}$ in-plane decreases significantly at a distance of 8 nm from the interface to a value of 10% of the lattice mismatch. This suggests that the mechanism for misfit accommodation at the interface in the 50 nm OA is not the same as in the bulk of the film.

A large compressive strain was calculated for specimen 4 at the interface in addition to compressive in plane strain. The Poisson ratio (ν) of a material is defined as the ratio of the transverse strain (ϵ_t) and longitudinal strain (ϵ_l) and is expressed as shown in equation 4.8.

$$\nu = -\frac{\epsilon_t}{\epsilon_l} \quad (4.8)$$

The Poisson ratio can take a value from -1 to 0.5. If ν is positive a material subjected to a transverse, or, axial compression it will extend its dimensions in the longitudinal directions in order to resist a change in volume ^[112]. In the case of (001) STO/CFO, the compressive mismatch strain which is in-plane would

lead to a longitudinal extension out of plane where $\nu > 0$. Valant *et al.* [112] previously report a negative Poisson ratio in OA STO/CFO thin films of thickness 25 – 100 nm of around $\nu = -0.85$. This corresponds to a decrease in all three cubic directions leading to a decrease in the CFO unit cell volume of -1.5%.

HRTEM results shown in table 4.2 suggest a positive ν in as-deposited 25 nm CFO films at the interface. In contrast, a negative ν was observed in the CFO thin film at the interface though ν was seen to be positive in the bulk. While the presence of a negative Poisson ratio in specimen 4 is in agreement with previous reports made by Valant *et al.* [112], the out of plane lattice strain calculated (-30%) would cause a much greater volume decrease than the -1.5%. Given the large strain calculated, it might be possible that a secondary phase may be present at the interface with a different unit cell structure to CFO. This could also be a consequence of the imaging conditions used to acquire this image though this seems more unlikely as this effect was not observed on other regions of the CFO film. However, the out of plane regions of interest over which lattice spacings could be reliably measured were also smaller than in-plane regions so artefacts, if present would have a stronger effect on lattice strains calculated for out-of plane. Further work is needed for an accurate and reliable characterisation of the out of plane strain and further discussions are therefore focused around in-plane results.

As previously discussed in section 1.6.1 Axelsson *et al.* [32] previously determined the microstrain and lattice strain in STO/CFO thin films by applying Scherrer's formula and the Nelson Riley formula respectively, to the (400) and (800) CFO diffraction lines in normal and GID scans.

From table 4.2 it is clear that for all specimens investigated, the lattice strain determined by XRD was compressive and much smaller in magnitude than the lattice mismatch. This clearly indicates that over the total volume of a given specimen, the mismatch is not relieved elastically. Given the small lattice strain calculated by XRD, a significant amount of the mismatch strain is expected to be

accommodated by dislocations which might suggest a value for microstrain much closer to the lattice mismatch in STO/CFO than previously reported [32]. From table 4.3, it is clear that the microstrain is low in all STO/CFO films in comparison to the mismatch, suggesting that over the total volume of the film, mismatch accommodation by dislocation nucleation is also small. It is possible that this disagreement may be a result of the reduced sampling volume available for HRTEM analysis in comparison to XRD. For a 50 nm STO/CFO film the approximate volume sampled by XRD would be $1.25 \times 10^{13} \text{ nm}^3$. Assuming a TEM specimen thickness of 100 nm, the maximum volume sampled in a single HRTEM image would be around $4 \times 10^4 \text{ nm}^3$.

While the lattice parameters and therefore lattice strain can be determined more precisely by XRD over a much larger sampling volume, XRD provides no site specific crystallographic information and the lattice strain and microstrain are average values. If misfit dislocations are localized to a small volume near the substrate/film interface in STO/CFO as HRTEM results show, it is possible that this volume might not represent a significant enough fraction of the total film volume for XRD analysis, which would explain the disagreement between XRD microstrain and HRTEM defect strain.

In a comparison of methods suitable for the determination of particle size in nanocrystalline anatase powders, Weibel *et al.* [113] determined the main error in TEM to be the limited sampling range but in XRD, the main source of error was associated with deconvolving four main sources of peak broadening in x-ray diffraction patterns. Weibel *et al.* [113] report this peak broadening to result from: microstrain (lattice deformation), faulting (extended defects), crystal domain size and distribution. Additional instrumental broadening is also reported. In determining particle sizes by the Scherrer approach Weibel *et al.* [113] state experimental errors of up to 50%. Axelsson *et al.* [32] report a line broadening contribution associated with the out of plane thickness for films of $h < 100 \text{ nm}$ and instrumentation but no contribution from crystal size in plane. No experimental error in the microstrain data determined by Axelsson *et al.* [32] was available for comparison

Lattice strain is typically determined with greater accuracy by XRD than HRTEM. Axelsson *et al.* [32] state an uncertainty in the lattice parameter of $\pm 0.0002 \text{ \AA}$. The uncertainty in the lattice parameter measured by HRTEM varied with the number of spacing measured. For 70 spacings measured in 7 sets of 10 spacings, the uncertainty of the in-plane lattice parameter of specimen 4 was found to be $\pm 0.03 \text{ nm}$. This increased to $\pm 0.08 \text{ nm}$ for 27 out of plane spacings measured in sets of 2-7 spacings.

From table 4.2, it can be seen that in general, there is qualitative agreement in the orders of magnitude of the in-plane lattice strains for 25 nm AD STO/CFO determined by XRD and HRTEM. Agreement was not observed within the stated error bars, possibly a consequence of the reduced sampling volume associated with HRTEM measurements in comparison to XRD. Overall, the results shown in table 4.2 suggest the degree of elastic relaxation at the interface is comparable to elastic relaxation in the bulk of 25 nm as-deposited films. Qualitative agreement between the in-plane lattice strains calculated by XRD and HRTEM was observed for 50 nm OA STO/CFO at a distance 8 nm from the interface. The lattice strain calculated at the interface by HRTEM does not agree with the lattice strain determined by XRD suggesting a change in misfit accommodation occurring in the in first 0-10 nm of the 50 nm OA film.

From table 4.2 it is apparent that tensile strain was observed in places, in particular, for the out of plane direction. This might be explained by the non-uniformity of the microstrain. A consequence of determining lattice strain by measuring interplanar spacings individually in HRTEM is that local variations associated with microstrain would also be measured. This effect would become stronger with reduced sampling volumes, which might explain why out of plane lattice strains determined by HRTEM were found to be tensile in most cases. If the tensile strains are taken as reliable, then these results would suggest a positive Poisson ratio for CFO, contradicting previous reports by Valant *et al.*[112].

4.3.1. Misfit Dislocations

In order to determine the degree of misfit accommodation by dislocation nucleation, (100) STO and (400) CFO planes were counted so that the in plane Burgers vector could be determined for STO/CFO specimens listed in table 4.1.

HRTEM images were split into regions of interest of that were 5 (100) STO planes in length, as shown in figure 4.5. (400) CFO planes were then counted for each marked region as shown in figure 4.5. The total length of a sampled region for a given HRTEM image was typically 15 – 25 nm (40 – 65 STO unit cells) in the in-plane direction.

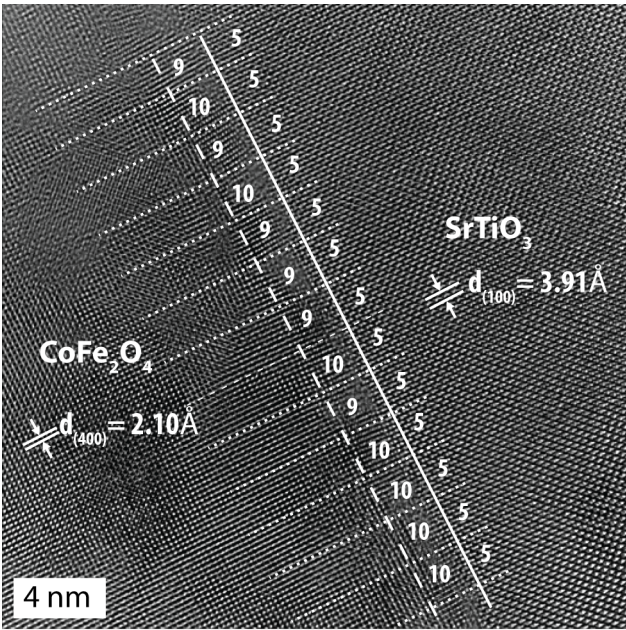


Figure 4.5 – HRTEM image ($C_s = -8.40 \text{ } \mu\text{m}$, $d = 24.07 \text{ nm}$) of 50 nm OA STO showing regions of interest used for plane counting. The numbers of planes are shown in the regions of interest, clearly indicating a number of missing planes as 10 (400) CFO spacings are expected for every 5 (100) STO spacings.

The in-plane Burgers vector was determined from partial Burgers circuits constructed with arbitrarily chosen out-of plane vectors ($\mathbf{m}$), and the number of CFO (n_1) and STO (n_2) planes counted. An illustration of a partial Burgers circuit is shown in figure 4.6. Missing or additional lattice planes in sampled regions as

shown in figure 4.5, were taken to be a result of misfit dislocations of $\mathbf{b} = a_0/4 [100]$ CFO.

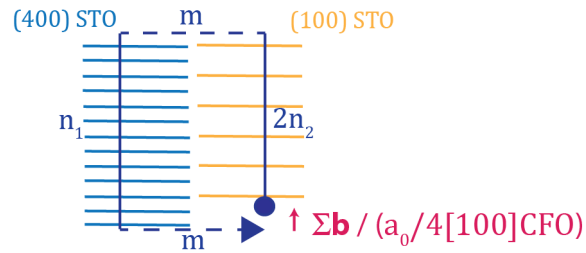


Figure 4.6 – Illustration of partial Burgers circuit showing how the in plane component of the Burgers vector was determined.

Defect strain (ϵ_{defect}) was defined as

$$\epsilon_{\text{defect}} = \frac{n_1 - 2n_2}{2n_2} \quad (4.9)$$

The defect strain and normalized Burgers vector were calculated over regions of interest at increasing distance from the substrate/film interface in order to determine the degree of misfit accommodation by dislocation nucleation at the STO/CFO and bulk of the STO/CFO thin films. Burgers vectors and defect strains calculated for the STO/CFO specimens listed in table 4.1 are summarized in table 4.4.

Table 4.3 – Normalised Burgers vectors and defect strain for as-deposited and oxygen post annealed SrTiO₃/CoFe₂O₄ thin films. The expected Burgers vector is the product of 1/s and n₂. The measured Burgers vector is as measured from a partial Burgers circuit; defect strain is as calculated by equation 4.9.

Specimen		r (nm)	b (normalised)	HRTEM: ϵ_{defect} (%)	XRD: ϵ_{micro} ⁴ (%)
<i>description</i>					
1	25 nm AD	1	1.13	-8.18	0.24 ^[32]
		6	1.06	-7.78	0.24 ^[32]
		10	0.88	-7.27	0.21 ^[32]
2	25 nm AD	1	0.98	-7.14	0.24 ^[32]
		5	0.76	-5.56	0.24 ^[32]
4	50 nm OA	0	0.33	-1.28	0.25 ^[32]
		6	1.67	-6.41	0.25 ^[32]
		8	1.00	-5.17	0.25 ^[32]
5	200 nm OA	1	0.69	-5.00	-
6	200 nm OA	1	1.02	-7.50	-
		3	0.91	-6.67	-

For the AD 25 nm STO/CFO film, the normalized Burgers vectors at the interface was close to 1, suggesting all of the mismatch strain was accommodated by misfit dislocations, which is supported by the values defect strain which were found to be close to the mismatch strain.

⁴ As microstrain was determined from line broadening using Scherrer's formula, microstrain values must always be positive. Positive values of microstrain do not necessarily correspond to tensile strain.

The normalised Burgers vector and defect strain calculated for a 50 nm OA STO/CFO were low at the substrate/interface but were found to increase in magnitude with distance from the substrate/film interface. The defect strain reached a value close to that expected from the lattice mismatch ~ 6 nm from the substrate film interface. Trends in the variation of defect strain with distance from the substrate/film interface were not identified for 200 nm films, as areas sampled far from the interface were unsuitable for accurate determination of defect strain.

The defect strain at the interface in 200 nm OA films was found to be similar to the mismatch strain suggesting an increased relaxation by dislocation formation as the film thickness of OA films is increased. Sampling regions were typically smaller for 200 nm specimens so further work would be needed to draw a firm conclusion in regard to variation with film thickness.

For all STO/CFO specimens analysed, the defect strain determined by HRTEM was in disagreement with microstrain results calculated from XRD results. Misfit dislocations were only identified in the near interface region of STO/CFO specimens (section 4.4). As the microstrain is an average of the non-uniform strain present in the sample, it is likely a significant microstrain would only be observed if the defects responsible for the peak broadening were distributed isotropically throughout the volume of a given CFO thin films. If misfit dislocations are present in the first 5 nm of a film only, the film volume containing the dislocations would only be 25% - 2.5% of the total film volume for films in thickness range 25 – 200 nm respectively. XRD is reportedly only sensitive for 5% which could explain the low microstrain calculated by Axelsson *et al* [32]. The disagreement between the calculated microstrain and defect strain supports the hypothesis that misfit dislocations are present in the near interface region of STO/CFO specimens only.

Misfit dislocations were observed directly in both 50 nm and 200 nm OA STO/CFO. Shown in figure 4.7 are HRTEM images that were acquired from specimen 4 and specimen 5, which are OA STO/CFO thin films of thickness

50 nm and 200 nm respectively. Dislocations are highlighted in figure 4.7a and figure 4.7c by dashed boxes. Burgers circuits are shown in figures 4.7b and 4.7d.

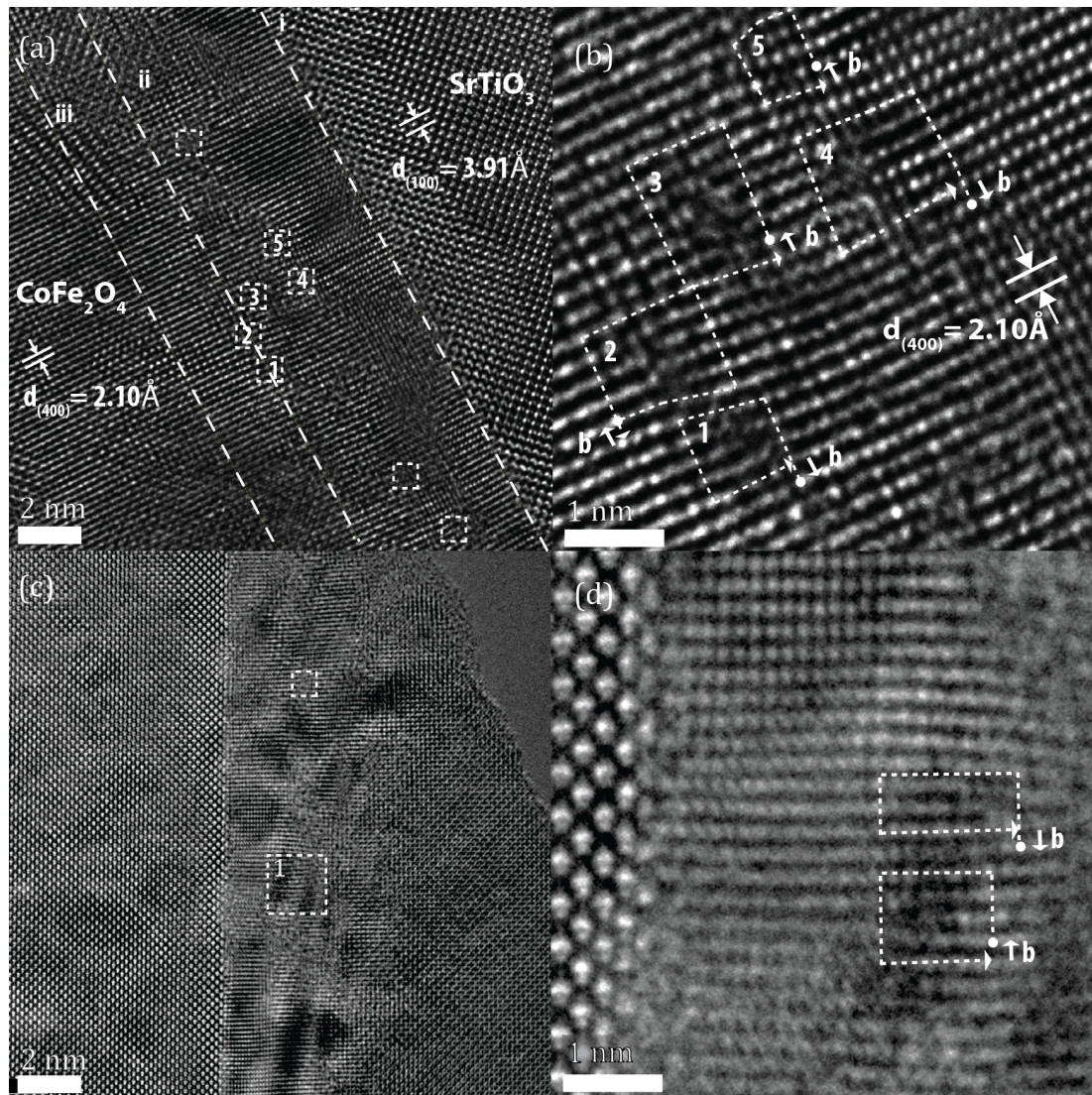


Figure 4.7 – HRTEM images ($C_s = -8.40 \mu\text{m}$, $d = 24.07 \text{ nm}$) of specimen 4, a 50 nm OA STO/CFO thin film showing: (a) misfit dislocations in a band $\sim 3 \text{ nm}$ from the film/substrate interface and (b) Burgers circuits showing selected dislocations. Equivalent HRTEM images ($C_s = -1.28 \mu\text{m}$, $d = 184 \text{ nm}$) of specimen 5, a 200 nm OA STO/CFO film are shown in (c) and (d). Inset (1) in image (c) corresponds to the misfit dislocation region shown in (d).

It is apparent from figure 4.7a and 4.7c that the misfit dislocations are found in a band standing off approximately 3 nm from the substrate/film interface. This is

in agreement with results shown in tables 4.2 and 4.3 that suggest a change in misfit accommodation mechanism in the bulk of an OA CFO film compared to the interfacial region. Misfit dislocations were not directly imaged for AD films.

From figure 4.7b and figure 4.7d it is clear that the Burgers vector of the dislocations visible in these images is $\mathbf{b} = a_0/4[100]$ CFO. The Burgers vector was found to be parallel to the substrate/film interface, in agreement with Sieber and Hess ^[43] who previously identified misfit dislocation in topotaxial films grown on substrates of high lattice mismatch. The sum of the Burgers vectors for the region shown for specimen 5 was found to be zero. For specimen 5 the dislocations identified cannot satisfy the lattice mismatch. For the region shown for specimen 4 in figure 4.7b, the sum of the Burgers vectors was found to be 0.42 nm. This corresponds to two misfit dislocations, which is close to the number expected for the region shown (2.4 dislocations).

4.3.1. Total Strain

Shown in table 4.5 are the in-plane lattice strains, defect strains, and total strains as determined by HRTEM. ϵ_{total} is given by $\epsilon_{\text{lattice}} + \epsilon_{\text{defect}}$.

Table 4.4 – Summary of elastic and defect strain results for SrTiO₃/CoFe₂O₄ thin films.

Specimen		r (nm)	HRTEM: $\epsilon_{\text{lattice}}$ (%)	HRTEM: ϵ_{defect} (%)	ϵ_{total} (%)
<i>Description</i>					
1	25 nm AD	1	-0.25 ± 0.02	-8.18	-8.44 ± 0.02
		6	0.27 ± 0.01	-7.78	-7.51 ± 0.01
		10	-0.68 ± 0.01	-7.27	-7.95 ± 0.01
2	25 nm AD	1	-0.94 ± 0.02	-7.14	-8.08 ± 0.2
		5	-2.54 ± 0.05	-5.56	-8.10 ± 0.2
4	50 nm OA	0	-4.64 ± 0.07	-1.28	-5.92 ± 0.05
		6	-1.39 ± 0.02	-6.41	-7.80 ± 0.03
		8	-0.77 ± 0.07	-5.17	-5.94 ± 0.01
5	200 nm OA	1	-2.23 ± 0.01	-5.00	-7.23 ± 0.01
			-0.35 ± 0.01		
			1.08 ± 0.01		
6	200 nm OA	1	1.98 ± 0.05	-7.50	-5.52 ± 0.05
		3	1.73 ± 0.03	-6.67	-4.94 ± 0.03
			0.42 ± 0.01	-5.00	-4.58 ± 0.01

From table 4.5, it is clear that for 25 nm as-deposited films the majority of the misfit strain is accommodated by misfit dislocation nucleation at the substrate film/interface.

For oxygen post-annealed films, it is clear that the misfit is accommodated elastically and by misfit dislocation nucleation. In the case of the 50 nm OA film it is clear that at the interface the majority of the misfit is accommodated elastically but at a distance of 6-8 nm from the interface the lattice strain decreases and the majority of the misfit is accommodated by misfit dislocation nucleation. The total strain was found to be close to the mismatch strain for all regions analysed.

4.4 Conclusion

Misfit dislocations were identified in AD and OA STO/CFO films of thickness 25 - 200 nm by HRTEM imaging. Misfit dislocations were not imaged directly in as-deposited films but were successfully imaged in 50 nm and 200 nm OA films, where misfit dislocations were found to have a Burgers vector of $\mathbf{b} = a_0/4[100]$.

In 50 nm and 200 nm OA STO/CFO, misfit dislocations were found to stand off approximately 3 nm from the substrate/film interface. In the 50 nm OA film, the normalized sum of the Burgers vectors for the region of interest analysed was found to be $0.83\mathbf{b}$, suggesting the majority of the mismatch strain in 50 nm OA/STO was accommodated by misfit dislocation formation. However, for the 200 nm OA film, the normalized sum of the Burgers vectors for the region analysed was found to be zero.

Lattice and defect strain were quantified in the AD and OA STO/CFO films by measuring lattice spacings directly and constructing partial Burgers circuits respectively. For 25 nm AD STO/CFO specimens, small compressive lattice strains were identified that qualitatively agreed with lattice strains determined by XRD by Axelsson *et al.*^[32]. The defect strain was found to be in close agreement with the lattice mismatch. In comparison to OA films, little variation in the lattice and defect strains determined by HRTEM was observed with distance from the interface, suggesting that the mismatch accommodation in as-deposited 25 nm was mostly misfit dislocation formation. Disagreements between defect strain determined from HRTEM and microstrain determined by XRD suggested the mismatch strain was accommodated by dislocations at the interface and not distributed isotropically in the 25 nm AD STO/CFO films.

Results showed that the misfit strain in OA STO/CFO was accommodated by a combination of elastic relaxation and misfit dislocation formation. In the case of a 50 nm OA STO/CFO film, a semi-coherent layer approximately 3 nm thick was observed at the interface in which 62% of the lattice mismatch was accommodated elastically. As the distance to the interface (r) increased, the

defect strain was found to increase as the lattice strain decreased. At a distance of 8 nm from the interface, the lattice strain measured by HRTEM agreed qualitatively with the lattice strain determined by XRD [32]. The defect strain was in close agreement with the mismatch strain indicating relaxation by dislocation formation after the coherent layer at the interface. Results showed that for both AD and OA STO/CFO films, the sum of the lattice strain and defect strain determined by HRTEM was in reasonable agreement with the mismatch strain.

Chapter 5 – Core Loss Electron Energy-Loss Spectroscopy of Iron and Cobalt Oxide Powders

5.1 Introduction

A method to determine the spinel degree of inversion (λ) by STEM-EELS is desirable for analysis of STO/CFO thin films as λ is known to vary with the spinel growth conditions (chapter 1). A method enabling λ to be determined by STEM-EELS would enable variations in λ in CFO thin films to be identified at nanoscale spatial resolution.

The fine structure of a core loss edge in the electron energy loss spectrum is dependent on the coordination environment of the atom undergoing excitation as well as atom type and valence, allowing atomic species to be identified from their characteristic “fingerprint” in the spectrum [56,114]. Krivanek and Paterson previously identified fine structural features in the iron $L_{2,3}$ -spectra of iron oxides that were directly attributed to the valence states and coordination environment of iron in a systematic study of binary iron oxides [61,62]. Similar trends were identified for the fine structure of oxygen K-spectra in iron oxides by Colliex *et al.*, and for cobalt-L spectra by Bazin *et al.*[115,116].

With suitable standards, λ may be calculated by multiple linear least squares (MLLS) fitting to EELS spectra acquired from CFO. Standards are required for $Fe^{3+} T_d$, $Fe^{3+} O_h$, $Co^{2+} T_d$ and $Co^{2+} O_h$. EELS spectra were acquired from commercially available iron and cobalt oxide powders in addition to a powder prepared using a sol-gel technique. In order to aid the interpretation of oxygen K-spectra, model spectra were calculated using the full multiple scattering code FEFF 8. A method to determine λ from metal $L_{2,3}$ -spectra was developed and tested using cobalt and iron $L_{2,3}$ -spectra acquired from CFO powder by Docherty [15].

5.2 Monochromated STEM-EELS

A list of oxides that were used as standards is given in table 5.1. ZnCo_2O_4 powder was prepared using the sol-gel synthesis technique previously reported by Wei *et al.* [117]. All other powders were commercially available (Sigma Aldrich, UK). Phase purity was confirmed by X-Ray powder diffraction.

Table 5.1 – List of the transition metal valence and coordination in the transition metal oxides analysed.

Cation	Coordination	Oxide
Fe^{2+}	O_h	FeO^5
Fe^{3+}	O_h	$\alpha\text{-Fe}_2\text{O}_3$
Fe^{2+}	O_h	Fe_3O_4
Fe^{3+}	T_d	Fe_3O_4
Co^{2+}	O_h	CoO
Co^{3+}	O_h	ZnCo_2O_4
Co^{2+}	T_d	Co_3O_4
Co^{3+}	O_h	Co_3O_4

In order to prepare TEM specimens from a powder sample, small quantities of powder were placed on folded filter paper (Whatman, UK) using a stainless steel spatula. The fold was closed over the powder, which was then ground in the paper using an Agate pestle. [118] The conventional technique to prepare a powder specimen is to grind in an Agate pestle and mortar. Trace amounts of

⁵ FeO is unstable and typically oxygen deficient (Fe_{1-x}O) [118].

iron were present in the filter paper (5 μ g/g). It was felt that the risk of contamination from oxide residue in the mortar was greater than that posed by the trace iron content of the filter paper.

After grinding, small quantities of the powders were suspended in isopropanol and dispersed using an ultrasonic bath. TEM specimens were prepared by dropping small volumes of isopropanol/oxide suspension onto holey carbon films (Agar, UK) using a pipette.

EELS spectra were acquired using an FEI Titan in filtered mode at an acceleration voltage of 300 kV. A decelerating gun lens was used at potential 3000 V and typical excitation 2.0 – 2.2. Imaging and analysis was performed at typical probe size of 0.48 nm and convergence and collection semi angles $\alpha = 5.4$ mrad and $\beta = 8.8$ mrad. Spectra were recorded at a dispersion of 0.05 eV per channel and acquisition time 60 s -120 s. The energy resolution under these conditions was typically 0.2 – 0.3 eV.

EELS spectra were acquired as spectrum images using the Digiscan tool in digital micrograph (Gatan, UK). A spectrum image (SI) is a three dimensional data set containing both spatial (x, y) and energy loss (dE) information. In order to acquire a SI, a STEM image must be acquired with the ADF or HAADF detector. An SI region is then defined that is divided into a user-defined number of pixels. Care must be taken to ensure the pixel size is not smaller than the probe size. A spatial drift region may also be defined before spectrum image acquisition. After defining the EELS acquisition time per pixel, the SI is acquired. Spectrum imaging is typically carried out remotely, giving the advantage of increased environmental stability during acquisition. An illustration of spectrum imaging showing the three dimensional (x,y, dE) data set is shown in figure 5.1.

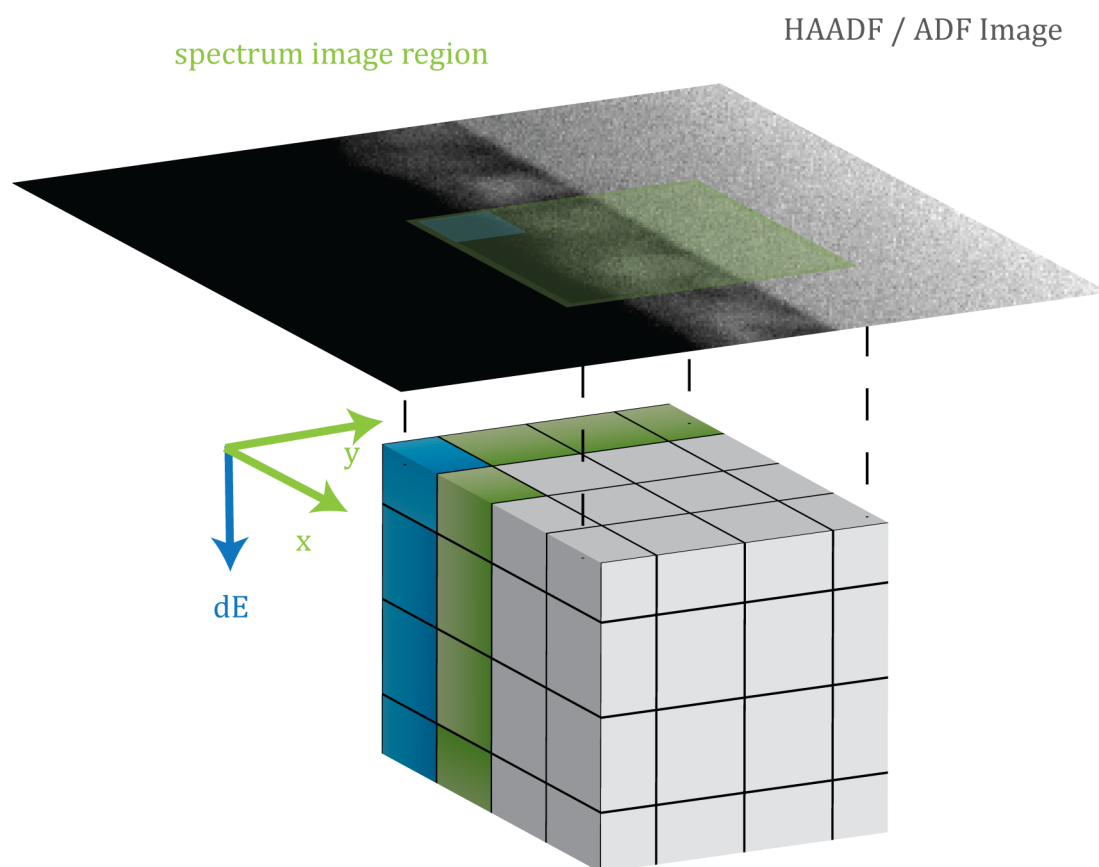


Figure 5.1 – Illustration of spectrum imaging showing the HAADF/ADF survey image, the spectrum image region and the data cube containing positional and energy loss information.

SI survey regions were typically chosen where the TEM specimen thickness was $0.3 < t/\lambda < 0.5$. Spatial drift regions were defined over features that were distinct in both the x and y directions. An example spectrum image of a CoO specimen is figure 5.2. The spectrum image and spatial drift regions are shown in figure 5.2a. Figure 5.2b shows unprocessed cobalt $L_{2,3}$ -spectra along the spectrum image region.

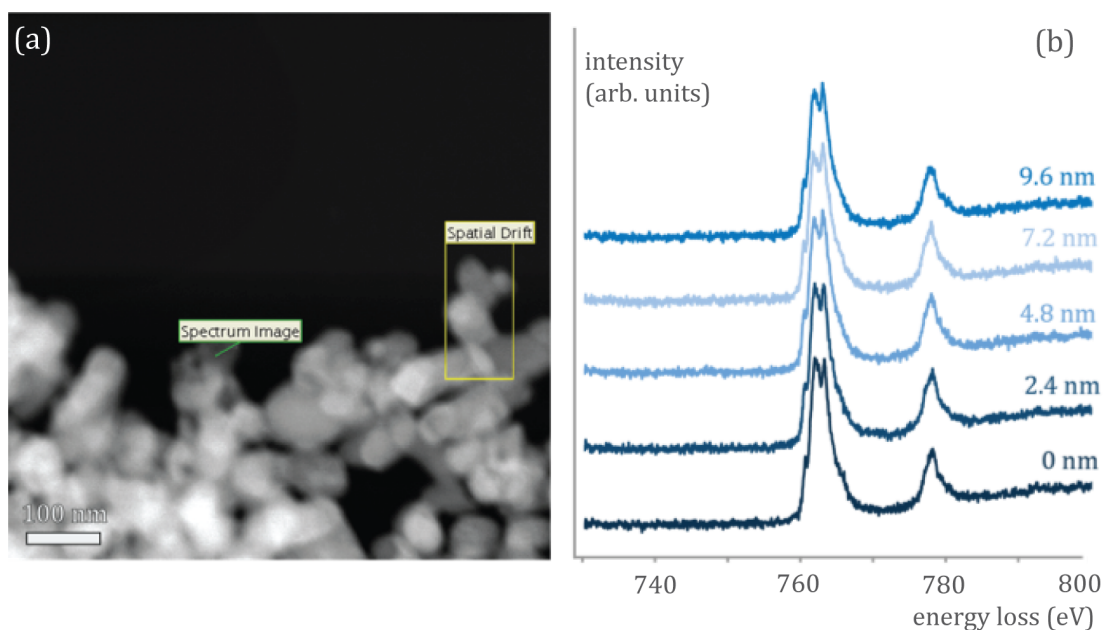


Figure 5.2 – Spectrum image acquired from CoO powder. (a) ADF image showing the spectrum image and spatial drift regions. (b) Unprocessed cobalt $L_{2,3}$ -spectra acquired at different pixels along the spectrum image region.

Spectrum images were acquired from the oxides listed in table 5.1 for use as Fe^{2+} , Fe^{3+} , Co^{2+} , Co^{3+} , O_h and T_d standards. In order to determine good standards from raw spectrum images, a number of processing steps were required. The component spectra of a raw spectrum image were aligned using the align peak function in the spectrum imaging tool set in Digital Micrograph, which performs a cross correlation alignment of EELS spectra over a user defined energy window [119]. The peak alignment window was defined across the metal L_3 -line for metal $L_{2,3}$ -spectra and the oxygen K-peak at 532 eV for oxygen K-spectra. These spectral features are explained in sections 5.5. An example alignment window for a cobalt $L_{2,3}$ -spectrum acquired from CoO is shown in figure 5.3a.

Following peak alignment, background subtraction was performed using an inverse power law model (chapter 2), fit over an energy window of width 20 - 30 eV preceding the onset of the target core loss edge. An example background subtraction window for the cobalt-L spectrum of CoO is shown in figure 5.3b.

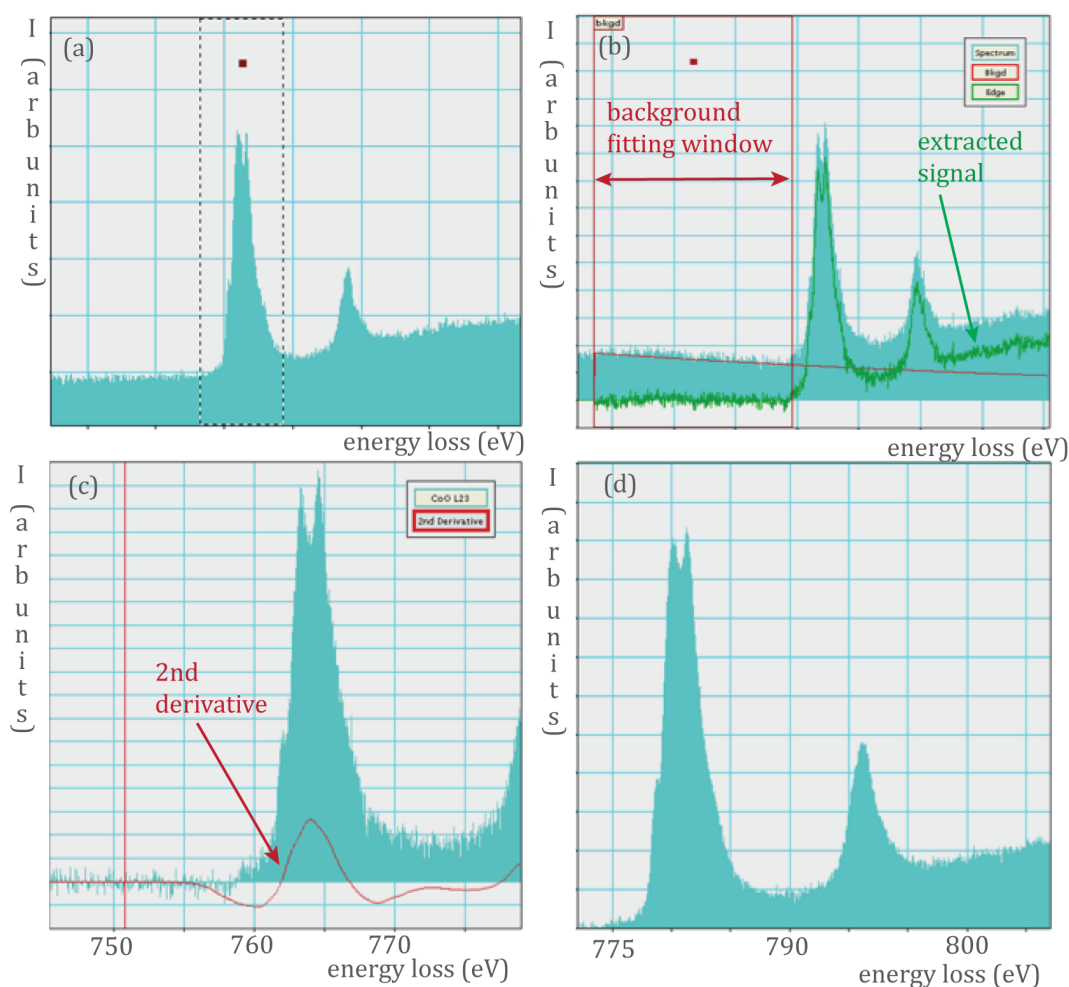


Figure 5.3 – Spectrum image processing steps for a cobalt $L_{2,3}$ -spectrum image acquired from CoO. (a) Peak alignment window, (b) background subtraction shown in red and signal extraction shown in green, (c) onset calibration as the 1st inflection point of the 1st derivative of the spectrum, (d) sum of processed spectra.

The edge onset was defined as the first inflection point of the 1st derivative of the transition metal L_3 line or the O K-peak. A cobalt $L_{2,3}$ -spectrum for CoO and the 2nd derivative are shown in figure 5.3c. Low loss spectrum images were typically acquired immediately before a given core-loss SI in order to determine the relative specimen thickness. Energy scale calibration was based on the drift tube voltage and absolute energy of the zero-loss peak in the low loss spectrum. EELS standards were then created by summing component spectra from a particular SI. 5 – 10 spectra were typically summed per SI. An example standard Co $L_{2,3}$ -spectrum for CoO formed is shown in figure 5.3d.

5.3 Electronic Structure and Bonding in the Transition Metal Oxides

The general electronic structure of elements in the transition row of the periodic table is $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^n$. As all atomic orbitals are filled other than the 3d orbital, the electronic properties of the transition metals are determined by 3d-electron chemistry.

d-orbitals have a degeneracy of 5 and consist of five suborbitals. Three of the five d-orbitals lie between the major cubic coordinate axes (d_{xy} , d_{yz} , d_{zx}) and two lie along major coordinate axes ($d_{x^2-y^2}$, d_{z^2}) [118]. Plots of the spatial distribution of electron density for the five 3d-orbitals are shown in figure 5.4.

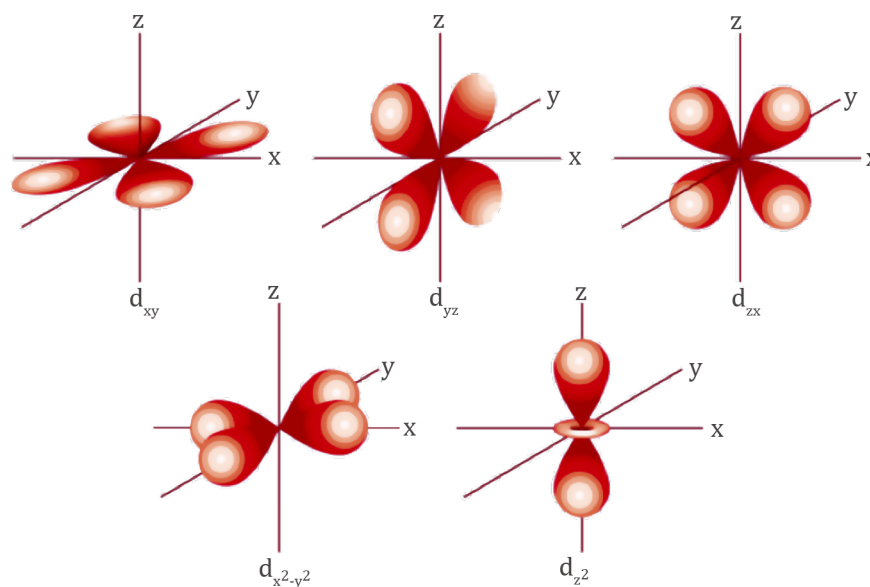


Figure 5.4 – Spatial distribution of electron density for the 3d atomic orbitals. Reprinted by permission from Macmillan Publishers Ltd [120] copyright (1999).

In the transition metal oxides the transition metal cations are surrounded by oxygen anions. The electronic configuration of oxygen is $1s^2 2s^2 2p^4$. The oxygen-2p state which is 3-fold degenerate has orbitals lying along the three major

coordinate axes. The axial d-orbitals of metal cations in octahedral coordination lie in close proximity to surrounding oxygen-2p orbitals. This causes the $d_{x^2-y^2}$ and d_{z^2} to increase in energy relative to the d_{xy} , d_{yz} , d_{zx} orbitals. For metal centres in tetrahedral coordination, the non-axial d-orbitals lie close to the oxygen-2p orbitals so the $d_{x^2-y^2}$ orbitals increase in energy relative to the d_{xy} , d_{yz} , d_{zx} orbitals. This splitting is known as crystal field splitting as illustrated in figure 5.6.

The crystal field splitting energy Δ depends on the type of anion responsible for the crystal field as well as the anion-cation separation. The electrostatic repulsion between cation d-orbitals and anion 2p-orbitals is stronger for highly electronegative anions, increasing Δ . An example two energy level system is shown in figure 5.5.

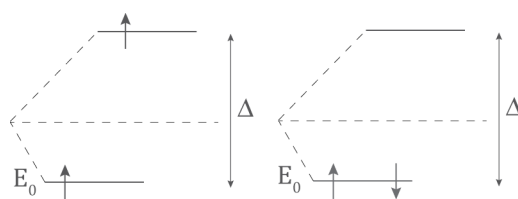


Figure 5.5 – Two energy level system populated with two electrons ^[121]

If one electron is placed in each energy level then the total energy (E) is given by,

$$E = E_0 + (E_0 + \Delta) \quad (5.1)$$

If two electrons are placed in the same energy level then the total energy must also include a pairing energy (P) associated with placing two electrons in the same orbital.

$$E = 2E_0 + P \quad (5.2)$$

It is clear from equations 5.1 and 5.2 that the lowest energy configuration is defined by the pairing energy and crystal field splitting energy such that if $\Delta < P$,

the electrons occupy separate levels and if $\Delta > P$ the electrons occupy the same level. As a result, d^4 , d^5 and d^6 and d^7 cations can form low spin or high spin complexes depending on the relative strength of the pairing and crystal field splitting energies [121]. The high spin and low spin electron configurations for a d^5 cation in O_h and T_d crystal fields are shown in figure 5.6.

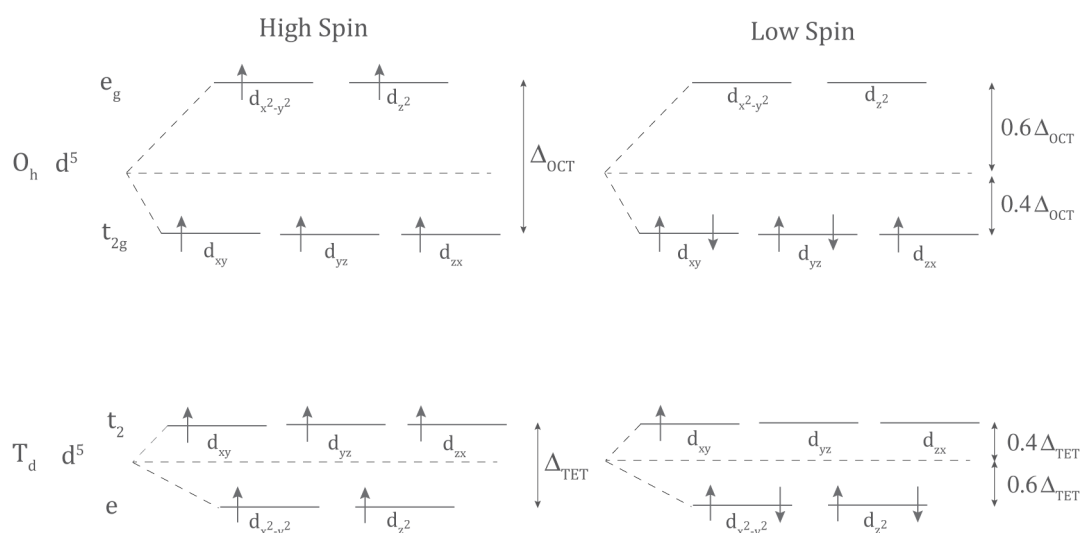


Figure 5.6 – Electron configurations for a d^5 cation in octahedral and tetrahedral crystal fields. Both high spin and low spin configurations are shown.

In a solid, atoms are in close proximity and the atomic orbitals of neighbouring atoms overlap. The electronic structure can be described in terms of molecular orbitals (MO) that are formed from a linear combination of atomic orbitals (LCAO) [118]. The spatial distribution of the electron density of the overlapping atomic orbitals is modified due to interference between the two wavefunctions. A molecular orbital is known as a bonding orbital if the electron density is maximised between the atom centres or an antibonding orbital if the electron density is minimised between the atom centres.

Molecular orbital assignments for TiO_2 were previously determined empirically by Grunes *et al.* [122]. The molecular orbital diagram for TiO_2 is shown in figure

5.6. To first approximation, the molecular orbital assignments give a good representation of the molecular orbital structure of the binary transition metal oxides of octahedral symmetry under investigation. From figure 5.7 it is clear that the molecular orbitals near the Fermi energy originate from interactions between metal 3d, 4s and 4p states, and oxygen 2p π and 2p σ orbitals.

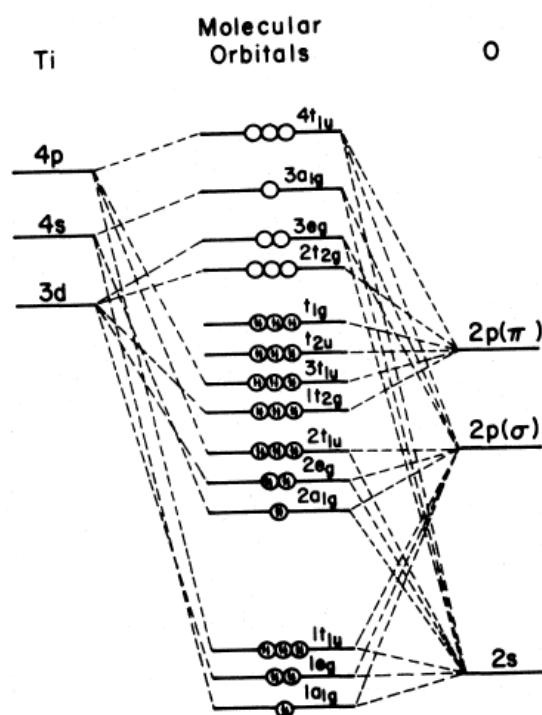


Figure 5.7 – Molecular orbital diagram for TiO₂. Unoccupied and occupied states are shown as empty and filled circles respectively ^[122].

5.4 Fine Structure Modelling by Full Multiple Scattering

5.4.1. Introduction

Electron solid interactions may be described by a many body Schrodinger equation in which the Hamiltonian is defined in terms of the electrons and nuclei of the solid ^[123,124]. The many body Schrodinger equation cannot be solved analytically and must be solved numerically ^[123].

A photoelectron ejected from an atomic absorption centre propagates outwards from the atomic site as a spherical wave ^[124]. The outgoing electron wave interacts with surrounding atoms and scattered electron waves interact with the primary photoelectron wave causing an interference pattern that is responsible for the near edge fine structure of a core loss edge in the energy loss spectrum ^[15,123-125].

In multiple scattering theory, the independent electron approximation is made so that the many body Schrodinger equation is reduced to a one body potential problem. This assumption is made in order to reduce the solution to a one-particle Greens function (G) ^[124]. A solid is spatially divided into shells around a common point of origin. Within a shell, scattering to all orders is defined in terms of a scattering matrix and solutions for individual shells are combined to give the total Green's function ^[123]. The Greens function describes the propagation of an electron wave from point r to r' and is given by

$$G(r, r', E) = \sum_n \frac{\psi_n(r) \psi_n^*(r')}{E + i0 - E_n} \quad (5.3)$$

where i0 is a constant included so that the denominator is non-zero for $E = E_n$.

The Greens function is linearly proportional to the electron density and may be expressed as a sum of all closed multiple scattering paths (Γ). The fine structure function is given by

$$\chi = \sum_{\Gamma} \text{Im} \left\langle e^{2i\phi_l} \sum_m \left\langle \text{Im} \left| G t_n \dots G t_2 G t_1 G \right| \text{Im} \right\rangle \right\rangle \quad (5.4)$$

where t_i is the scattering matrix for site i and ϕ_l is the partial wave phase shift at the absorber ^[126].

The real space Green's function (RSGF) is directly equivalent to the the Koringa-Kohn-Rostocker (KKR) method for determination of bandstructure ^[125]. The RSGF approach is argued to be a less precise but does not have symmetry constraints allowing non-periodic structures can be modelled ^[125].

5.4.1. Multiple Scattering Calculations in FEFF 8

FEFF 8 is a self-consistent full multiple-scattering code capable of calculating X-Ray absorption spectroscopy (XAS) spectra and the symmetry and site projected densities of states ^[127]. XAS spectra calculated using FEFF 8 can be used to aid the interpretation of core loss EELS spectra due to similarities in the X-Ray absorption and electron energy-loss scattering cross sections for high angle low energy scattering. Good agreement between model XAS spectra and EELS spectra was previously observed for spinel structured materials by Eustace ^[128], and for polyaromatic hydrocarbons by Husain ^[65].

FEFF version 8.2 has been used for all multiple scattering calculations in this thesis and for ease of discussion is referred to as FEFF 8. All calculations were carried out with the inclusion of a core hole.

Before performing a multiple scattering calculation using FEFF 8 it is necessary to generate a FEFF input file. FEFF input files were generated using ATOMS 2.50 written by Bruce Ravel. ATOMS generates the FEFF input file from an ATOMS input file in which the structural parameters for the material of interest are defined.

Within the ATOMS input file, the unit cell parameters and edge type are defined. It is possible to prompt ATOMS to generate a P1 file. The P1 is a secondary ATOMS input file in which the atomic positions are defined individually within a generic space group. P1 type input files were used for all oxides of spinel structure.

ATOMS is then used to generate the FEFF input file which consists of a file header containing a number of simulation parameters, followed by a list of atomic positions for atoms in a radial cluster centering on an absorber of a type defined in the ATOMS or P1 file. A number of control cards can be included or excluded from the header section of the FEFF input file. These control cards modify calculation parameters and dictate the data sets generated, for example, XAS spectra or the DOS.

The first stage in a FEFF calculation is the determination of a self consistent set of free atomic potentials using a relativistic Dirac-Fock method ^[127]. A Hedin-Lundqvist self energy term is included to account for the effect of the core hole in the final excited state ^[127]. Scattering potentials are then generated by overlapping the free atom potentials and placing any excess charge in a flat interstitial potential between the spheres. This is referred to as a muffin tin potential ^[124].

Following calculation of the scattering potentials, the electron scattering amplitude and phase are calculated for all atoms in the cluster, which are used to calculate full multiple scattering fine structure functions (equation 5.4) ^[124]. Atomic potentials are recalculated iteratively until the fine structure functions converge ^[124,125]. The scattering potentials, fermi energy (E_f) and charge transfer

are calculated self consistently which improves accuracy in the calculation of near edge fine structure ^[125].

A relatively small cluster size is needed for convergence of the scattering potentials (SCF radius). A larger cluster size is needed to calculate the multiple scattering paths (FMS radius) as the cluster must be sufficiently large to include all the scattering paths responsible for features in the ELNES. In order to determine whether a calculation has converged, calculations are performed at different FMS radii and the calculated spectra compared ^[125].

It is conventional to determine the SCF convergence radius before the FMS convergence radius. Shown in figure 5.8 are oxygen K-spectra calculated to identify SCF and FMS convergence radii for a calculation for Fe₃O₄.

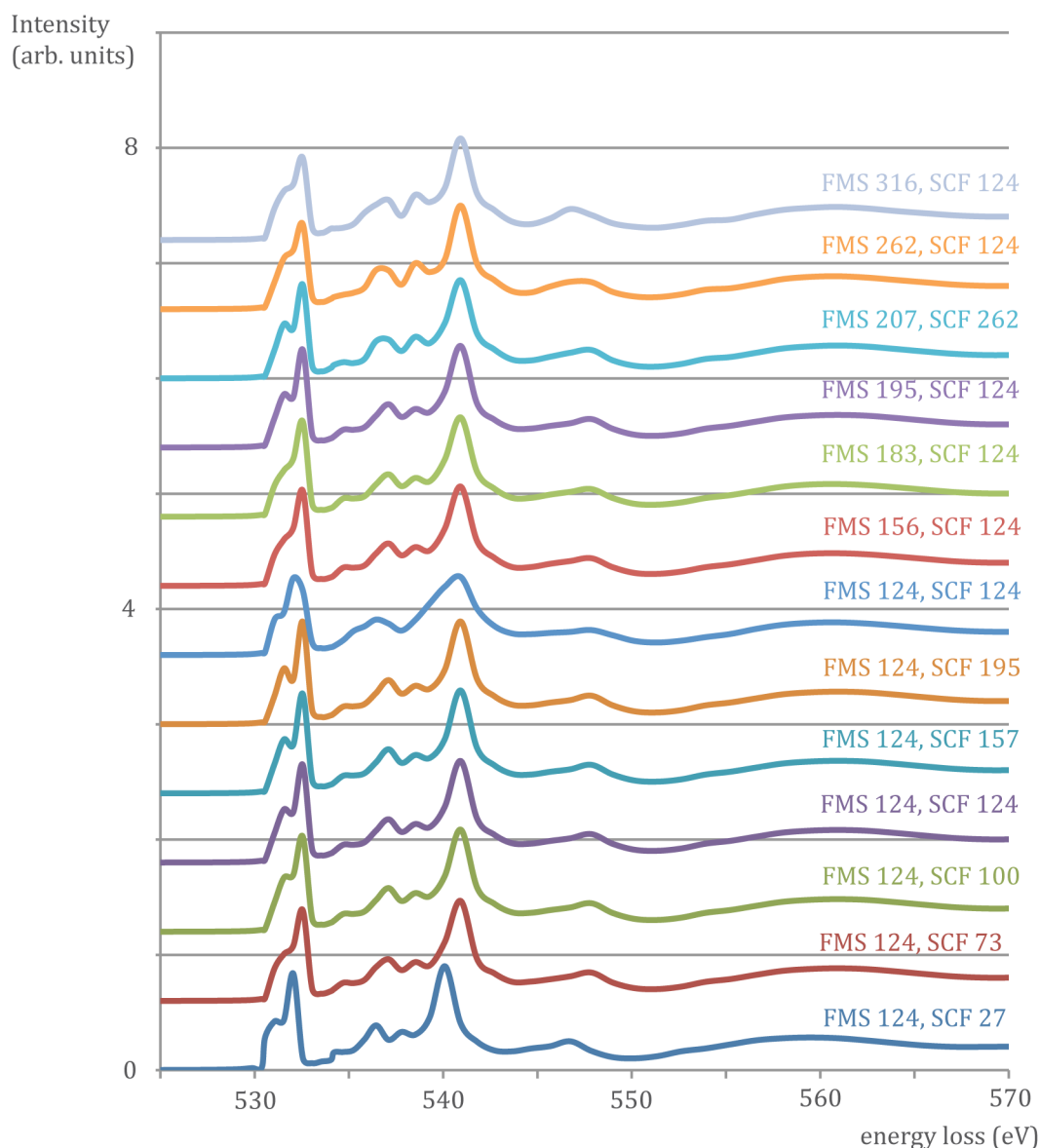


Figure 5.8 – FMS and SCF convergence parameters for calculation of the oxygen *K*-spectra for Fe_3O_4 .

To determine the SCF convergence radius, the SCF cluster size was increased from 27 atoms to 124 atoms (radius = 4.09 Å – 7.78 Å) while maintaining a fixed FMS cluster size of 124 atoms (radius = 6.63 Å). To determine the FMS convergence radius, the FMS cluster size was increased from 124 atoms to 316 atoms (radius = 6.63 Å – 9.19 Å) while maintaining a fixed FMS cluster size of 124 atoms. Cluster size was increased in both the SCF and FMS convergence investigations, in complete coordination shells.

Results shown in figures 5.8 show that for an SCF cluster size ≥ 27 atoms, the fine structure in the energy loss range 535 eV – 550 eV is well converged. A loss in fine structure was observed when the SCF radius was equal to the FMS radius, though the fine structure became apparent as the FMS radius was increased. It is apparent from figure 5.8 that for all FMS cluster sizes ≥ 124 atoms, the fine structure in the energy loss range 535 eV – 550 eV is also well converged. Convergence of the fine structure in the energy range 530 eV – 535 eV was not observed, possibly due to an error in the placement of the Fermi energy in the FEFF calculation.

As FEFF 8 calculates the scattering potentials from free atom potentials, the Fermi energy is typically calculated incorrectly, with an error of up to 1 eV for self-consistent potentials [127]. As the metal-3d band in the transition metal oxides is partially occupied, there is a high density of unoccupied states at the Fermi level. Due to hybridization between metal 3d and oxygen 2p (section 5.3) orbitals, the fine structure of calculated oxygen-K is highly sensitive to the placement of the Fermi energy.

The symmetry and site projected DOS was calculated using FEFF 8 before calculating model oxygen K-spectra, in order to verify the Fermi energy placement in the calculation. The symmetry projected DOS was integrated across energy range $(E_f - 50)$ eV to $(E_f + 10)$ eV, to ensure important oxygen and metal valence electron states (O 2s, O 2p, M 3d) were present in the calculation.

The integral of the total DOS up to E_f is equal to the number of valence electrons included in the FEFF calculation. The correct E_f was determined by comparing the total number of valence electrons included in the calculation from the atomic potentials, with the total number expected for ionic potentials. The E_f placement was then adjusted using the CORRECTIONS card in the FEFF input file. SCF and FMS cluster sizes of 124 and 207 atoms were typically used for the calculation of model spectra that were compared to experimental EELS results. Calculated spectra were broadened by 0.7 eV to aid comparison with experimental spectra.

5.5 Fine Structural Analysis

5.5.1. Oxygen K-spectra

Oxygen K-standard spectra prepared from spectrum images acquired from FeO, α -Fe₂O₃ and Fe₃O₄ powders, as described in section 5.2, are shown in figure 5.9. Model spectra calculated in FEFF 8, as described in section 5.4, are overlaid for comparison. Model K-spectra were normalised against the peak b maximum of the equivalent experimental EELS spectrum as shown in figure 5.9.

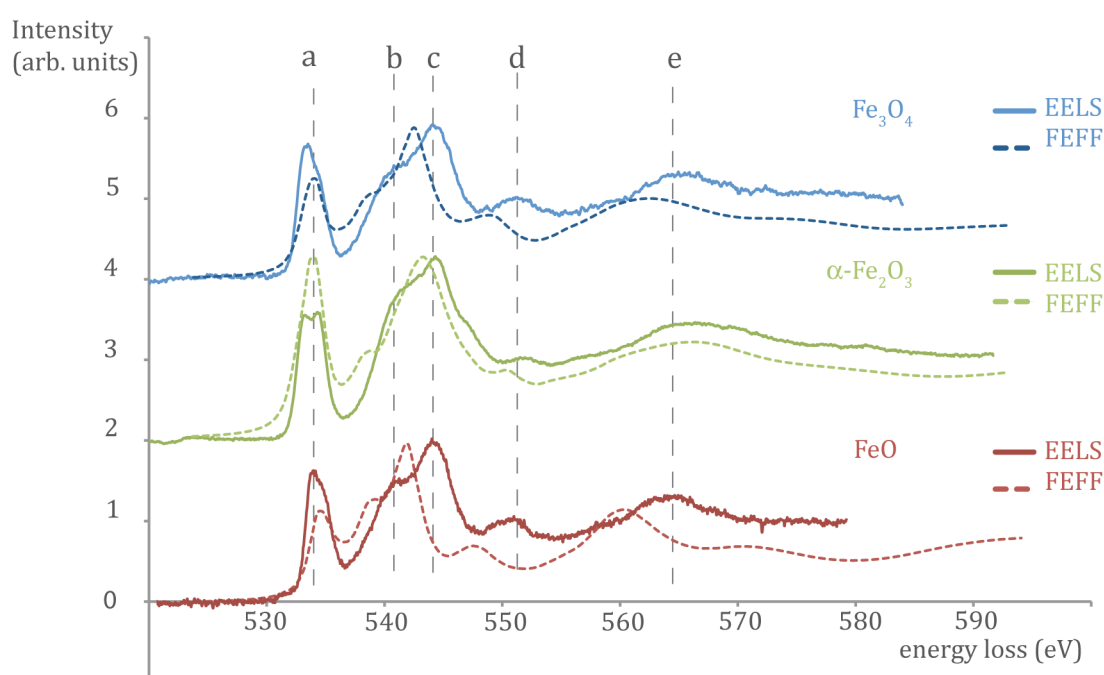


Figure 5.9 – Standard oxygen K-spectra for FeO, α -Fe₂O₃ and Fe₃O₄ determined from spectrum images acquired by monochromated STEM-EELS (solid) and oxygen-K spectra calculated using FEFF 8.

From figure 5.9, it is clear that the ELNES of oxygen K-spectra for the iron oxides under investigation consists of five peaks in the energy loss range 530 eV - 570 eV. A narrow high intensity peak was observed at 532 eV, labelled peak a, followed by a broader maximum at ~ 545 eV that can be sub divided into two distinct features at 541 eV and 545 eV labelled b and c in figure 5.9 respectively. A lower intensity peak was observed at 551 eV followed by a second broader low

intensity peak at ~ 565 eV. As plasmon losses become significant at energy losses of around 30 eV beyond the edge onset, it is possible that peak e is an effect of multiple scattering. Variations in peak e intensity are therefore not discussed [115].

The fine structure seen in oxygen K-spectra shown in figure 5.9 For α -Fe₂O₃ and Fe₃O₄ is in agreement with EELS data and full multiple scattering models previously presented by Colliex *et al.* and Wu *et al.* [115,129]. The fine structure for the FeO oxygen K-spectrum is not in agreement with the literature, with the relative intensity of peak a shown in figure 5.9 higher than previously observed by Colliex *et al.* [115]. Peaks b and c were previously classified by Colliex *et al.* as a single peak though this is likely to differences in energy resolution of the experiments. An energy resolution of 1 eV was stated by Colliex *et al.* [115] and spectra shown in figure 5.9 were acquired at typical energy resolution of 0.25 eV – 0.3 eV. From figure 5.9, it is apparent that the majority of peak positions and peak intensities are reproduced in model oxygen-K spectra for the iron oxides.

By comparing the relative intensity of peaks a, b and c from oxygen K-spectra shown in figure 5.9, it is clear that there is variation in fine structure between the different iron oxides. The relative intensity of peak a to peak c was found to decrease from α -Fe₂O₃ to Fe₃O₄ and decrease from Fe₃O₄ to FeO, in agreement with the literature [115]. It is also clear that relative intensity of peak b to peak c increases from FeO to Fe₃O₄ and increases further from Fe₃O₄ to α -Fe₂O₃. Results showed a peak splitting for peak a in the oxygen-K spectrum for α -Fe₂O₃ in agreement with spectra previously acquired by Mitterbauer *et al.* [63,115]. The peak splitting is attributed to crystal field splitting due to the O_h field in α -Fe₂O₃.

Standard oxygen K-spectra prepared from spectrum images acquired from CoO, ZnCo₂O₄ and Co₃O₄ are shown in figure 5.10. Model spectra calculated with FEFF

8 are overlaid for comparison. As previously observed for iron oxides, the fine structure in oxygen K-spectra acquired from CoO, ZnCo₂O₄ and Co₃O₄ consists of five peaks that occur between and energy loss of 530 eV and 570 eV. In the case of CoO the peak positions are in good agreement with peak positions identified in iron oxides. From figure 5.10, it is apparent that there is a sharp peak at 532 eV, followed by a broader maximum that is divided into peak b occurring at 538 eV and peak c at 542 eV. Lower intensity peaks were observed at 548 eV and ~ 565 eV.

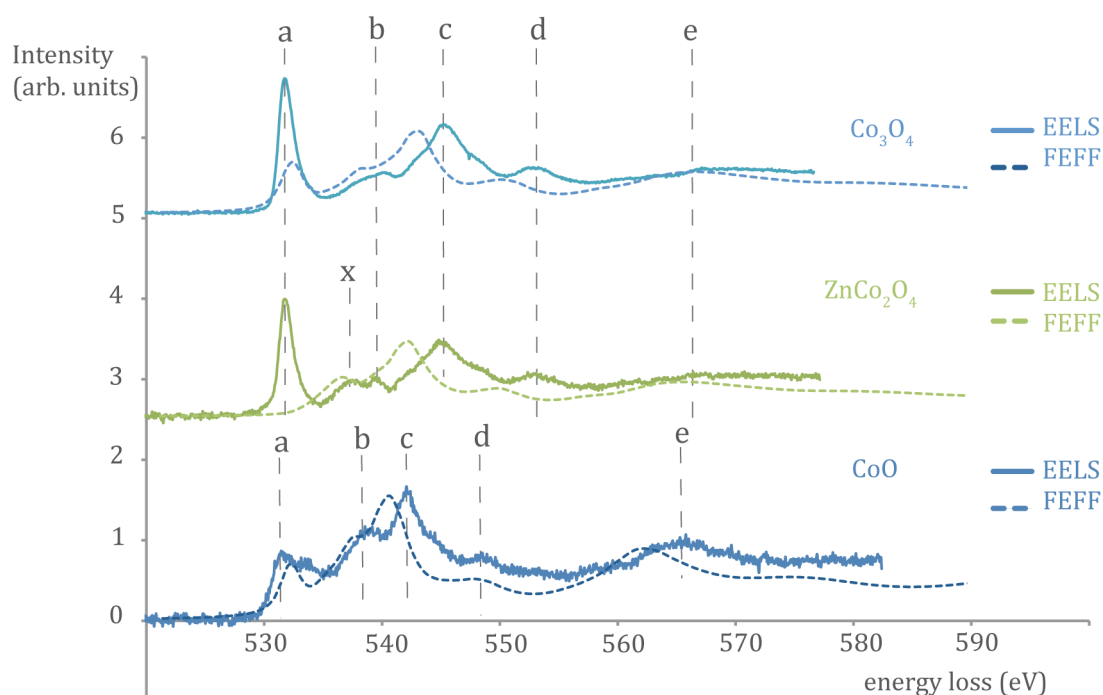


Figure 5.10 – Standard oxygen K-spectra for CoO, ZnCo₂O₄ and Co₃O₄ determined from spectrum images acquired by monochromated STEM-EELS (solid) and oxygen K-spectra calculated using FEFF 8.

From figure 5.10 it is clear that there is a chemical shift of peaks b-d in oxygen K-spectra acquired from ZnCo₂O₄ and Co₃O₄ in comparison to oxygen-K spectra from other oxides. For ZnCo₂O₄ and Co₃O₄, peak b was found to be a low intensity peak occurring at 540 eV followed by a higher intensity peak at 545 eV (peak c). A shoulder was observed on peak c at 543 eV in the oxygen-K spectrum for

Co₃O₄. Low intensity peaks were observed at 550 eV and ~ 565 eV labelled d and e respectively.

It is apparent from figure 5.10 that the fine structure and relative peak intensities for oxygen K-spectra acquired from Co₃O₄ and ZnCo₂O₄ are in close agreement, with the exception of peak x at 538 eV that was only observed for ZnCo₂O₄. Both oxygen K-spectra show a high relative intensity of peak a compared to peaks b-e in contrast to the oxygen K-spectrum for CoO in which peak a was not the strongest peak. In contrast to the iron oxides, poor agreement was observed between model spectra and experimental spectra for most of the cobalt oxides. Features of the experimental and model spectra are discussed further in the following section following in terms of the structural and electronic differences across the iron and cobalt oxide series.

The initial state for an oxygen K-transition is an oxygen 1s state. Under the dipole approximation, the final state for a transition from 1s state must be a state with p-character. de Groot *et al.* previously assigned the threshold peak of the oxygen K-edge at 532 eV to 1s → 2p transitions [130]. If bonding in transition metal oxides were purely ionic the intensity of the onset peak (peak a) would be zero. de Groot *et al.* attribute the strength of peak a to the degree of covalency in a transition metal oxide [130]. Hybridization between metal 3d orbitals and oxygen 2p orbitals in transition metal oxides is reported to significantly affect the fine structure of the transition metal oxide oxygen K-spectra [63,115,122]. de Groot *et al.* previously assign the fine structure near the edge onset, to states of oxygen 2p character, hybridized with metal 3d hybridized states. The second maximum was assigned to transitions to states of oxygen 2p character hybridized with the metal 4sp band [130].

Colliex *et al.* previously attribute the decreasing intensity of peak a from α-Fe₂O₃ to Fe₃O₄ and From Fe₃O₄ to FeO, to a decrease in the number of unoccupied states above E_f, due to a decreasing number of d-holes with increasing iron valence [115]. This is clearly seen by comparing the occupancy of Fe³⁺ and Fe²⁺ in table 5.2.

Table 5.2 – Transition metal occupancy for iron, cobalt and zinc cations.

Cation	Occupancy
Fe ²⁺	[Ar] 3d ⁶ 4s ⁰
Fe ³⁺	[Ar] 3d ⁵ 4s ⁰
Co ²⁺	[Ar] 3d ⁷ 4s ⁰
Co ³⁺	[Ar] 3d ⁶ 4s ⁰
Zn ²⁺	[Ar] 3d ¹⁰ 4s ⁰

de Groot *et al.* ^[130] report a relatively constant density of metal 4sp states in the transition metal oxides, which explains the relatively unchanging intensity of the 540 eV peak reported by Colliex *et al.* ^[115]. This does not explain the differences in peak intensities of peak b and c observed in figure 5.9. As peak b was seen to decrease in intensity from α -Fe₂O₃ to Fe₃O₄ and from Fe₃O₄ to FeO this might suggest that 2p 3d hybridization also plays a role in determining fine structure at energy loss 540 eV in the oxygen K-spectra of the iron oxides.

In the case of CoO, the intensity of peak a was much lower than the intensity of peak b, suggesting relatively low 2p 3d hybridization which would be expected; Co²⁺ has only 3 d-holes so that the number of unoccupied 3d states in the system is low. Given the agreement in the oxygen K-edge fine structure for CoO shown in figure 5.10 with that observed by de Groot *et al.* ^[130], Colliex *et al.* ^[115] as well as observations for iron oxides shown in figure 5.9, peaks b and c in the CoO oxygen K-spectrum are likely to be due to transitions to 4sp states.

It is clear that the fine structure observed between 535 eV and 550 eV in the oxygen K-spectra acquired from Co₃O₄ and ZnCo₂O₄ differs from the fine structure observed in this energy-loss range for the remaining oxides under investigation. Davoli *et al.* ^[131] attributed fine structural features between 538 eV and 562 eV in oxygen K-spectra acquired from NiO to effects of electron correlation, which are generally well described by single electron models ^[131].

Both Co_3O_4 and ZnCo_2O_4 contain a large number of d electrons, as seen in table 5.2, which might suggest the presence of electron correlation in the fine structure of their respective oxygen K-spectra. The strong onset peak in oxygen K-spectra acquired from Co_3O_4 and ZnCo_2O_4 indicates significant covalency.

It is apparent from figures 5.9 and 5.10 that the main peaks of the oxygen K-spectra are reproduced by the multiple scattering calculation with the exception of the model spectrum for ZnCo_2O_4 in which peak a is completely absent. In the case of ZnCo_2O_4 better agreement with the experimental spectrum was observed before correction of E_f . The E_f corrected spectrum is shown in figure 5.10 in order to maintain consistency with other model spectra. As peak a is absent from the model spectrum, E_f for ZnCo_2O_4 has been overestimated by the correction procedure outlined in section 5.4.1. As pre-peak intensities, and therefore E_f , were reproduced well for other most other oxides investigated, the missing peak may be the result of a calculation artefact or error specific to the ZnCo_2O_4 calculation.

The crystal field splitting of the pre-peak seen in the experimental spectrum for $\alpha\text{-Fe}_2\text{O}_3$ was not reproduced in the FEFF 8 calculation, though was reproduced in a model oxygen-K spectrum previously calculated by Wu *et al.* [129], using the “CONTINUUM” full multiple scattering code.

The transition metal monoxides (FeO , CoO) are reported as Mott insulators, displaying a band gap in the 3d band due to strong intra-atomic d-d coulomb interactions [132]. Anisimov [132] previously suggested single-particle band structure theory can not be used to accurately describe Mott insulators as the single particle model does not account for electron correlation effects. During E_f correction, it was clear that FEFF incorrectly calculated the metal 3d band structure for both FeO and CoO as no band gap was predicted in the site projected 3d DOS. In spite of this calculation error, model spectra for the transition metal monoxides agreed well with experimental spectra after correction of the Fermi level.

Correction of the Fermi energy also led to good agreement between model and experimental spectra for α -Fe₂O₃ and Fe₃O₄ though for Co₃O₄ and the ZnCo₂O₄ the pre-peak intensity was not well reproduced. α -Fe₂O₃ is widely reported to be semiconducting, the accepted band gap being 2.2 eV [118,133]. Cornell indicates the band gap in FeO and α -Fe₂O₃ results from a forbidden energy region between occupied 3d and unoccupied 3d bands [118]. Fe₃O₄ is also reported as semiconducting with a band gap of 0.1 eV [118]. Co₃O₄ thin films prepared by chemical vapour deposition were found to be p-type semiconductors with band gap energies of 1.50 – 1.52 eV by Cheng *et al.* [134] and ZnCo₂O₄ films grown by magnetron sputtering by Kim *et al.* are also reported to have semiconducting properties depending on the oxygen pressure during film growth, with p-type, n-type and insulating type films identified [135,136].

As the main source of disagreement between model spectra and experimental spectra was the intensity of peak a, it is expected that errors result from the placement of E_f . Band gaps reported in the literature were not reproduced in the FEFF calculation of the symmetry and site projected DOS. As E_f intersected the 3d band in the DOS calculation for most iron and cobalt oxides investigated, any error would lead to a significant change in the intensity of peak a in calculated oxygen K-spectra due to oxygen 2p metal 3d hybridization.

Better agreement might be achieved in the Co₃O₄ and ZnCo₂O₄ models by adjusting the placement of the Fermi level further using the CORRECTIONS card. This might also be improved further by accounting for magnetic effects in the electronic structure of the structures investigated [128].

5.5.2. Metal $L_{2,3}$ -spectra

The transition metal $L_{2,3}$ -spectra involve transitions between metal 2p states and metal s states or d states. The $L_{2,3}$ -spectra are dominated by the transitions to unoccupied 3d states due to the high intensity and narrow bandwidth of the 3d bands in transition metals around the Fermi energy. The hybridization between the 2p and 3d orbitals give rise to features in the transition metal $L_{2,3}$ -spectra that cannot be explained by a single electron model. The $L_{2,3}$ -edges must be described in terms of a $2p^6 3d^n \rightarrow 3d^{n+1}$ instead of a simple $2p \rightarrow 3d$ transition, in order to account for electron correlation effects ^[115].

The orbital momentum (l) and spin (s) components of a wavefunction interact through spin-orbit (SO) coupling. The total angular momentum (j) is given by

$$j = l \pm s \quad (5.5)$$

For a p-state, $l = 1$ so that $j = 1/2$ or $j = 3/2$. The transition metal L-edges are dominated by two sharp peaks referred to as white lines. The white lines correspond to excitations from the $2p_{3/2}$ or $2p_{1/2}$ states. The higher intensity L_3 line is due to transitions from $2p_{3/2}$ and the lower intensity L_2 line due to transitions from the $2p_{1/2}$ level. The L_2 line is broader than the L_3 due to the availability of a Coster-Kronig decay channel for transitions from the $2p_{1/2}$ state that shorten the final state lifetime ^[91].

The relative intensity of the L_3 line is expected to be twice that of the L_2 line, due to the spin-orbit coupling interaction. Leapman and Grunes observed significant deviations from the 2:1 ratio expected that were later attributed to coulomb and exchange, p-d and d-d interactions ^[137]. Crystal field effects (section 5.3) also affect the fine structure of the transition metal $L_{2,3}$ -spectra by splitting both the L_3 and L_2 lines satellite peaks associated with transitions to the 3d t_{2g} and e_g states in an O_h field, or t_2 and e states in a T_d field.

5.5.2.1. Iron Oxides

Figure 5.11 shows standard iron $L_{2,3}$ -spectra determined from spectrum images acquired from FeO, α -Fe₂O₃ and Fe₃O₄ powders by monochromated STEM-EELS. Spectra calculated by configuration interaction (CI) models, by Crocombette *et al.* [138], are overlaid for comparison. The CI model for Fe₃O₄ is a weighted sum of the Fe³⁺ T_d, Fe³⁺ O_h and Fe²⁺ O_h models. Model spectra were smoothed using a low pass filter in digital micrograph to aid comparison with experimental spectra. The iron L₃ maximum of each model spectrum was normalised against the iron L₃ maximum of the equivalent experimental spectrum.

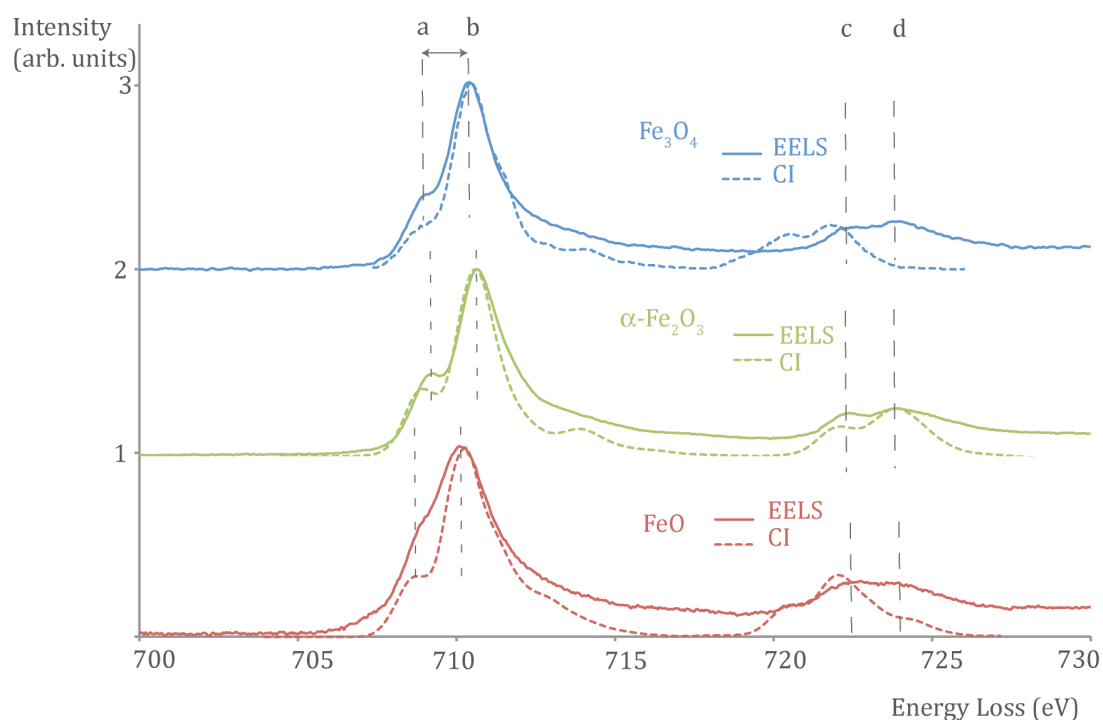


Figure 5.11 – Standard Iron $L_{2,3}$ -spectra for FeO, α -Fe₂O₃ and Fe₃O₄ determined from spectrum images acquired by monochromated STEM-EELS (solid) and CI model spectra previously calculated using by Crocombette *et al.* [138].

From figure 5.11, it is clear that the iron- $L_{2,3}$ spectrum consists of two main peaks, the L₃ line at around 709 eV and the L₂ line at around 720 eV. The L₃ and L₂ lines were observed to split into satellite peaks labelled a-d. This splitting was

not as apparent in the experimental spectrum for FeO as observed in experimental spectra for α -Fe₂O₃ and Fe₃O₄ though the splitting is clear in the [FeO₆]¹⁰⁻ CI model spectrum calculated by Crocombette *et al.* [138] From figure 5.11 it is also apparent that the relative intensities of peaks a-d vary over the iron oxide series. The relative intensity of peak a to peak b was seen to decrease from α -Fe₂O₃ to FeO and decrease further from FeO to Fe₃O₄. Peak positions and the energy separations of peaks a and b, and peaks c and d are given in table 5.3.

Table 5.3 – Iron L₃ and L₂ peak maxima and peak separations for iron L_{2,3}-spectra for iron oxides as shown in figure 5.11.

Oxide	L ₃			L ₂		
	a	b	b-a	c	d	d-c
FeO	707.6	708.75	1.15	721.5	722.45	1.30
α -Fe ₂ O ₃	707.75	709.20	1.45	720.9	722.45	1.55
Fe ₃ O ₄	709.02	710.42	1.40	722.52	723.92	1.40

The peak splittings b-a and d-c for α -Fe₂O₃ are in reasonable agreement with splittings previously reported by Krivanek and Paterson of 1.55 eV and Krishnan of 1.6 eV [61,62,139]. This splitting was previously attributed to the crystal field splitting energy for Fe³⁺ O_h. It is likely that the reduction in the splitting energy between α -Fe₂O₃ and FeO is due to the different Fe-O bond lengths in the two oxides. The Fe-O bond length in α -Fe₂O₃ is 1.91 – 2.06 Å and 2.15 Å in FeO [138]. The decreased bond length in α -FeO would lead to reduced repulsion between oxygen 2p and iron 3d orbitals which could explain the reduced peak splitting.

Krishnan previously attributed peak a and c to transitions to the O_h t_{2g} state and peaks c and d to transitions to the O_h e_g [139]. The decrease in the relative intensity of peak a from Fe₂O₃ can be explained by a decrease in the number of unoccupied d states with a valence change of Fe³⁺ to Fe²⁺ as seen from table 5.4. The decrease

in peak a intensity from $\alpha\text{-Fe}_2\text{O}_3$ to Fe_3O_4 is likely to be a combination of a decrease in the number of unoccupied d-states due to the presence of Fe^{2+} in Fe_3O_4 , in addition to the presence of $\text{Fe}^{3+} \text{ T}_d$, which will not contribute to either of the t_{2g} or e_g octahedral peak.

Cornell and Schwertmann [118] suggest the fine structure in iron $L_{2,3}$ -spectra is a result of electronic interactions within the 1st coordination shell of the excited atom. CI model spectra calculated from simple molecular orbital clusters by Crocomette *et al.* [138] shown in figure 5.11 are in good agreement with experimental spectra, which also suggests the iron- $L_{2,3}$ fine structure is defined within the 1st coordination shell. $\alpha\text{-Fe}_2\text{O}_3$ has a slightly distorted cubic symmetry though this did not appear to affect the fine structure significantly, in agreement with previous reports by Crocombette *et al.* [138]. A summary of the molecular orbital clusters relevant to FeO , $\alpha\text{-Fe}_2\text{O}_3$ and Fe_3O_4 is given in table 5.4.

Table 5.4 – Molecular orbital clusters for FeO , $\alpha\text{-Fe}_2\text{O}_3$ and Fe_3O_4 .

Oxide	MO Cluster	Empty d-States
FeO	$\text{Fe}^{2+} \text{ O}_h$ $[\text{FeO}_6]^{10-}$	4
$\alpha\text{-Fe}_2\text{O}_3$	$\text{Fe}^{3+} \text{ O}_h$ $[\text{FeO}_6]^{9-}$	5
Fe_3O_4	$\text{Fe}^{2+} \text{ O}_h$ $[\text{FeO}_6]^{10-}$	4
	$\text{Fe}^{3+} \text{ O}_h$ $[\text{FeO}_6]^{9-}$	5
	$\text{Fe}^{3+} \text{ T}_d$ $[\text{FeO}_4]^{5-}$	5

As the fine structure of iron- $L_{2,3}$ is defined within one coordination shell, the iron- $L_{2,3}$ spectrum for Fe_3O_4 may be approximated as a linear superposition of $\text{Fe}^{2+} \text{ O}_h$, $\text{Fe}^{3+} \text{ O}_h$ and $\text{Fe}^{3+} \text{ T}_d$ iron- $L_{2,3}$ spectra. The crystal field splitting energies of the $\text{Fe}^{3+} \text{ T}_d$ fields is approximately 0.69 eV [140]. This peak splitting is not observed in the iron- $L_{2,3}$ spectrum for Fe_3O_4 possibly because the $\text{Fe}^{3+} \text{ T}_d$

component of the iron-L_{2,3} spectrum comprises only 1/3 of the total integrated intensity (section 5.6). From figure 5.11, a peak splitting of 1.4 eV was observed for Fe₃O₄. This peak splitting was not previously observed in iron-L_{2,3} spectra acquired from Fe₃O₄ by Krivanek and Paterson [61,62]. Krivanek and Paterson [61,62] attributed the loss in fine structure to the chemical shift between Fe³⁺ and Fe²⁺ components of the spectrum, which Taftø and Krivanek previously found to be 1.3 eV [141]. Crocombette *et al.* previously report a much lower chemical shift of 0.7 eV [138].

As more fine structure was observed in Fe₃O₄ iron L_{2,3}-spectra collected by monochromated STEM-EELS than previously shown by Krivanek and Paterson [61,62], it is possible that the chemical shift is less than 1.3 eV. This is discussed further in section 5.6 and chapter 6.

5.5.2.2. Cobalt Oxides

Figure 5.12 shows cobalt $L_{2,3}$ -spectra acquired from CoO, $ZnCo_2O_4$ and Co_3O_4 by monochromated STEM-EELS. XAS spectra acquired by Bazin *et al.* [116] and CI model spectra calculated by Kumagai *et al.* [142] are overlaid for comparison. Spectra shown in figure 5.12 were normalised against the cobalt L_3 maximum to aid comparison of fine structural features. The energy loss of cobalt $L_{2,3}$ -spectra shown in figure 5.12 were calibrated according to L_3 peak energies determined experimentally by XAS, by Bazin *et al.* [116] and Morales *et al.* [143].

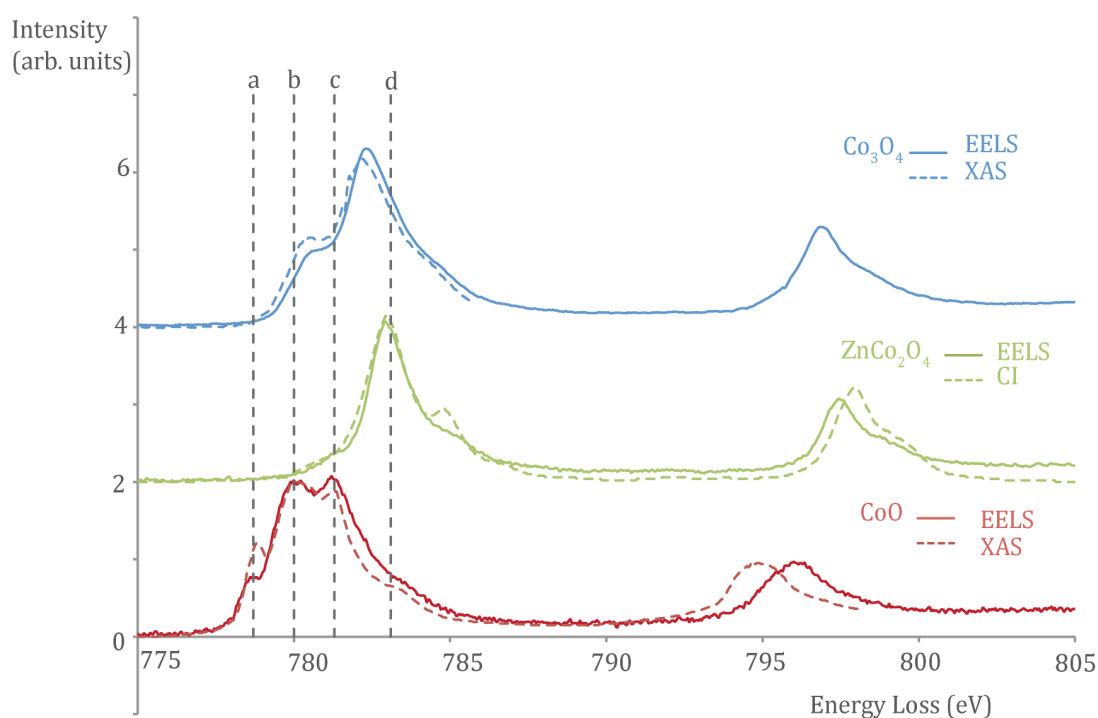


Figure 5.12 – Standard cobalt $L_{2,3}$ -spectra determined from spectrum images acquired from for CoO, $ZnCo_2O_4$ and Co_3O_4 by monochromated STEM-EELS (solid). XAS and CI model spectra acquired by Bazin *et al.* [116] and calculated by Kumagai *et al.* [142] are shown for comparison. The CI model spectrum compared with $ZnCo_2O_4$ was calculated by Kumagai *et al.* [142] from a $[Co^{3+}O_6]^{-9}$ cluster.

From figure 5.12, it is clear that the fine structure of cobalt $L_{2,3}$ -spectra consists of two white lines that occur at around 779 eV (L_3) and 800 eV (L_2). A significant amount of fine structure is superimposed on the L_3 line that is clearly

seen to vary with cobalt valence. Fine structural variations in the cobalt-L₂ line were less significant L₃ line and are therefore not discussed.

The cobalt-L₃ line for CoO was seen to consist of four satellite peaks labelled a-d in figure 5.12, occurring at 778.7 eV, 780 eV, 781.3 eV and 783.1 eV respectively. The b-c splitting and c-b splitting were both found to be 1.3 eV, which is in reasonable agreement with the ligand field splitting energy previously reported for CoO by Terakura ^[140] and Mattheiss ^[144]. The d-c splitting was equal to 1.8 eV.

Major satellite peaks were not observed in the experimental cobalt L₃ line for ZnCo₂O₄. The peak maximum was observed at 783.1 eV, clearly indicating an increase in onset energy with increasing cobalt valence. It is apparent from figure 5.12, that the ZnCo₂O₄ L₃ line is asymmetric with a shoulder present at ~785 eV. If the experimental spectrum is compared with the CI model spectrum it is clear that the shoulder observed in experiment coincides with a peak in the model spectrum.

The cobalt L₃ line for Co₃O₄ consisted of two major peaks occurring at 780.4 eV and 782.2 eV, giving a splitting of 1.8 eV. As the peak splitting is relatively high in comparison to the crystal field splitting, it is possible that the shoulder might represent the Co²⁺ T_d component of the Co₃O₄ cobalt L_{2,3}-spectrum. Co₃O₄ is a normal spinel with 1/3 of the cobalt present as Co²⁺ T_d.

Trends in fine structural variation in cobalt-L_{2,3} spectra with change in valence and cobalt coordination were not in agreement with trends observed for iron-L_{2,3}-spectra. While iron L_{2,3}-spectra acquired from FeO, α -Fe₂O₃ and Fe₃O₄ showed common fine structural features that changed in relative intensity with changes in valence or coordination, cobalt L_{2,3}-spectra showed major abrupt changes in fine structure. It is likely that this will have significant impact on the effectiveness of fitting routines based on cobalt standards. A detailed discussion of MLLS fitting results is given in section 5.6.

5.6 Multiple Linear Least Squares Fitting

The spinel degree of inversion (λ) may be determined by performing MLLS fitting on a metal $L_{2,3}$ -spectrum acquired from a spinel, with suitable T_d and O_h standards. This is justified as the $L_{2,3}$ fine structure is determined by interactions in the first coordination shell.

Molecular orbital clusters centering on oxygen anions for the perfect normal and inverse spinel structure, given by Grimes *et al.* ^[12] are summarised in table 5.5.

Table 5.5 – Molecular orbital clusters centering on oxygen anions in normal and inverse spinel structures ^[12].

Normal	Inverse
$[OAB_3]^{+9}$	$[OA_3B]^{+7}$
	$[OA_2B_2]^{+8}$
	$[OAB_3]^{+9}$
	$[OB_4]^{+10}$

From table 5.5 it is clear that an attempt to determine λ by performing MLLS fitting on an oxygen K-spectrum acquired from a spinel, a minimum of five standards are required in contrast to the two standards required for metal $L_{2,3}$ fitting. Additional problems are likely to arise, as the fine structure of oxygen K-spectra are not limited to the first coordination shell of excited oxygen atoms ^[63].

Given the reduced complexity of MLLS fitting with metal $L_{2,3}$ -spectra it seemed more likely that λ would be successfully calculated by this approach and attempts to fit to oxygen K-spectra were not made.

5.6.1. Iron L_{2,3}

In order to determine λ from iron L_{2,3}-spectra, standards are needed for Fe³⁺ T_d and Fe³⁺ O_h. Iron L_{2,3}-spectra acquired from α -Fe₂O₃ were found to be a good match to spectra calculated for [FeO₆]⁹⁻ octahedra by Crocombette *et al.* [138]. Poorer agreement between the iron L_{2,3}-spectra for acquired from FeO and previous calculations for [FeO₆]¹⁰⁻ by Crocombette *et al.* was observed, though good agreement was observed with an Fe²⁺ O_h iron L_{2,3}-spectrum acquired by Krishnan [139]. Given this agreement, iron L_{2,3}-spectra for α -Fe₂O₃ and FeO were taken as representative standards for Fe³⁺O_h and Fe²⁺ O_h respectively. A simple binary oxide for use as a Fe³⁺ T_d standard was not identified. Fe₃O₄ is an inverse spinel and therefore contains Fe³⁺ in tetrahedral and octahedral coordination environments and Fe²⁺ in an octahedral coordination environment. The chemical formula may be expanded as



Taking Fe₃O₄ as fully inverse, the integrated intensity (I) of an iron L_{2,3}-spectrum acquired from Fe₃O₄ may be taken as the sum of the tetrahedral and octahedral components.

$$k_1 \sum I\left(\text{Fe}\left[\text{L}_{23}\right]\right)_{\text{Fe}_3\text{O}_4} = k_2 \sum I\left(\text{Fe}\left[\text{L}_{23}\right]\right)_{\text{Fe}_{\text{O}_h}^{2+}} + k_3 \sum I\left(\text{Fe}\left[\text{L}_{23}\right]\right)_{\text{Fe}_{\text{O}_h}^{3+}} \quad (5.7)$$

$$+ K_4 \sum I\left(\text{Fe}\left[\text{L}_{23}\right]\right)_{\text{Fe}_{\text{T}_d}^{3+}}$$

where $k_2 = k_3 = k_4 = 1/3k_1$ are normalization constants.

Fe³⁺ T_d standard spectra were calculated by subtracting Fe³⁺ O_h and Fe²⁺ O_h standards from the standard iron L_{2,3}-spectrum acquired from Fe₃O₄. This is only valid where the onset energies of standard spectra are well defined, as the form

of a spectrum calculated with equation 5.7 depends strongly on the relative positions of peak maxima in the standards.

Crocombette *et al.* previously calculated the iron $L_{2,3}$ -spectrum for Fe_3O_4 as a linear superposition of $Fe^{3+} O_h$, $Fe^{2+} O_h$ and $Fe^{3+} T_d$ standards. (figure 5.11) [138]. Tafto and Krivanek previously report a chemical shift of 1.3 eV between Fe^{3+} and Fe^{2+} iron $L_{2,3}$ -spectra though Crocombette *et al.* found a shift of 0.7 eV gave the closest matching iron $L_{2,3}$ -spectrum for Fe_3O_4 [138,141]. Garvie and Buseck [145,146] previously report the iron L_3 maxima for Fe^{2+} and Fe^{3+} bearing minerals as 708.5 eV and 709.5 eV respectively, giving a chemical shift of 1 eV. In an independent study by Van Aken *et al.* [147] the L_3 maxima for Fe^{2+} and Fe^{3+} bearing compounds was found to be 707.8 eV and 709.5 eV giving a splitting of 1.7 eV. Given the variation in the values of this chemical shift found in the literature, chemical shifts between standards were modified iteratively in order calculate a number of $Fe^{3+} T_d$ standards under different conditions.

The onset for the iron $L_{2,3}$ -spectrum (708.4 eV) for Fe_3O_4 was defined as a fixed reference point. Under this condition, the L_3 maximum was found at an energy-loss of 709 eV. Taking the $Fe^{3+}:Fe^{2+}$ ratio in Fe_3O_4 as 2:1, the L_3 maximum is not in agreement with the equivalent value (709.2 eV) derived from Fe^{3+} and Fe^{2+} L_3 maxima reported by Garvie and Buseck [146]. Chemical shifts were applied to the $Fe^{2+} O_h$ and $Fe^{3+} O_h$ standard spectra so that at the initial condition, the onset energy of the $Fe^{2+} O_h$, $Fe^{3+} O_h$ and Fe_3O_4 standards were 708.4 eV. All spectra were normalised against the integrated intensity of the $Fe^{2+} O_h$ spectrum over energy loss range 705 – 730 eV.

Chemical shifts were applied to the $Fe^{3+} O_h$ spectrum from 0.1 eV to 0.7 eV, in 0.2 eV increments. For each $Fe^{3+}O_h$ shift, further chemical shifts were applied to the $Fe^{2+}O_h$ spectrum over the approximate range -0.1 eV to -1.1 eV in increments of 0.2 eV. Renormalization was carried out after any chemical shift and the $Fe^{3+} T_d$ spectrum was then calculated using equation 5.7.

Figures 5.13 – 5.16 show iron $L_{2,3}$ -spectra calculated for $\text{Fe}^{3+} T_d$. For small positive shifts to the $\text{Fe}^{3+} O_h$ spectrum and large negative shifts to the $\text{Fe}^{2+} O_h$ spectrum, negative intensity regions were observed preceding the L_3 peak. For large positive shifts to the $\text{Fe}^{3+} O_h$ spectrum and large negative shifts to the $\text{Fe}^{2+} O_h$ spectrum, negative intensity regions were observed following the L_3 peak. These features are unphysical, clearly showing that the optimum values for chemical shifts are around 0.1 eV for $\text{Fe}^{3+} O_h$ and -0.5 eV $\text{Fe}^{2+} O_h$.

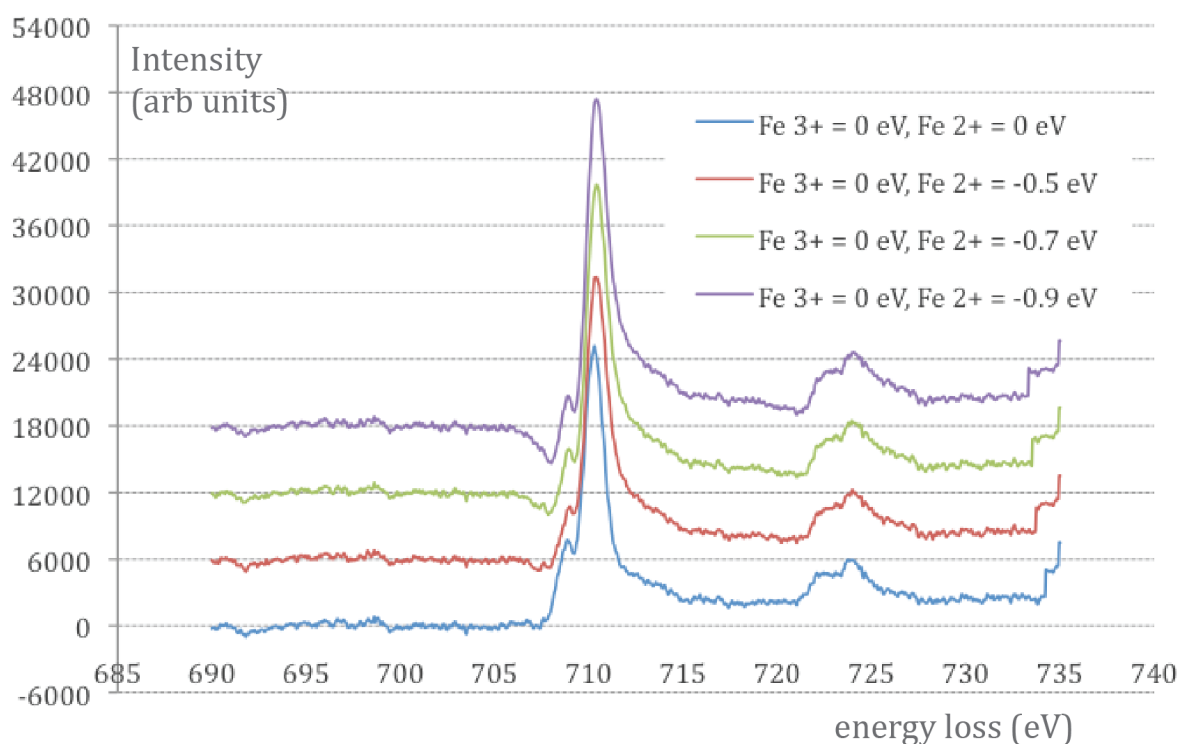


Figure 5.13 – $\text{Fe}^{3+} T_d$ spectra calculated for an $\text{Fe}^{3+} O_h$ onset shift of 0 eV.

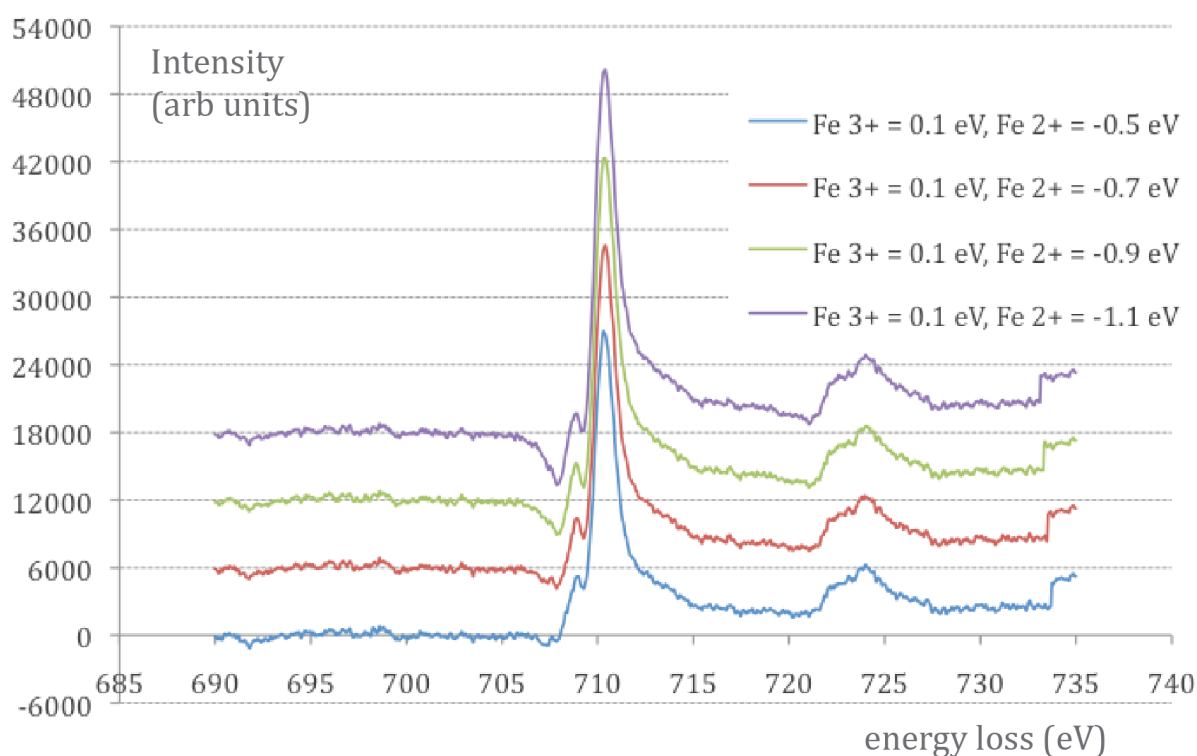


Figure 5.14 – $\text{Fe}^{3+} T_d$ spectra calculated for an $\text{Fe}^{3+} O_h$ onset shift of 0.1 eV.

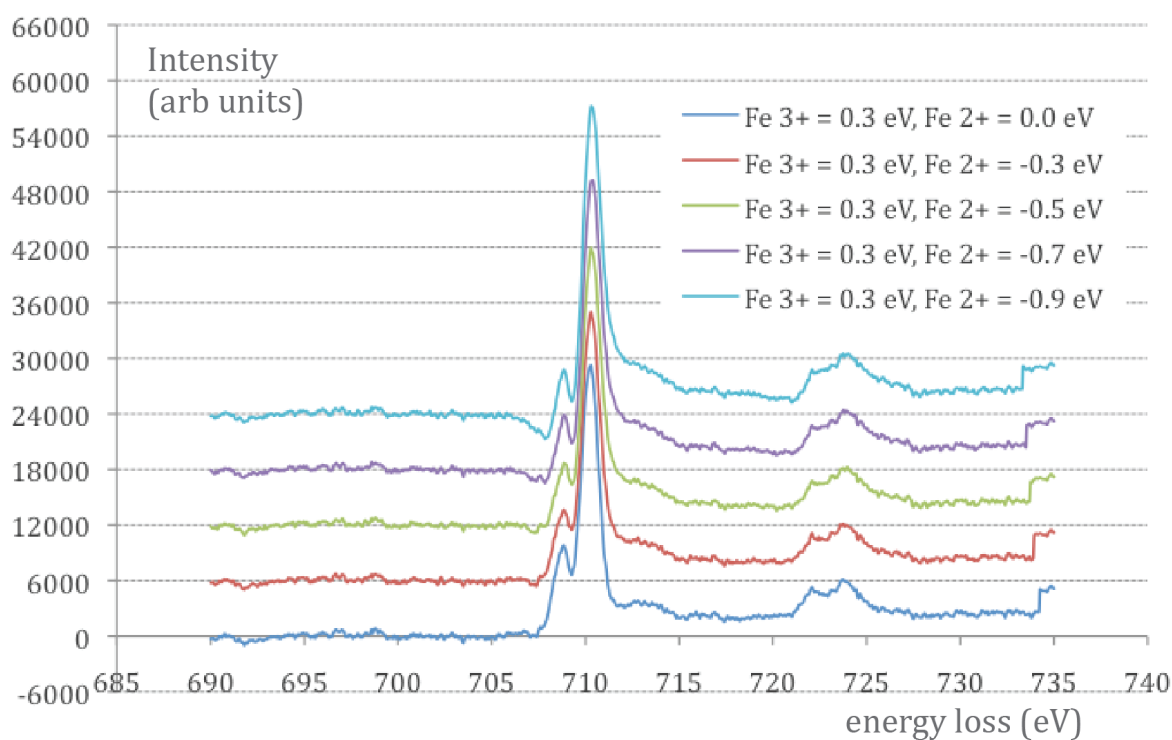


Figure 5.15 – $\text{Fe}^{3+} T_d$ spectra calculated for an $\text{Fe}^{3+} O_h$ onset shift of 0.3 eV.

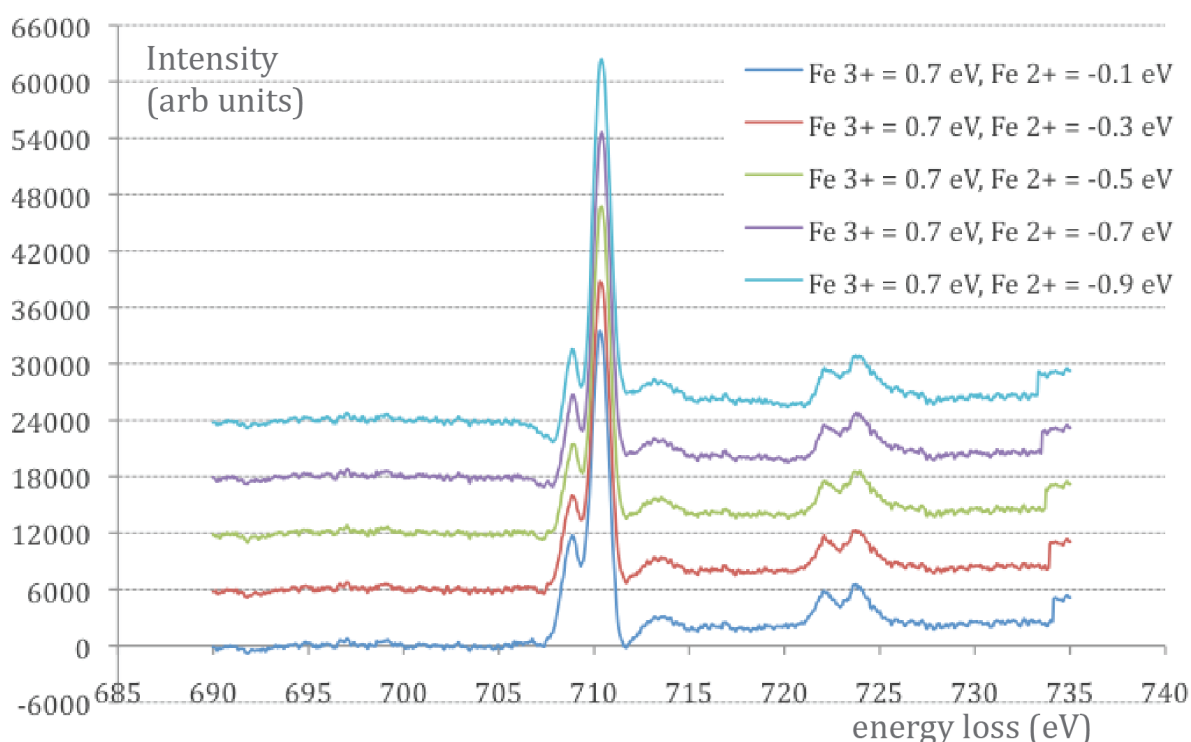


Figure 5.16 – $\text{Fe}^{3+} \text{T}_d$ spectra calculated for an $\text{Fe}^{3+} \text{O}_h$ onset shift of 0.7 eV.

From the investigation of iron oxide standards (section 5.5.2.2), a characteristic fine structural feature of the iron $\text{L}_{2,3}$ peak that varies with both iron valence and coordination environment was found to be the relative intensity of peak a to peak b in the iron $\text{L}_{2,3}$ -spectrum (figure 5.11). For iron $\text{L}_{2,3}$ -spectra shown in figures 5.13-5.16, the relative intensity of peak a was found to decrease as the $\text{Fe}^{2+} \text{O}_h$ chemical shift became more negative. Chemical shifts of the $\text{Fe}^{3+} \text{O}_h$ and $\text{Fe}^{2+} \text{O}_h$ spectra minimising the intensity of peak a in the spectrum for $\text{Fe}^{3+} \text{T}_d$ were found to give the closest matching $\text{Fe}^{3+} \text{T}_d$ spectrum to that published by Crocombette *et al.* [138]. The values of chemical shift that minimised the intensity of peak a whilst also minimising unphysical negative intensity in the $\text{Fe}^{3+} \text{T}_d$ spectrum were shifts of 0.1 eV and -0.4 eV for the $\text{Fe}^{3+} \text{O}_h$ and $\text{Fe}^{2+} \text{O}_h$ spectra respectively. The $\text{Fe}^{3+} \text{T}_d$ standard calculated under these conditions is shown in figure 5.17. The $\text{Fe}^{3+} \text{O}_h$ standard and CI models calculated by Crocombette *et al.* are included for comparison.

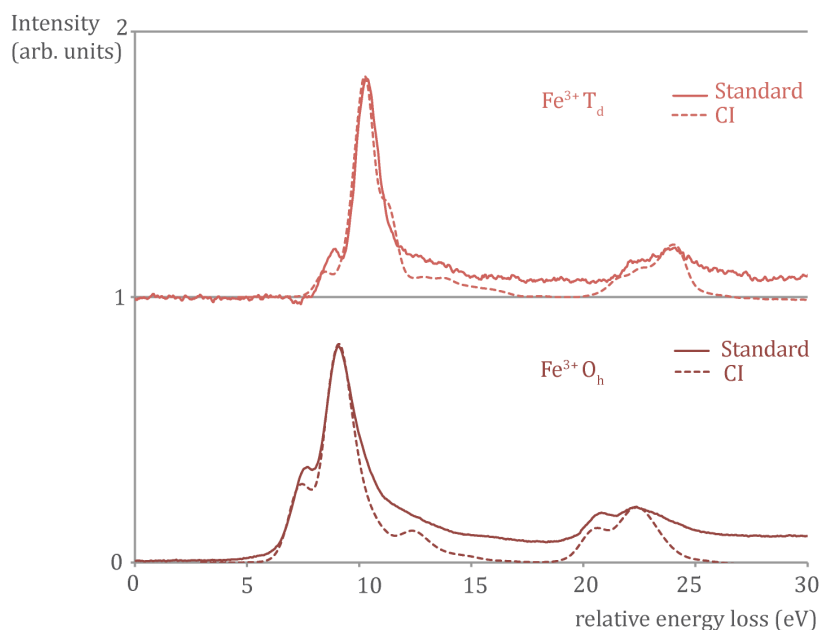


Figure 5.17 – Comparison of iron $L_{2,3}$ -standard spectra for $Fe^{3+} O_h$ and $Fe^{3+} T_d$ with CI models calculated by Crocombette et al. [138].

Both the $Fe^{3+} T_d$ and $Fe^{3+} O_h$ standards shown in figure 5.19 show qualitative agreement with CI model spectra in terms of the relative peak positions and intensities observed. This suggests that both standards are suitable for MLLS fitting.

Docherty [15] previously prepared bulk CFO using a basic solid state technique and determined a degree of inversion in the bulk CFO of $\lambda = 0.82$, by neutron diffraction. Docherty also carried out an investigation of the fine structure of iron $L_{2,3}$ -spectra acquired from $CoFe_2O_4$ by STEM EELS. In this thesis, MLLS fitting was performed on an iron $L_{2,3}$ -spectrum previously acquired by Docherty from CFO, using the $Fe^{3+} O_h$ and $Fe^{3+} T_d$ standards shown in figure 5.17. Fitting was performed on this iron $L_{2,3}$ -spectrum as λ was well defined, allowing the fitting parameters to be optimised.

MLLS fitting was performed using the MLLS fitting routine in Digital Micrograph. This routine forms a model spectrum that consists of a linear combination of specified standards or models. The standards represent linear terms in a model

function used to match an experimental spectrum. The best fit is identified by varying fit coefficients of the linear terms, to minimise the square deviation between the model function and experimental spectrum ^[148].

On completion, the MLLS fitting function plots the optimised model function and gives the minimised square of the deviation (χ^2) from the experimental spectrum and the integrated intensities of the modified standards used to form the model. Two or more standards must be specified to carry out MLLS fitting. The fitting results are highly sensitive to a number of experimental conditions, which include the absolute energy scale in the experimental and standard spectra.

As the Fe³⁺ T_d iron L_{2,3}-standard is calculated from the Fe₃O₄, Fe³⁺ O_h and Fe²⁺ O_h standards, the Fe³⁺ T_d iron L_{2,3}-fine structure depends on the relative energy scales of the three experimental standards. The relative energy scales of the Fe³⁺ T_d, Fe³⁺ O_h and Fe²⁺ O_h standards cannot be changed without modifying the Fe³⁺ T_d iron L_{2,3}-fine structure. To optimise the MLLS fit, the CFO onset was varied in the range 710.3 eV – 710.7 eV. The optimum condition was found to be where the CFO iron L₃ maximum occurred at an energy loss of 710.6 eV. Absolute energy scales for the optimised MLLS fit are given in table 5.5.

Table 5.6 – Edge onsets of iron L_{2,3}-spectra for standards and CoFe₂O₄.

Cation	L ₃ maximum (eV)
Fe ³⁺ O _h	710.7
Fe ³⁺ T _d	710.3
CFO	710.6

In addition to a well defined absolute energy scale, MLLS fitting must be performed over a suitable energy window. Iron L_{2,3}-spectra for Fe³⁺ O_h, Fe³⁺ T_d standards and bulk CFO are shown in figure 5.18.

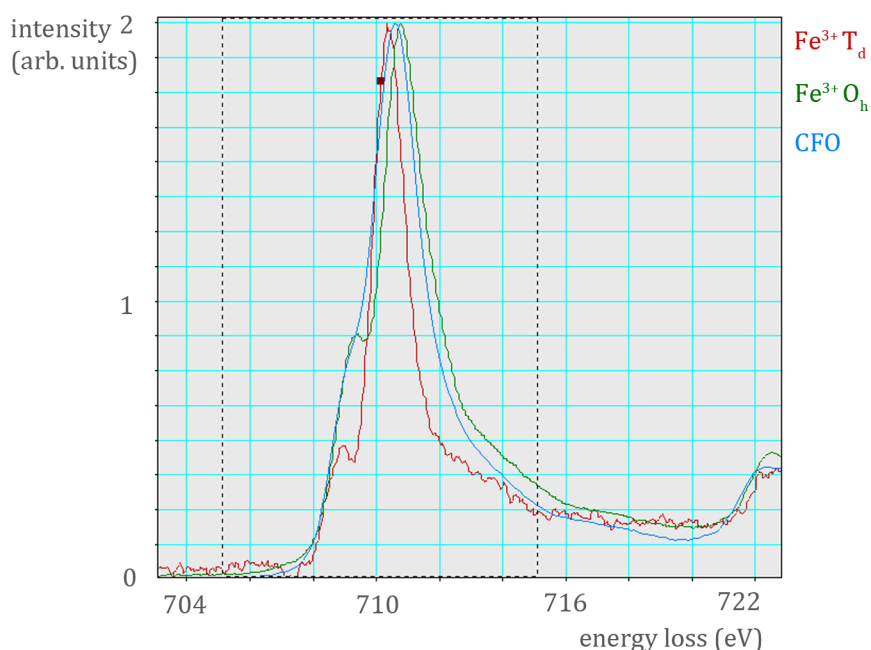


Figure 5.18 – Example MLLS fitting window showing the Iron $L_{2,3}$ -spectrum for bulk CFO acquired by Docherty ^[15] and the $Fe^{3+} T_d$ and $Fe^{3+} O_h$ standard spectra. An example 10 eV fitting window is also shown.

Fitting was carried out over the iron L_3 line as in this region, standard and experimental iron $L_{2,3}$ -spectra displayed a high signal to noise ratio. This was expected to improve the quality of fit.

Fitting must be performed using standard and experimental spectra that have been acquired under the same conditions ^[148]. The iron $L_{2,3}$ -spectrum acquired from CFO by Docherty was acquired at probe convergence and collection semiangles of $\alpha = 11$ mrad and $\beta = 12$ mrad respectively at an energy resolution of 0.5 – 0.6 eV ^[15]. The $Fe^{3+} O_h$ and $Fe^{3+} T_d$ standards were acquired at convergence and collection semiangles of $\alpha = 5.4$ mrad and $\beta = 8.8$ mrad and an energy resolution of 0.2 – 0.3 eV. In both cases $\alpha < \beta$ and β was small, making the dipole approximation valid ^[91]. To account for differences in the energy resolution at which standard and CFO iron $L_{2,3}$ -spectra were acquired, standard spectra were broadened by convolving with Gaussian functions.

In order to determine the quality of fit, it is necessary to assess the χ^2 value and the model function generated by the fitting routine. In order to determine the

validity of the fitting parameters, it is also necessary to calculate the degree of inversion from the integrated intensity of the modified standards given out by the fitting routine. The degree of inversion is given by

$$\lambda = 2 \left(\frac{\sum I(\text{Fe}[L_{23}])_{\text{Fe}^{3+}_{\text{Td}}}}{\sum I(\text{Fe}[L_{23}])_{\text{Fe}^{3+}_{\text{Oh}}} + \sum I(\text{Fe}[L_{23}])_{\text{Fe}^{3+}_{\text{Td}}}} \right) \quad (5.8)$$

Absolute energy scales for $\text{Fe}^{3+} \text{ T}_d$, $\text{Fe}^{3+} \text{ O}_h$ and CFO iron $L_{2,3}$ -spectra were defined based on iron L_3 maxima listed in table 5.6. MLLS fitting was performed over energy loss windows: 705.0 – 715.0 eV, 706.5 – 713.0 eV and 706.5 – 715.0 eV. For each window, MLLS fitting was performed with standards that had been broadened using Gaussian functions of FWHM 0 eV, 0.6 eV, 0.7 eV and 1.0 eV. λ was calculated using equation (5.9). For a given MLLS fitting, the same broadening energy was used for all standards as all were acquired under at the same energy resolution and under the same experimental conditions. Plots of broadening energy (b) against the calculated inversion parameter and χ^2 are shown in figures 5.19 and 5.20 respectively. Plots shown are for a fitting window of 705 – 715 eV

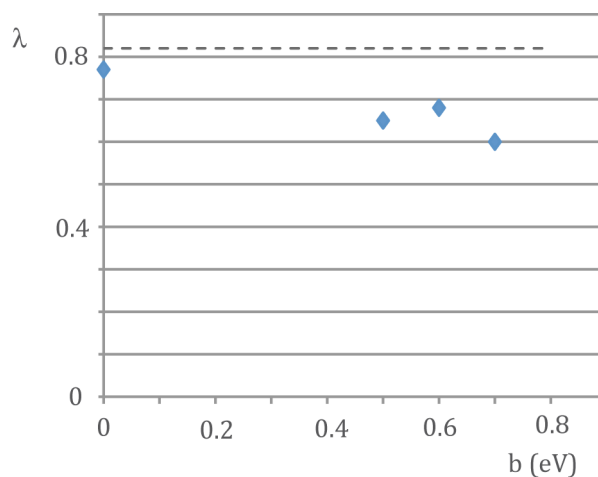


Figure 5.19 – Plot of λ against broadening energy for MLLS fitting of the iron $L_{2,3}$ -spectrum for CFO using $\text{Fe}^{3+} \text{ T}_d$ and $\text{Fe}^{3+} \text{ O}_h$ standards. The plot shown is for a fitting window of 705 – 715 eV.

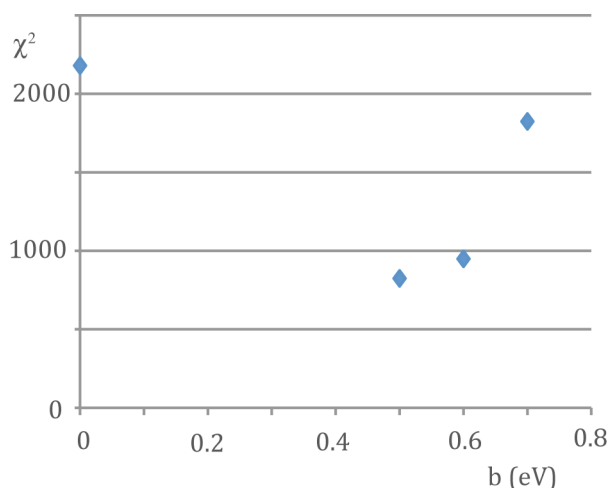


Figure 5.20 – Plot of χ^2 against broadening energy for MLLS fitting of the iron $L_{2,3}$ -spectrum for CFO using $Fe^{3+} T_d$ and $Fe^{3+} O_h$ standards. The plot shown is for a fitting window of 705 – 715 eV.

The optimum fitting parameters are those that give the value of λ closest to the literature value whilst also minimising χ^2 . It is clear from figure 5.20 that λ decreases as the broadening energy is increased. The closest agreement with the literature value for the inversion parameter ($\lambda = 0.82$) was given for $b = 0.0$ eV and fitting window 705.0 – 715.0 eV, where the calculated inversion parameter from the MLLS fit was $\lambda = 0.77$.

It is also apparent from figure 5.22 that χ^2 is minimised for $b = 0.5$ eV. The minimum value of χ^2 was found to be 824. Under the optimised χ^2 ($b = 0.5$ eV), the degree of inversion was found to be $\lambda = 0.65$.

5.6.2. Cobalt $L_{2,3}$

In order to determine λ from cobalt $L_{2,3}$ -spectra acquired from CFO, standards are needed for $Co^{2+} T_d$ and $Co^{2+} O_h$. Cobalt $L_{2,3}$ -spectra acquired from CoO were found to closely match cobalt $L_{2,3}$ -spectra acquired from CoO by XAS, by Bazin *et al.* [116]. Reasonable agreement between cobalt $L_{2,3}$ -spectra acquired from $ZnCo_2O_4$ and calculations for $[CoO_6]^{9-}$ octahedra by Kumagai *et al.* was also

observed [142]. Given this agreement, cobalt $L_{2,3}$ -spectra for CoO and ZnCo_2O_4 were taken as representative standards for Co^{2+}O_h and Co^{3+}O_h respectively. A simple binary oxide for use as a Co^{2+}T_d standard was not identified. Co_3O_4 is a normal spinel and therefore contains Co^{2+} in tetrahedral coordination and Co^{3+} in octahedral coordination. The chemical formula may be expanded as [149]

$$\left(\text{Co}_{\text{TET}}^{2+}\right)\left(\text{Co}_{\text{OCT}}^{3+}\right)_2\text{O}_4 \quad (5.9)$$

Taking Co_3O_4 as fully normal ($\lambda = 0$), the integrated intensity of a cobalt $L_{2,3}$ -spectrum acquired from Co_3O_4 may be taken to be the sum of the tetrahedral and octahedral components.

$$k_1 \sum I\left(\text{Co}\left[L_{2,3}\right]\right)_{\text{Co}_3\text{O}_4} = k_2 \sum I\left(\text{Co}\left[L_{2,3}\right]\right)_{\text{Co}_{\text{TET}}^{2+}} + k_3 \sum I\left(\text{Co}\left[L_{2,3}\right]\right)_{\text{Co}_{\text{OCT}}^{3+}} \quad (5.10)$$

where k_n are normalization constants and $k_1 = k_2 + k_3$ and $2k_2 = k_3$.

Co^{2+}T_d standard spectra were calculated by subtracting Co^{3+}O_h standards from the cobalt $L_{2,3}$ -spectrum acquired from Co_3O_4 based on equation 5.11. A similar method was followed as previously used for determining the Fe^{3+}T_d standard. Chemical shifts between the standard spectra were modified iteratively in order to calculate a number of Co^{2+}T_d standards under different conditions.

The onset for the cobalt $L_{2,3}$ -spectrum (780.35 eV) for Co_3O_4 was defined as the fixed reference point. A chemical shift was applied to the Co^{3+}O_h standard so that the onset was 780.35 eV. Spectra were normalised against the integrated intensity of the Co^{3+}O_h spectrum over energy loss range 775 – 790 eV. Chemical shifts were then applied to the Co^{3+}O_h spectrum from 0.1 eV to 1.2 eV, in 0.1 eV increments. Renormalization was carried out after each chemical shift and Co^{2+}T_d spectra were calculated using equation 5.10.

Cobalt $L_{2,3}$ -spectra calculated for Co^{2+}T_d are shown in figure 5.21. It is clear that as the chemical shift is increased an unphysical negative peak is present at low values of chemical shift. The maximum of this negative peak increases in energy

loss as the chemical shift is increased. As the chemical shift tends to 0.8 eV the relative intensity of the negative peak decreases so that the best agreement with the $\text{Co}^{2+} T_d$ spectrum falls in the chemical shift range 0.8 – 1.2 eV.

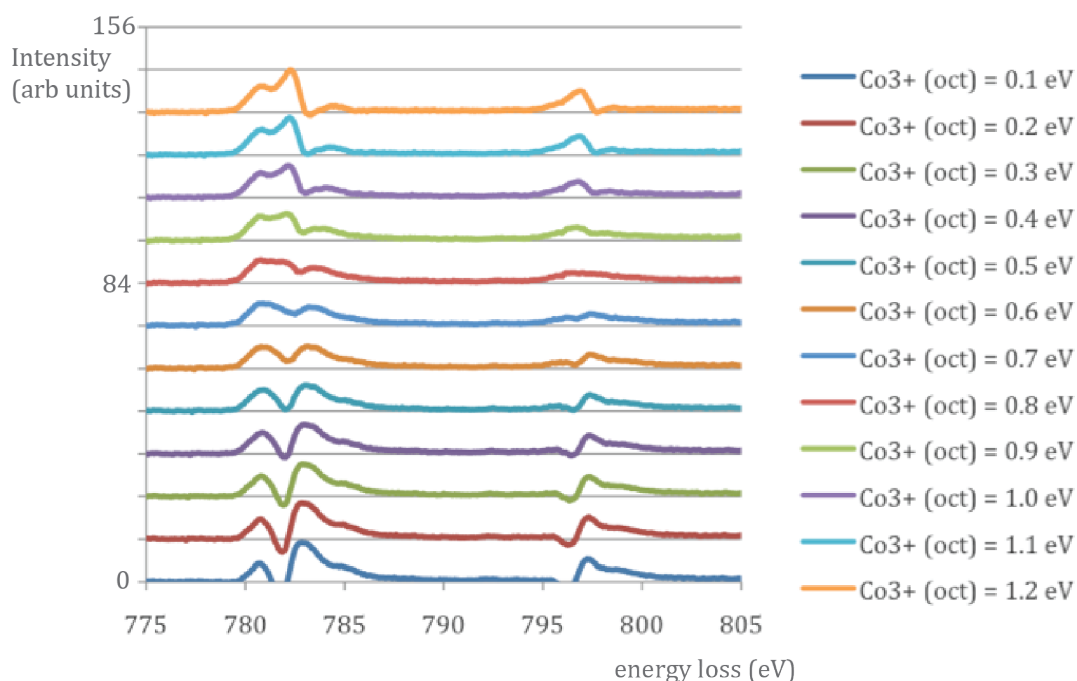


Figure 5.21 – $\text{Co}^{2+} T_d$ standards calculated for $\text{Co}^{3+} O_h$ onset shifts of 0.1 – 1.2 eV.

$\text{Co}^{2+} T_d$ standards calculated for $\text{Co}^{3+} O_h$ chemical shifts of 0.8 – 1.2 eV are shown in figure 5.22. The calculated spectrum for a $\text{Co}^{3+} O_h$ shift of 0.8 eV is in closest agreement with previously published data [116].

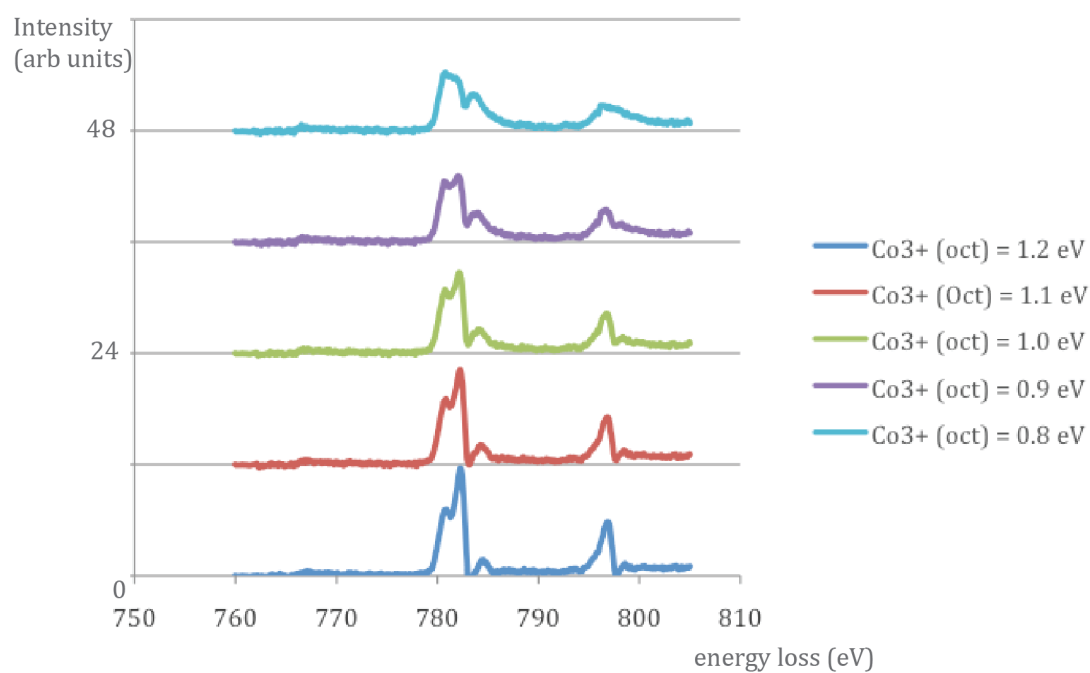


Figure 5.22 – $\text{Co}^{2+} T_d$ standards calculated for $\text{Co}^{3+} O_h$ onset shifts of 0.8 – 1.2 eV.

$\text{Co}^{2+} T_d$ and $\text{Co}^{2+} O_h$ standards are shown in figure 5.23. Cobalt $L_{2,3}$ -spectra determined experimentally by XAS by Bazin *et al.* and calculated using a CI model by Kumagai *et al.* [142] are shown for comparison.

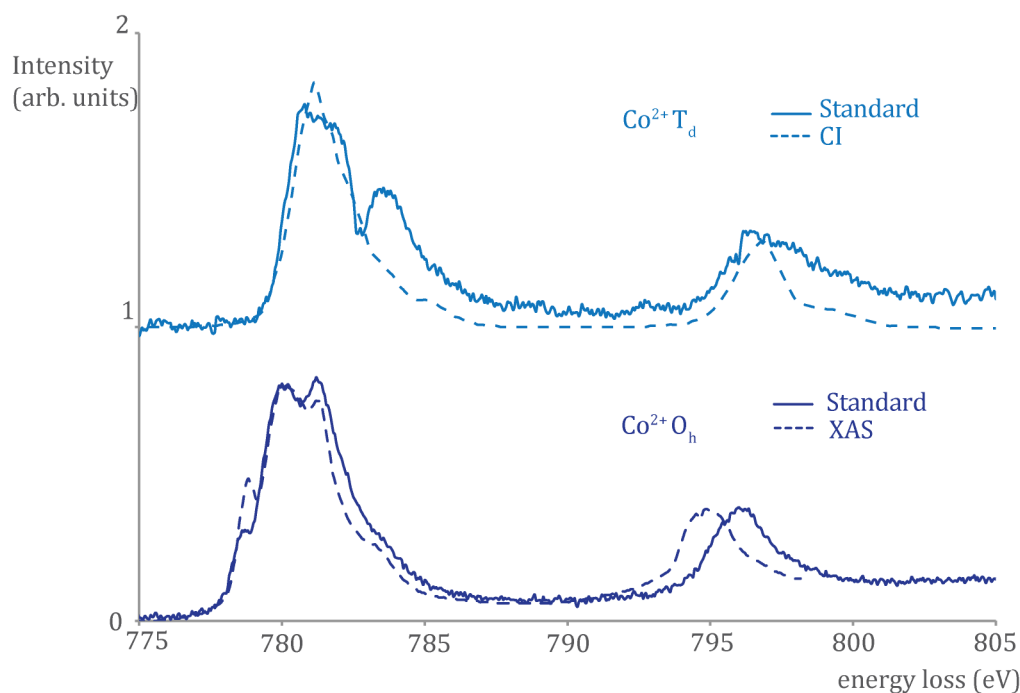


Figure 5.23 –Comparison of cobalt $L_{2,3}$ -spectra for $\text{Co}^{2+} \text{O}_h$ and $\text{Co}^{2+} \text{T}_d$ with spectra acquired by XAS and calculated by a CI model by Bazin et al. and Kumagai et al. [116].

From figure 5.23 it is clear that the fine structure of the $\text{Co}^{2+} \text{T}_d$ standard does not agree with that seen in the CI model. The $\text{Co}^{2+} \text{T}_d$ standard calculated showed two major peaks on the cobalt L_3 line where the CI model has only one major peak. The presence of the two peaks in the $\text{Co}^{2+} \text{T}_d$ is likely to be an artefact of the subtractive technique used to generate the standard. It is clear from figure 5.21 that this artefact is always present and can only be minimised, and not removed, by optimising the $\text{Co}^{3+} \text{O}_h$ chemical shift.

In order to optimise the fitting parameters, fitting was performed on a cobalt $L_{2,3}$ -spectrum previously acquired by Docherty under experimental conditions stated in the section 5.6.1 [15]. Fitting was performed over the cobalt L_3 line only.

$\text{Co}^{2+} \text{O}_h$ and $\text{Co}^{2+} \text{T}_d$ standards and the cobalt $L_{2,3}$ -spectrum acquired by Docherty are shown in figure 5.24. The spectrum for CFO agrees well with the spectrum for $\text{Co}^{2+} \text{O}_h$ between 778 eV and 781 eV and shows poor agreement with the $\text{Co}^{2+} \text{T}_d$ spectrum. If the cobalt $L_{2,3}$ -spectrum can be modelled as a linear combination

of the O_h and T_d components, this is as would be expected; the major component in CFO is $Co^{2+} O_h$. From figure 5.24, it is clear that the agreement between the CFO cobalt $L_{2,3}$ -spectrum and the $Co^{2+} O_h$ and $Co^{2+} T_d$ standard spectra is poor.

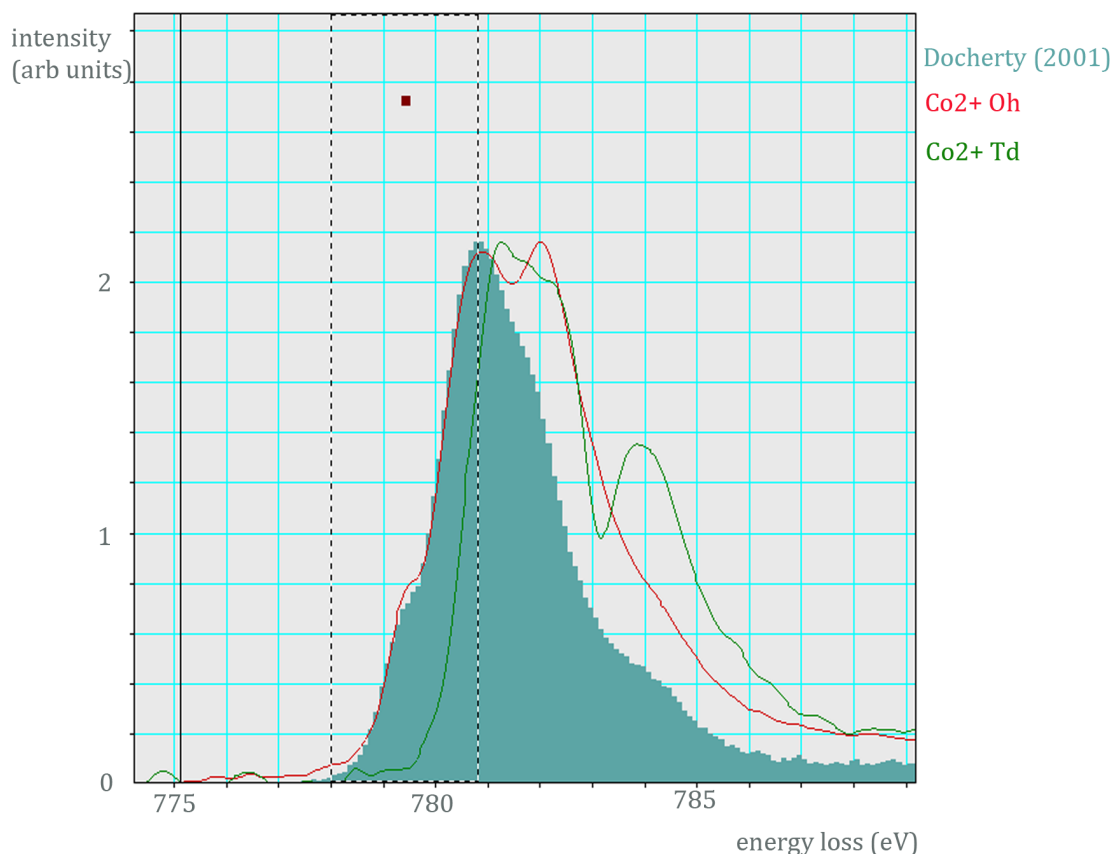


Figure 5.24 –Comparison of $Co^{2+} O_h$ and $Co^{2+} T_d$ standards with the CFO cobalt $L_{2,3}$ -spectrum^[15]. An example fitting window (778 – 780.8 eV) is shown.

Plots of λ and χ^2 against broadening energy for various MLLS fitting windows are shown in figures 5.25 and 5.26. For the 778.0 – 780.8 eV fitting window the degree of inversion calculated by MLLS was in good agreement with the literature value. The closest agreement was for $b = 0$ where the inversion parameter was calculated to be $\lambda = 0.82$. In contrast to results for the iron $L_{2,3}$ fitting, χ^2 was found to increase as b was increased. It is clear from the plots shown in figures 5.25 and 5.26 that the MLLS fitting procedure breaks down as unphysical values for the inversion parameter ($\lambda > 1.00$) are calculated and χ^2 is seen to increase in magnitude dramatically.

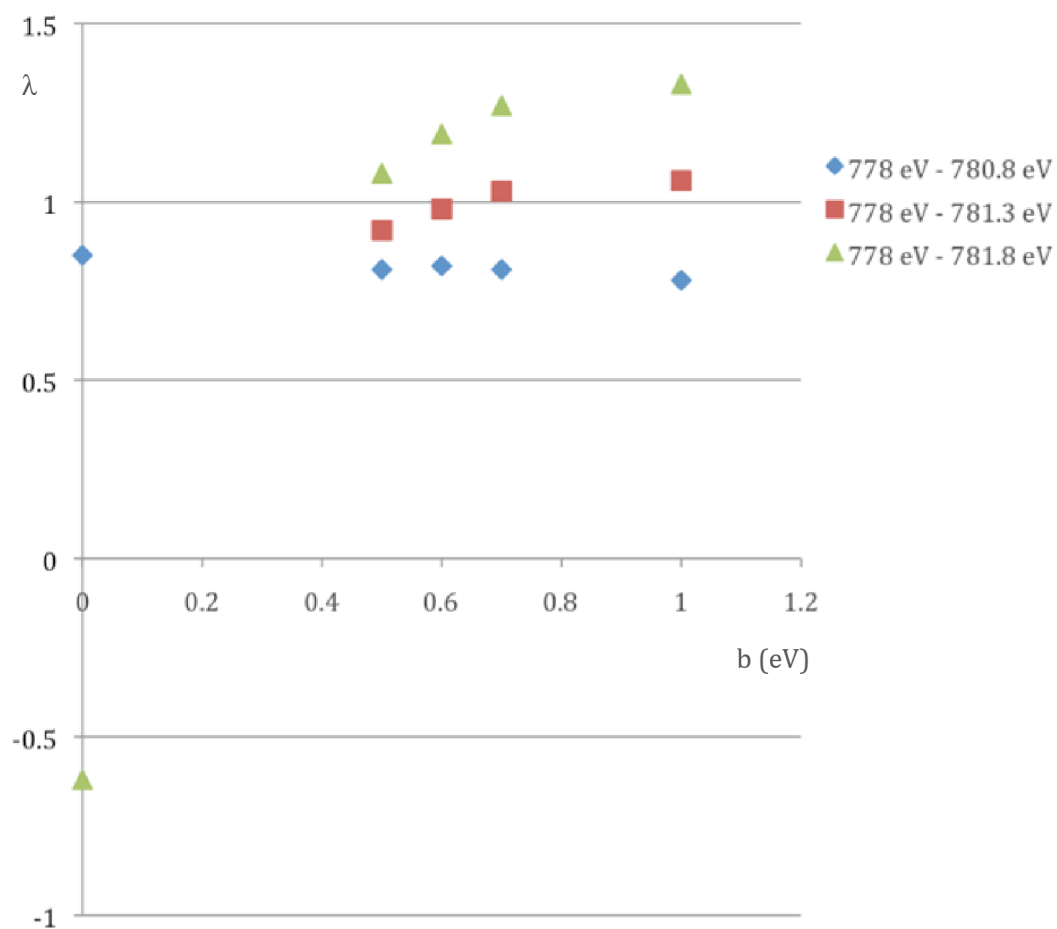


Figure 5.25 – Plot of λ against broadening energy for MLLS fitting of the cobalt $L_{2,3}$ -spectrum for CFO using $Co^{2+} T_d$ and $Co^{2+} O_h$ standards. Plots are shown for fitting windows of 778.0 – 780.8 eV, 778.0 eV -781.3 eV and 778.0 – 781.8 eV.

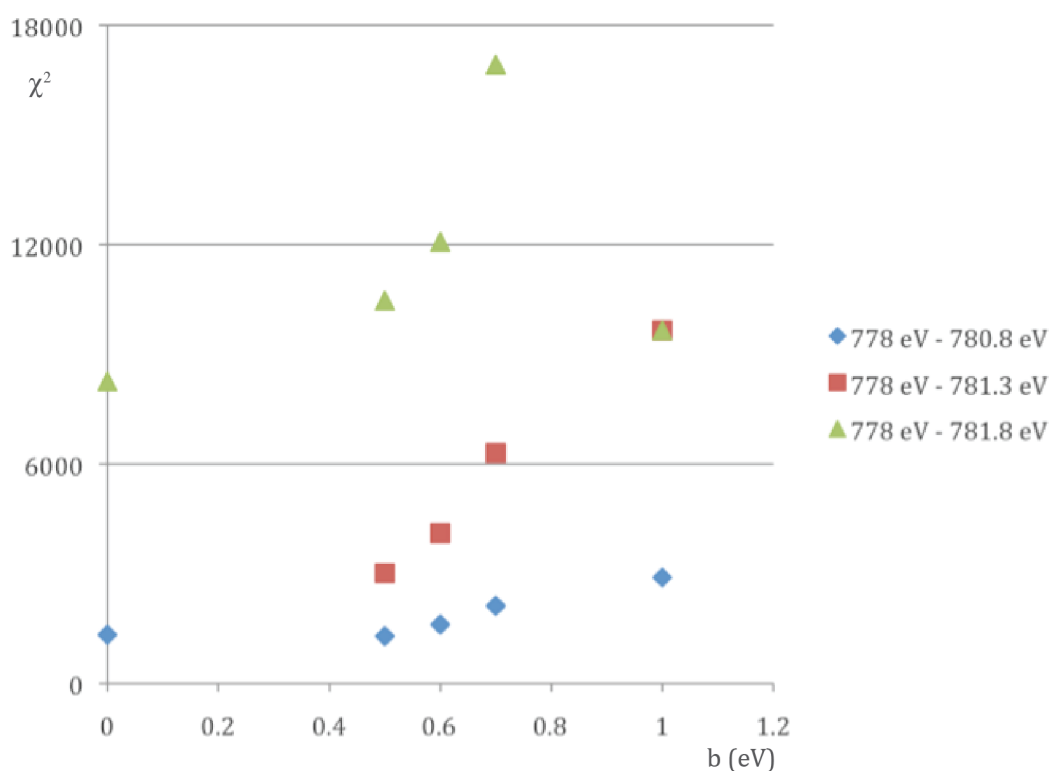


Figure 5.26 – Plot of χ^2 against broadening energy for MLLS fitting of the cobalt $L_{2,3}$ -spectrum for CFO using $Co^{2+} T_d$ and $Co^{2+} O_h$ standards. Plots are shown for fitting windows of 778.0 – 780.8 eV, 778.0 eV-781.3 eV and 778.0 – 781.8 eV.

MLLS model functions and the cobalt $L_{2,3}$ -spectrum for CFO are shown in figure 5.27. It is clear that as the width of the fitting window is increased over the cobalt L_3 line, the agreement between the model function and the CFO spectrum worsens. This is in agreement with the poor prediction of λ and large χ^2 values seen in figures 5.28 and 5.29. It is clear that the degree of inversion cannot be reliably reproduced by MLLS fitting standards to the CFO cobalt $L_{2,3}$ -spectrum under the conditions applied.

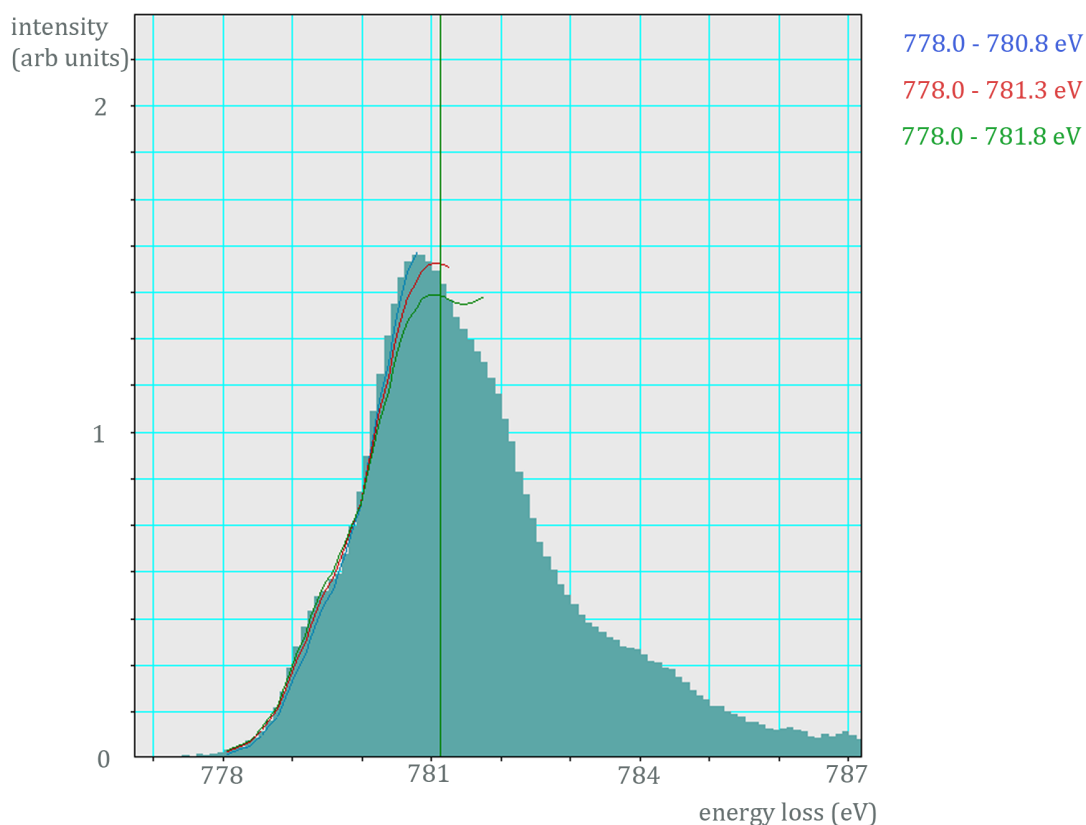


Figure 5.27 – MLLS model functions of the cobalt $L_{2,3}$ -spectrum for CFO. Model functions are shown for fitting windows 778.0 – 780.8 eV, 778.0 eV -781.3 eV and 778.0 – 781.8 eV. The solid spectrum shown is the cobalt $L_{2,3}$ -spectrum for CFO.

It would be possible to introduce chemical shifts between the cobalt $L_{2,3}$ -spectra of either standard or the CFO spectrum. It would also be possible to repeat the fitting procedure using a different Co^{2+} Td standard in order to try and improve the fit. However, as previously discussed the major component of the cobalt $L_{2,3}$ -spectrum for CFO is expected to be $\text{Co}^{2+} \text{O}_h$.

Referring to figure 5.24 and figure 5.12, it is clear that a strong peak is present at 782 eV in the $\text{Co}^{2+} \text{O}_h$ standard spectrum that is not present in the CFO cobalt $L_{2,3}$ -spectrum. By inspection it is also clear that a shift in the relative positions of the $\text{Co}^{2+} \text{O}_h$ or CFO cobalt $L_{2,3}$ -spectrum could not improve the fit over a large fitting window. Broadening the $\text{Co}^{2+} \text{O}_h$ spectrum does not improve the quality of fit, as the peak width observed for the cobalt L_3 line for $\text{Co}^{2+} \text{O}_h$ is greater than

the peak width of the L_3 line in the CFO spectrum, due to the presence of the additional peak at 782 eV in the $\text{Co}^{2+} \text{O}_h$ cobalt $L_{2,3}$ -spectrum.

Fine structural changes in the cobalt L_3 line in XAS spectra acquired by Bazin *et al.* acquired from CoO and Co_2SiO_4 can be attributed to slight differences in the symmetry of $\text{Co}^{2+} \text{O}_h$ sites in CoO and Co_2SiO_4 . The u parameter for CFO was previously found to be 0.25641 by Docherty meaning there is a small deviation from perfect octahedral symmetry on the octahedral sites in CoFe_2O_4 [15]. However, the changes to the fine structure of the cobalt- L_3 line in XAS spectra acquired by Bazin *et al.*, were small; the linewidth and number of peaks present was the same [116]. Further work is needed to explain the fine structural differences between the cobalt $L_{2,3}$ -spectra for CFO and $\text{Co}^{2+} \text{O}_h$.

As the degree of inversion could only be reproduced for a fitting window of 3 eV and the $\text{Co}^{2+} \text{T}_d$ and $\text{Co}^{2+} \text{O}_h$ standards do not seem to be representative components of the cobalt $L_{2,3}$ -spectrum for CoFe_2O_4 , calculation of the degree of inversion from the cobalt-L spectra is argued to be unreliable. It is further argued that for unknown reasons, the cobalt-L spectrum cannot be modelled as a linear combination of the O_h and T_d standard spectra due to the poor agreement between the CoFe_2O_4 and $\text{Co}^{2+} \text{O}_h$ cobalt-L spectra.

5.7 Conclusion

The near edge fine structure in oxygen K-spectra acquired from iron and cobalt oxides was found to vary with metal valence and coordination environment. Trends in the variation of fine structure in the oxygen K-spectra for the iron oxides was well described by a simple molecular orbital model based around oxygen 2p and metal 3d hybridization close to the edge onset, and 4sp hybridization at higher energy loss. Fine structural variations in the oxygen K-spectra of the cobalt oxides were not well described by the molecular orbital model, a possible consequence of an increasing importance of electron correlation effects due to the higher occupancy of the 3d states in cobalt oxides. Model spectra calculated in FEFF 8 were in good agreement with experimental spectra for the transition metal monoxides, α -Fe₂O₃ and Fe₃O₄ after correcting the Fermi energy. Model spectra for ZnCo₂O₄ and Co₃O₄ were in poor agreement with experimental spectra.

Variations in fine structure of iron L_{2,3}-spectra for the iron oxides were well described by crystal field theory. The relative intensity of satellite peaks in the L₃ and L₂ lines were attributed to changes in the relative occupancy of the t_{2g} and e_g 3d levels in the octahedral field in FeO, α -Fe₂O₃ and Fe₃O₄ in agreement with previous reports by Krishnan^[139]. Significant fine structural variations were observed in cobalt L_{2,3}-spectra for cobalt oxides. A large chemical shift was observed with an increase in cobalt valence of 2+ to 3+. In contrast to iron L_{2,3}-spectra, variation in the satellite peak intensity for cobalt L_{2,3}-spectra did not correlate well with structural or changes in cobalt valence.

Fe³⁺ T_d and Co²⁺ T_d standards were determined empirically from iron L_{2,3} and cobalt L_{2,3}-spectra acquired from Fe₃O₄ and Co₃O₄. This allowed the spinel degree of inversion to be calculated to within 20% of the bulk value, by MLLS fitting Fe³⁺ T_d and Fe³⁺ O_h standard spectra to an iron L_{2,3}-spectrum acquired from bulk CFO by Docherty ^[15]. The degree of inversion was also calculated by fitting Co²⁺ T_d

and $\text{Co}^{2+} \text{O}_h$ standards to a cobalt $\text{L}_{2,3}$ -spectrum acquired from CFO by Docherty [15].

The empirical procedure used to successfully calculate the $\text{Fe}^{3+} \text{T}_d$ standard failed to generate a satisfactory $\text{Co}^{2+} \text{T}_d$ standard. In addition, poor agreement was observed between the fine structure of the $\text{Co}^{2+} \text{O}_h$ and CFO cobalt $\text{L}_{2,3}$ -spectra. Given the poor agreement with both standards, it was not possible to calculate λ reliably by fitting to cobalt $\text{L}_{2,3}$ -spectra.

Chapter 6 – Local Chemistry in SrTiO₃/CoFe₂O₄ Thin Films

6.1 Introduction

The functional properties of a nanomaterial are often different from the bulk due to an increase in the significance of interfaces at the nanoscale. Analysing nanomaterials by STEM-EELS allows the local electronic environment to be probed at nanoscale spatial resolution. The electronic properties of interfaces can be measured directly by analysing the fine structure of core loss edges in the EELS spectrum.

Axelsson *et al.* [3] attribute variations in the M_s of as-deposited and oxygen post-annealed CFO films to cation reordering and oxidation processes during post-annealing [3]. Bulk magnetometry and XRD results support this hypothesis though a nanoanalytical investigation was not previously undertaken. In order to correlate the magnetic properties of CFO films with local chemistry, cobalt and iron $L_{2,3}$ -spectrum images were acquired from specimen 4, a 50 nm post-annealed (001) STO/CFO film. XTEM specimens prepared from as-deposited (001) STO/CFO were found to be unsuitable for STEM-EELS analysis and do not form part of the discussion in this chapter.

An analysis of the near-edge fine structure of cobalt and iron $L_{2,3}$ -spectra acquired from specimen 4 was undertaken to verify a chemical model previously proposed by Axelsson *et al.* [3]. Previous analyses of the fine structure of iron and cobalt standards presented in chapter 5 were used to aid interpretation of the near-edge fine structure of metal $L_{2,3}$ -spectra acquired from specimen 4. MLLS fitting was performed on iron $L_{2,3}$ -spectra using $Fe^{3+} T_d$ and $Fe^{3+} O_h$ standards to determine local variations in λ . Fitting was carried out with $Fe^{2+} O_h$ and $Fe^{3+} O_h$ standards to determine Fe^{2+} content in specimen 4. EELS quantification was performed on a non-monochromated dataset to support EELS analysis by MLLS.

6.2 Experimental Technique

Spectrum images were acquired using an FEI Titan in filtered and unfiltered modes at 300 kV. Monochromated data was acquired using a decelerating gun lens. Spectra were acquired with a typical probe size of 0.48 nm and convergence and collection semiangles of $\alpha = 5.4$ mrad and $\beta = 8.8$ mrad. Spectra were acquired at a dispersion of 0.05 eV per channel and typical acquisition times of 90 s – 120 s per pixel and typical energy resolution, 0.25 – 0.3 eV. The spectrometer drift voltage was set so that the iron and cobalt $L_{2,3}$ lines could be acquired simultaneously.

Non-monochromated spectrum images were acquired using a typical probe size of 0.2 nm and probe convergence and collection semiangles of $\alpha = 6.74$ mrad and $\beta = 8.81$ mrad. Low loss and core loss spectrum images were acquired at a dispersion of 0.3 eV per channel so that the Ti $L_{2,3}$, O K, Fe $L_{2,3}$ and Co $L_{2,3}$ edges could be acquired simultaneously. Low loss and core loss spectrum images were acquired at dwell times of 0.01 s and 15 s per pixel respectively. Core loss spectrum images were acquired immediately after low loss spectrum images, from the same survey region and under the same conditions, so that the low loss spectrum image could be used to perform a Fourier ratio deconvolution in order to determine the single scattering distribution from the core loss spectrum image (chapter 2). The energy resolution during non-monochromated EELS acquisition was typically 0.7 eV.

For both monochromated and non-monochromated EELS spectra, background subtraction was performed using background models of the form AE^{-r} . Iron $L_{2,3}$ MLLS fitting parameters were previously found to be optimised where the iron L_3 peak was found at 710.6 eV. The absolute energy scale for EELS spectra acquired from the CFO film was defined so that the iron L_3 maximum was 710.6 eV in order to optimise MLLS fitting routines performed on spectra acquired from the CFO film.

6.3 Variations in Near-Edge Fine Structure

6.6.1. Cobalt $L_{2,3}$

An ADF image of specimen 4, a 50 nm oxygen post-annealed STO/CFO thin film acquired in filtered mode is shown in figure 6.1. This specimen is as previously defined in chapter 4.

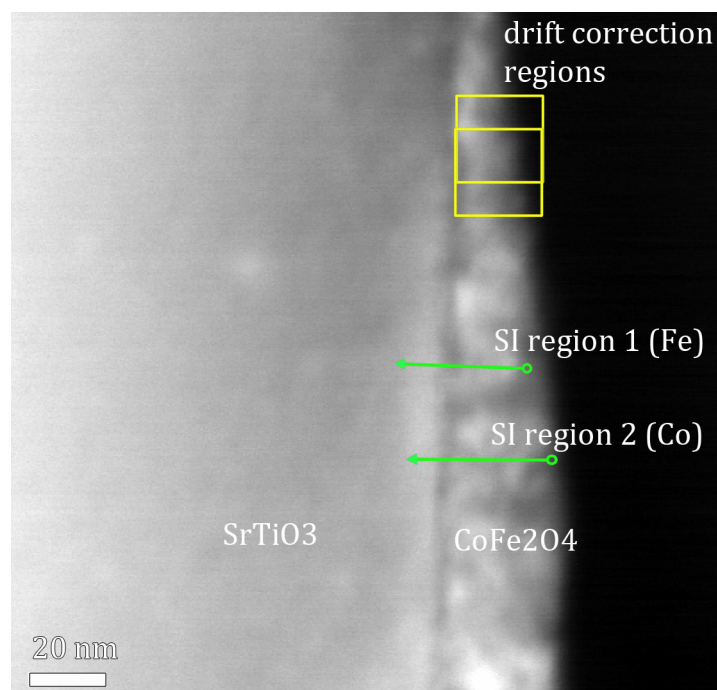


Figure 6.1 – STEM-ADF image of a 50 nm oxygen post-annealed STO/CFO thin film acquired in filtered mode. The STO substrate, CFO film, spectrum image regions and spatial drift correction regions are marked.

The substrate/film interface is clearly resolved in figure 6.1 but in contrast to images acquired in unfiltered mode (figure 3.7b), the substrate/film interface does not appear sharp. A large probe size (~ 0.48 nm) was necessary to ensure good signal to noise ratio in EELS spectra acquired in filtered mode. Consequently, the substrate and film lattice were not resolved when acquiring monochromated STEM images and the interface does not appear sharp.

Shown in figure 6.1 are the spectrum image and spatial drift correction regions used for the acquisition of a 17 pixel two-dimensional spectrum image (x, dE) of pixel length 2.4 nm, which is labelled as SI region 1. Cobalt $L_{2,3}$ -spectra for pixels 1-11 for SI region 2 are shown in figure 6.2. Cobalt $L_{2,3}$ -spectra for pixels 1-9 were normalised against the cobalt L_3 maximum so that fine structure in the EELS spectra could be compared. Spectrum for pixels 10 and 11 were not normalised due to a significant decrease in the cobalt signal. The cobalt signal for pixels 12 to 17 was found to be zero. Spectra for these pixels are not shown.

Shown in figure 6.4, is a higher magnification region ADF image showing the individual pixel positions of SI region 2. It is clear from figure 6.4 that the closest pixel to the substrate/film is pixel 9 and pixel 8 and pixel 10 lie in the CFO and STO layers respectively. It is apparent from figure 6.2 that there is a weak Co L_3 signal in the spectrum for pixel 10, which might suggest some interdiffusion in agreement with previous investigations for annealed CFO films carried out by Hu *et al.* [36] and Schnittger *et al.* [47] or interface roughness. It is also clear from figure 6.4 that there is a fine structural change in the cobalt L-spectrum for pixel 9 relative to spectra acquired from the bulk of the film. Fine structural changes in spectra acquired from the bulk of the film were not observed.

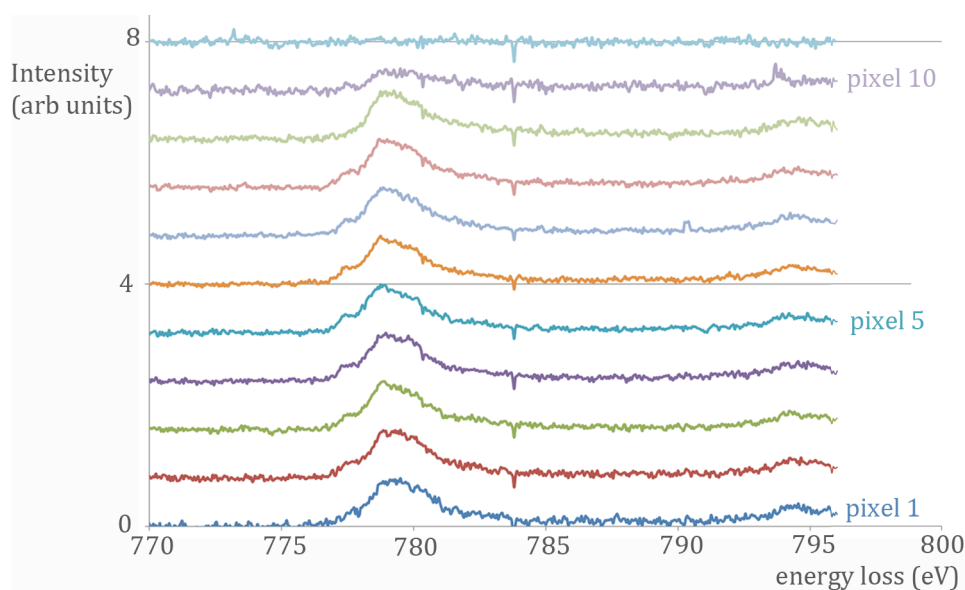


Figure 6.2 – Cobalt $L_{2,3}$ -spectra acquired from a 50 nm oxygen post-annealed CFO thin film. Spectra are shown for pixels 1-11 of SI region 2.

Shown in figure 6.3 are cobalt $L_{2,3}$ -spectra acquired from the near interface region of specimen 4. Two major peaks were identified labelled peak a and peak b. The near edge fine structure of cobalt $L_{2,3}$ -spectra from within the bulk of the 50 nm OA STO/CFO film was in good agreement with fine structure in the cobalt $L_{2,3}$ -spectrum acquired from bulk CFO powder by Docherty [15]. Cobalt $L_{2,3}$ -spectra for bulk CFO are overlaid with spectra acquired from the CFO film for comparison in figure 6.3. EELS spectra acquired from the thin film are shown as solid lines and reference spectra are shown as dashed lines.

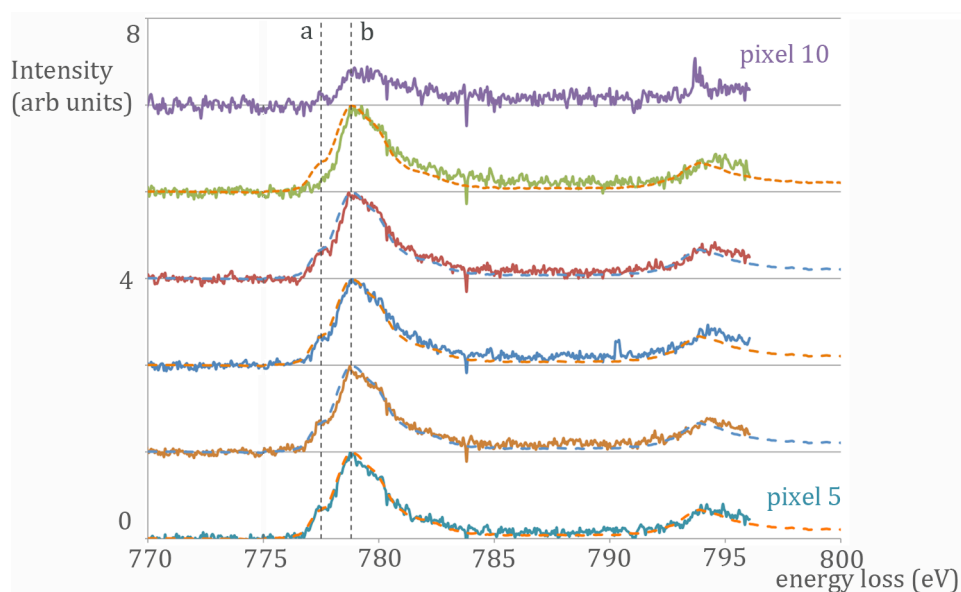


Figure 6.3 – Cobalt $L_{2,3}$ -spectra acquired from the near interface region of specimen 4 (solid) in comparison to reference cobalt $L_{2,3}$ -spectra for bulk CFO (dashed) [15].

It is clear from figure 6.3 that cobalt $L_{2,3}$ -spectra acquired from the bulk of specimen 4 are in good agreement with the cobalt $L_{2,3}$ -spectrum for bulk CFO powder. Chemical shifts were not observed between any spectra shown and it is clear by comparing bulk CFO spectra with spectra from the film that the relative intensity of peak a and b does not change significantly. The peak splitting (b-a) was found to be 1.3 eV for all spectra shown in figure 6.3 other than for spectrum 9.

It is clear that there is a discrete change in the fine structure of spectrum 9, with peak a not present in this spectrum. Comparing to figure 6.4a, an ADF image of the interfacial region of specimen 4, it is clear that this discrete change in fine structure occurs at the substrate/film interface.

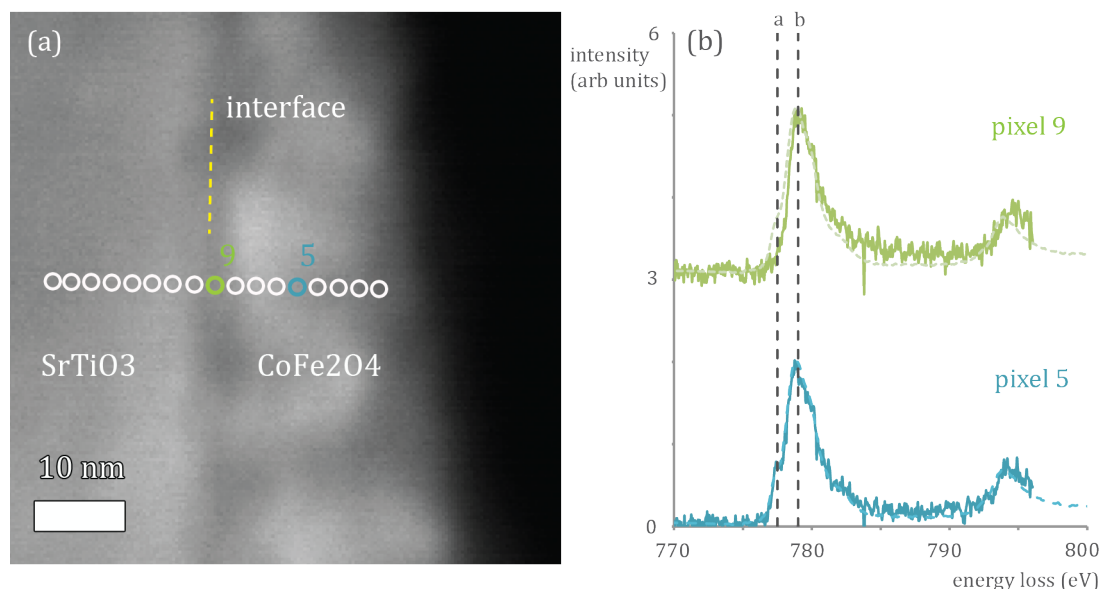


Figure 6.4 –(a)STEM-ADF image of specimen 4 showing individual pixel positions for SI region 2 and (b) Cobalt $L_{2,3}$ -spectra for pixels 5 and 9. It is clear that the relative intensity of peak a is not the same in the bulk of specimen 4 as at the substrate/film interface.

In the octahedral cobalt oxides four major satellite peaks were previously identified in the cobalt L_3 line (chapter 5) in agreement with the literature [116,143]. The energy losses at which these peaks are found in the EELS spectrum are summarised in table 6.1. Abrupt fine structural variations in cobalt $L_{2,3}$ -spectra acquired from the cobalt metal oxides were previously linked to changes in valence. Oxidising cobalt in an octahedral coordination environment from Co^{2+} to Co^{3+} was found to cause a chemical shift in the maximum intensity peak in the cobalt $L_{2,3}$ -spectrum of around 3 eV [143].

Table 6.1 – Summary of the major satellite peaks identified in cobalt $L_{2,3}$ -spectra for Co O_h

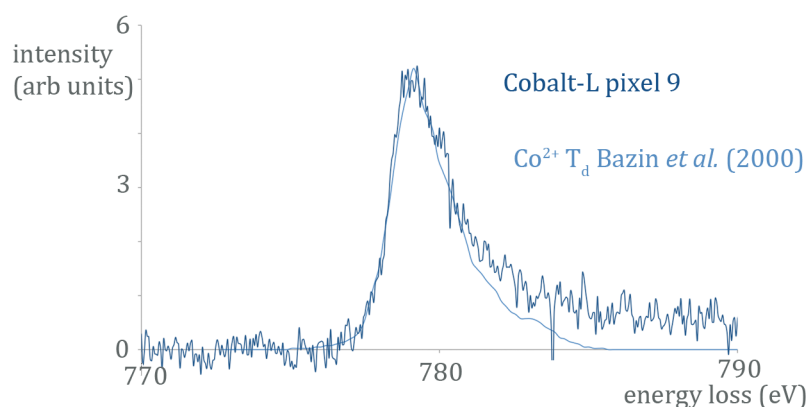
peak	energy loss (eV)
a	778.7
b	780.0
c	781.3
d	783.1

Docherty previously determined the degree of inversion in bulk CFO as $\lambda = 0.82$. Taking the cobalt $L_{2,3}$ -spectrum for $CoFe_2O_4$ as a combination of the O_h and T_d cobalt-L spectra, $\sim 80\%$ of the integrated intensity of the cobalt $L_{2,3}$ -spectrum acquired for bulk CFO originates from the $Co^{2+} O_h$ component. Given the close agreement between cobalt $L_{2,3}$ -spectra acquired from specimen 4 and spectra acquired from bulk CFO, it is argued that cobalt is mostly present in the CFO thin film as $Co^{2+} O_h$. Given that no chemical shift is observed for the main intensity peak in figure 6.3, it is further argued that there is no oxidation of Co^{2+} to Co^{3+} in the 50 nm oxygen annealed film.

The peak splitting observed (b-a) observed in cobalt $L_{2,3}$ -spectra acquired from the CFO film is consistent with the splitting previously observed in bulk CFO and CoO. Terakura *et al.* [140] and Mattheiss [144] previously report experimental and theoretical values for the ground state ligand field splitting in CoO of 1.2 eV. Given the close agreement between the ligand field splitting and peak splitting observed in cobalt $L_{2,3}$ -spectra it is argued that the satellite peaks a and b in the cobalt $L_{2,3}$ -spectrum correspond to transitions to the t_{2g} and e_g states respectively for Co^{2+} in an octahedral crystal field. The peak splitting of $4/9\Delta_{OCT} = 0.53$ eV for $Co^{2+} T_d$ is not resolved, possibly due to the weak contribution of the $Co^{2+} T_d$ component to the CFO cobalt $L_{2,3}$ -spectrum. Split peaks were not identified in a model $Co^{2+} T_d$ cobalt $L_{2,3}$ -spectrum calculated by Bazin *et al.* [116].

Given that peak a and peak b are likely to result from crystal field splitting, it is possible that the intensity of peak a and peak b will be proportional to respective occupancies of the t_{2g} and e_g states. However, given previous observations for cobalt $L_{2,3}$ -spectra acquired from cobalt oxide powders, it is more likely different multiplet structures would be present in the L_3 line for $\text{Co}^{2+} T_d$ and $\text{Co}^{2+} O_h$. Comparing $\text{Co}^{2+} T_d$ and $\text{Co}^{2+} O_h$ spectra previously calculated by CI model [116,142] and acquired by XAS [116,143] supports this hypothesis.

Shown in figure 6.5, are the cobalt $L_{2,3}$ -spectrum for pixel 9 of SI region 2 and cobalt $L_{2,3}$ -spectrum calculated for $\text{Co}^{2+} T_d$ by Bazin *et al* [116]. It is clear from figure 6.5 that there is good agreement between the experimental and model cobalt $L_{2,3}$ -spectra which would suggest that the majority of cobalt in the interfacial region of the CFO film is in T_d coordination.



*Figure 6.5 – Cobalt $L_{2,3}$ -spectrum for SI region 2 pixel 9 in comparison to a $\text{Co}^{2+} T_d$ spectrum calculated using a CI model by Bazin *et al.* [116].*

From HRTEM results presented in chapter 4, the $(001)_{\text{STO}}// (001)_{\text{CFO}}$ orientation relationship in STO/CFO reported in the literature was confirmed [32,34,35]. HRTEM results also showed that in the 50 nm OA film, an in-plane strain of -5.52% at near the interface region due to the substrate/film lattice mismatch.

From crystal field theory it is known that the crystal field energy is inherently sensitive to local symmetry and interatomic spacing. Decreasing the cation-anion spacing would increase electrostatic repulsion, possibly leading to an increase in the crystal field splitting energy. Changes in local symmetry could change the crystal field symmetry and completely change the relative energy separation of the five d orbitals.

By comparing with literature spectra ^[15] it is clear that Co^{2+} is in majority O_h coordination in the bulk. In contrast, results suggest that Co^{2+} was in majority T_d coordination at the interface. Given that CFO is known to be under compression close to the interface, it is possible that the decreased interatomic spacing would lead to an increase in the crystal field splitting energy. It is possible that due to the interfacial strain, the Co^{2+} T_d majority coordination is energetically favourable due to the reduced splitting energy in a T_d crystal field.

6.6.1. Iron $L_{2,3}$

Shown in figure 6.1 are SI and spatial drift correction regions used in the acquisition of a two-dimensional spectrum image of 10 pixels of length 2.4 nm. Shown in figure 6.6 are iron $L_{2,3}$ -spectra for SI region 1. Iron $L_{2,3}$ -spectra for pixels 1 to 7 were normalised against the iron L_3 maximum in order to aid comparisons of near-edge fine structure. Spectra for pixels 8 – 10 were not normalised, as the iron signal was weak.

Shown in figure 6.7, is a higher magnification ADF image of specimen 4 showing the pixel positions of SI 1. From figure 6.7 it is clear that pixel 7 is the closest pixel to the substrate/film interface and pixel 6 and pixel 8 lie in the CFO and STO layers respectively. In contrast to cobalt $L_{2,3}$ -spectra that showed a discrete change in fine structure at the interface, the near-edge fine structure of iron $L_{2,3}$ -spectra shown in figure 6.6.a was seen to vary steadily with pixel position.

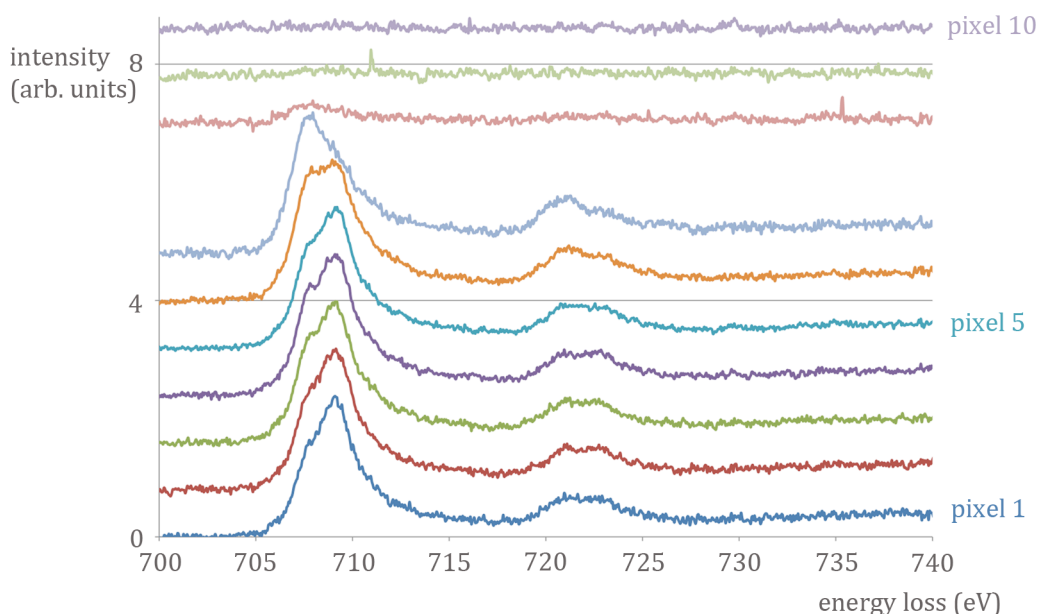


Figure 6.6 – iron $L_{2,3}$ -spectra acquired from specimen 4 by spectrum imaging. Spectra shown are taken from SI region 1 as shown in figure 6.1.

Figure 6.7 shows iron $L_{2,3}$ -spectra acquired from the near interface region of specimen 4. Four major peaks were identified labelled peaks a-d. Iron $L_{2,3}$ -

spectra acquired by Docherty from bulk CFO are overlaid for comparison [15]. From figure 6.7, it is clear that the relative intensity of peak a to peak b is greater for iron $L_{2,3}$ -spectra acquired from the bulk of the film (pixels 1-3) than observed in the reference iron $L_{2,3}$ -spectrum for bulk CFO.

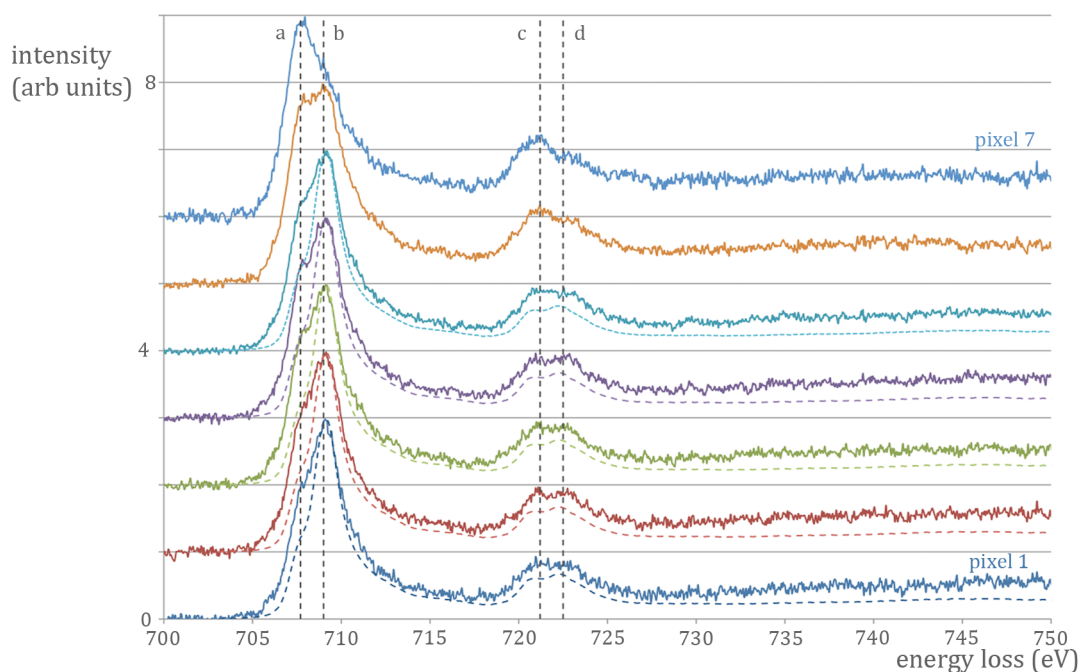


Figure 6.7 – iron $L_{2,3}$ -spectra (solid) acquired from specimen 4. Spectra shown are for pixels 1-7 of SI region 1. Iron $L_{2,3}$ -spectra for bulk CFO [15] (dashed) are shown for comparison.

Results shown in figure 6.7 show that the a/b and c/d peak ratios in spectra acquired from the thin film increase gradually toward the substrate/film interface. Iron L_3 lines for spectra acquired from pixels 1-7 in SI region 1 are shown in figure 6.8. For iron $L_{2,3}$ -spectra acquired from pixels 1-5, the relative intensity of peak b is greater than a. It is clear that for pixel 6, the relative intensity of peak a and b are approximately equal and for pixel 7 peak a is the stronger peak. From figure 6.8 and figure 6.9, it is clear that this significant fine structural change occurs in the spectrum acquired closest to the substrate/film interface.

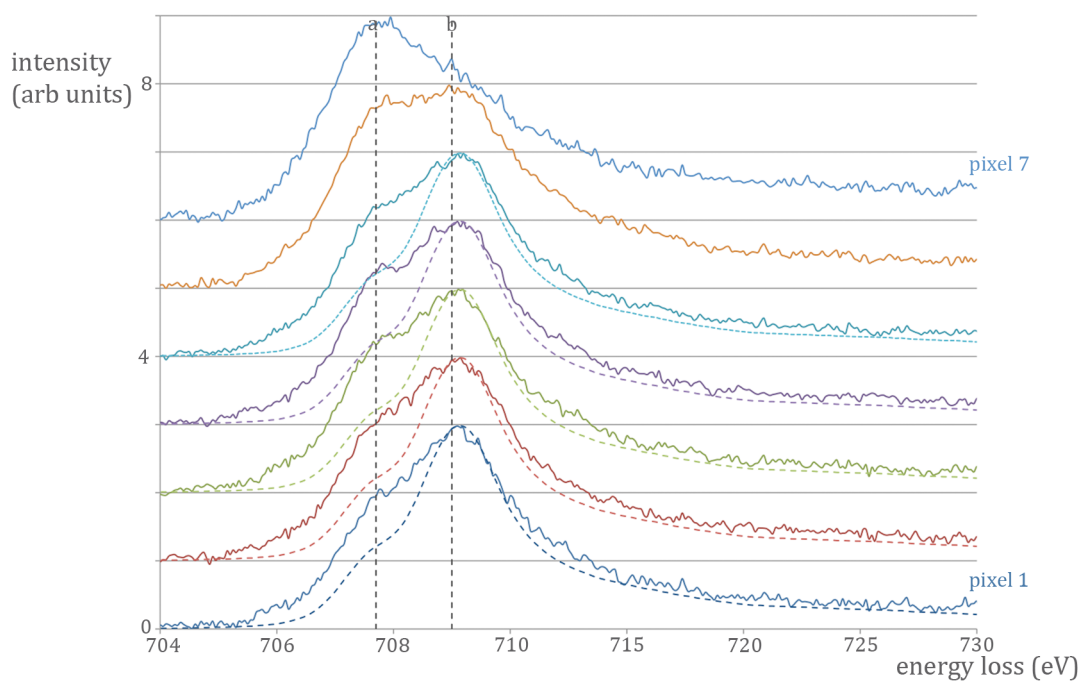


Figure 6.8 – Iron L_3 lines acquired from the specimen 4. Spectra are shown for pixels 1-7 of SI region 1.

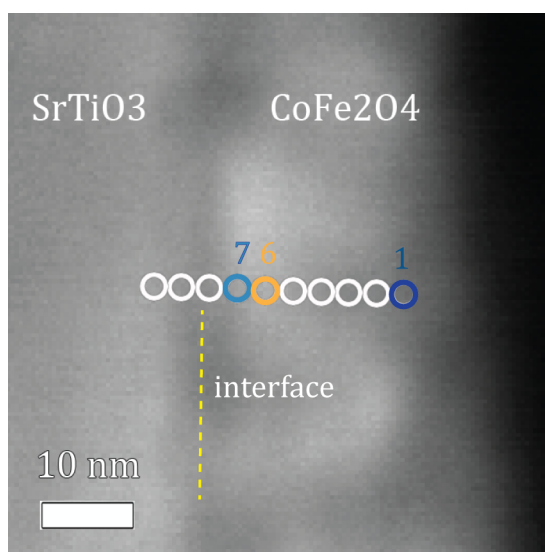


Figure 6.9 – STEM-ADF image of specimen 4 showing individual pixel positions for SI region 1.

The near-edge fine structure of the iron $L_{2,3}$ -spectrum was previously shown to be sensitive to iron valence and coordination environment [61,62,141]. The relative

energy calibration of the iron $L_{2,3}$ -spectra of iron standards was previously defined by an MLLS procedure used to determine λ in bulk CFO. The iron- L_3 maxima for iron standards and bulk CFO are summarised in table 6.2.

Table 6.2 – Summary of iron- L_3 maxima for iron standards and bulk CFO

	Energy-loss (eV)
$\text{Fe}^{2+} \text{O}_h$	710.1
$\text{Fe}^{3+} \text{T}_d$	710.3
$\text{Fe}^{3+} \text{O}_h$	710.7
CFO	710.6

The peak splitting (b-a) observed in figures 6.7 and 6.8 was found to be 1.4 eV. This peak splitting is in reasonable agreement with the peak splitting previously determined for bulk CFO of 1.5 eV and the close to a theoretical value reported by Terakura *et al.* for the ligand field splitting energy in FeO of 1.1 eV ^[140].

For $\lambda = 0.82$, approximately 40% of the total integrated intensity of the iron $L_{2,3}$ -spectrum for CFO is due to $\text{Fe}^{3+} \text{T}_d$. A smoothing filter of width 0.2 eV was applied to the iron $L_{2,3}$ -spectra for pixels 1-7 of SI region 1. The smoothed spectra are shown in figure 6.10. Smoothed spectra shown in figure 6.10 show a feature at energy loss 710.3 eV labelled peak c. The peak spacing b-c is consistent with the expected energy difference of the $\text{Fe}^{3+} \text{T}_d$ and $\text{Fe}^{3+} \text{O}_h$ L_3 maxima shown in table 6.3.

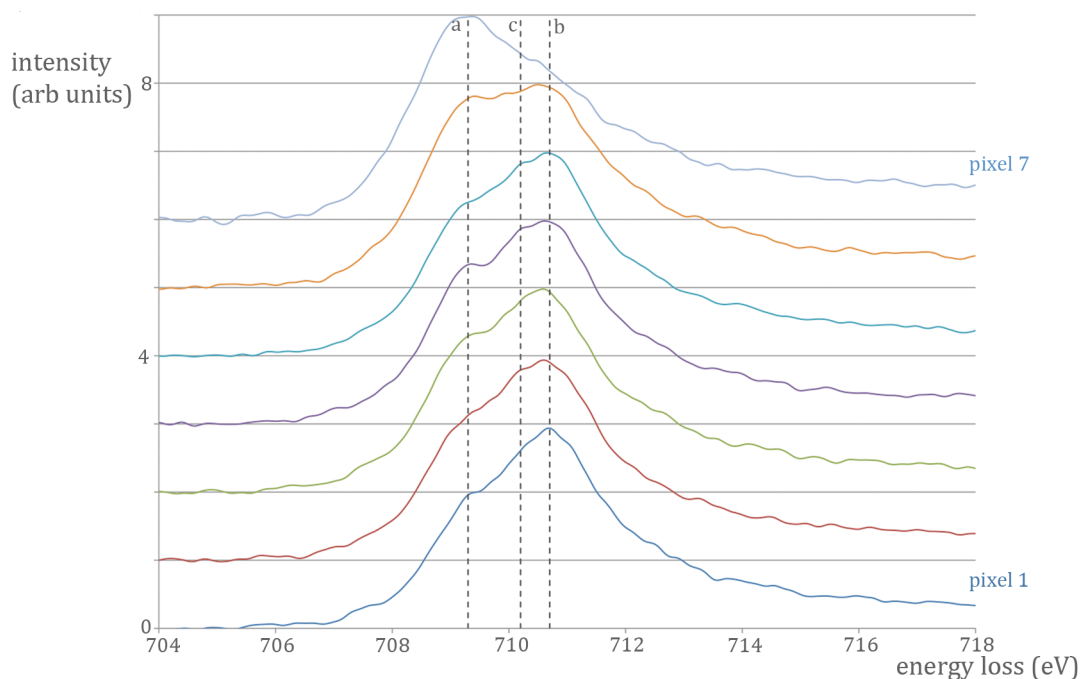


Figure 6.10 – Iron L_3 lines acquired from specimen 4. Spectra smoothed using a 0.2 eV smoothing filter in digital micrograph are shown for pixels 1-7 of SI region 1.

Krishnan ^[139] previously argued that the intensity of the iron $L_{2,3}$ satellite peaks a and b, was directly related to the relative population of the t_{2g} and e_g states oxides. If peak a is correctly assigned and proportional to the t_{2g} population this might suggest that $Fe^{3+} O_h$ is in a majority high spin configuration at the interface and majority low spin configuration in the bulk.

However, this seems unlikely as the magnetic moment of bulk CFO suggests a high spin configuration of both the cobalt and iron cations ^[3]. MLLS fitting and quantification of cobalt and iron $L_{2,3}$ -edges was performed to aid interpretation of the fine structural variations seen in monochromated EELS spectra acquired from specimen 4.

6.4 Multiple Linear Least Squares Fitting

A method to determine the spinel degree of inversion was developed which enabled λ to be calculated by MLLS fitting iron standards to an iron $L_{2,3}$ -spectrum acquired from bulk CFO by Docherty [15].

MLLS fitting was performed using fitting parameters previously optimised for bulk CFO, on iron $L_{2,3}$ -spectra acquired from specimen 4. Fitting was performed on spectra previously discussed in section 6.3 for SI region 1. The energy scale for spectra acquired from CFO was calibrated by defining the peak b maximum (figure 6.13) to 710.7 eV. Energy scales for standard spectra were defined as described in chapter 5, section 5.6. MLLS fitting was performed over a fitting window of 705 – 715 eV. Broadening was not performed on any spectra as all standard and experimental spectra were acquired under the same conditions.

In contrast to previous iron $L_{2,3}$ fitting results for bulk CFO, MLLS fitting performed on spectra acquired from specimen 4 with $\text{Fe}^{3+} \text{O}_h$ and $\text{Fe}^{3+} \text{T}_d$ standards was poor. An example MLLS model function for SI region 1 pixel 3 is shown in comparison to the equivalent experimental spectrum in figure 6.11. By comparing the MLLS fit and experimental spectrum, it is clear that the fine structure of the experimental iron $L_{2,3}$ -spectrum is poorly reproduced by the model. The quality of fit worsened as the pixel number was increased.

$\text{Fe}^{3+} \text{T}_d$ and $\text{Fe}^{3+} \text{O}_h$ standards are shown in figure 6.12a in comparison to the experimental iron $L_{2,3}$ -spectrum for SI region 1 pixel 3. From figure 6.12a, it is apparent that the $\text{Fe}^{3+} \text{T}_d$ and $\text{Fe}^{3+} \text{O}_h$ standards cannot reproduce the relative intensities of peak a and peak b seen in experimental data which would explain the poor fit seen in figure 6.11. χ^2 values shown in figure 6.14b are 1-2 orders of magnitude greater than observed for the best fit to bulk CFO, clearly indicating a poor fit of $\text{Fe}^{3+} \text{T}_d$ and $\text{Fe}^{3+} \text{O}_h$ standards to iron $L_{2,3}$ -spectra acquired from the post-annealed 50 nm STO/CFO sample. Given the poor fit, λ was not calculated.

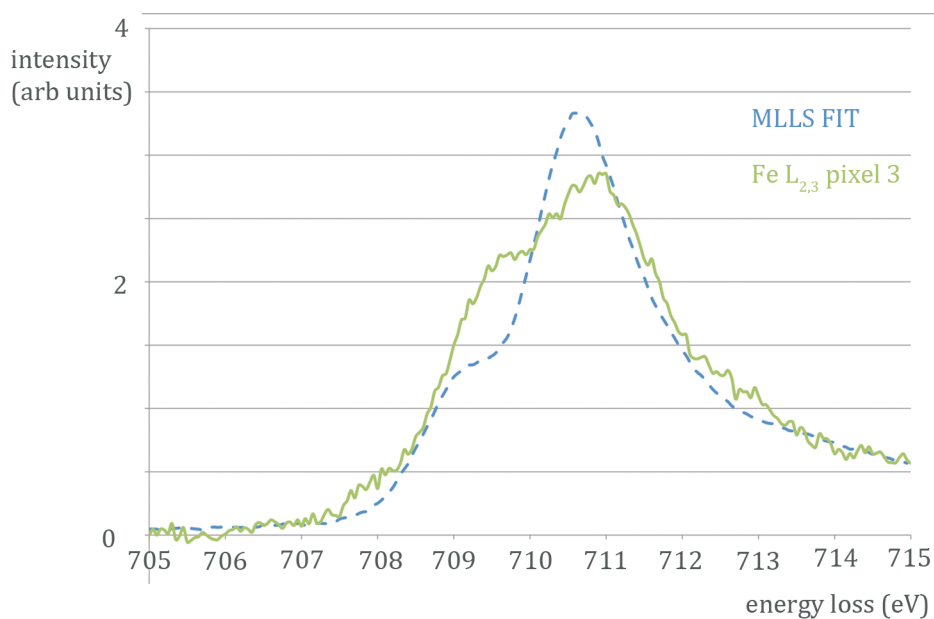


Figure 6.11 – MLLS model function generated from fitting Fe^{3+}O_h and Fe^{3+}T_d standards to an iron $\text{L}_{2,3}$ -spectrum from pixel 3 of SI region 1.

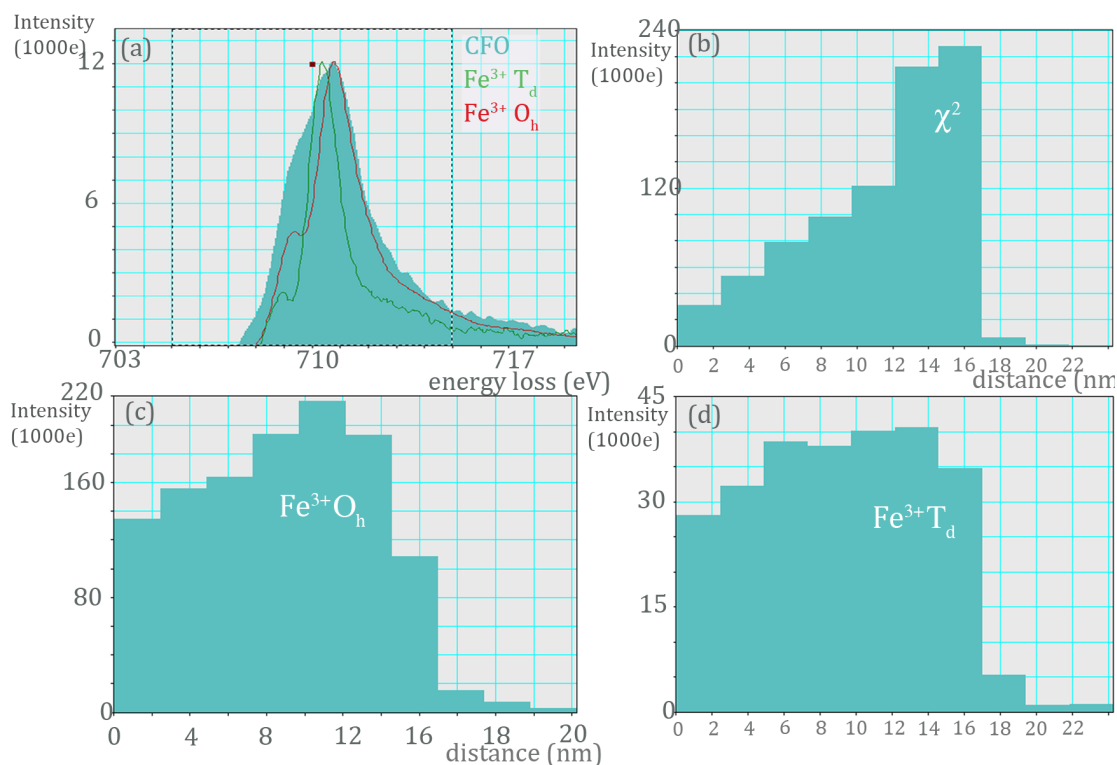


Figure 6.12 – MLLS fitting parameters and results for specimen 4. (a) Standard spectra and iron $\text{L}_{2,3}$ -spectrum for STO/CFO, (b) χ^2 vs distance, (c) integrated intensity of Fe^{3+}O_h vs distance and (d) integrated intensity of Fe^{3+}T_d vs distance.

Large values of χ^2 calculated during MLLS fitting are reported to be a possible indication of an absence of fitting components necessary for an accurate fit to experiment [148]. Given the poor fit for $\text{Fe}^{3+} \text{O}_h$ and $\text{Fe}^{3+} \text{T}_d$, a second fit was performed using $\text{Fe}^{3+} \text{O}_h$ and $\text{Fe}^{2+} \text{O}_h$ standards. MLLS model functions for $\text{Fe}^{3+} \text{O}_h$ and $\text{Fe}^{2+} \text{O}_h$ fitting are shown in figure 6.13 in comparison to experimental spectra for SI 1, pixels 3 and 6.

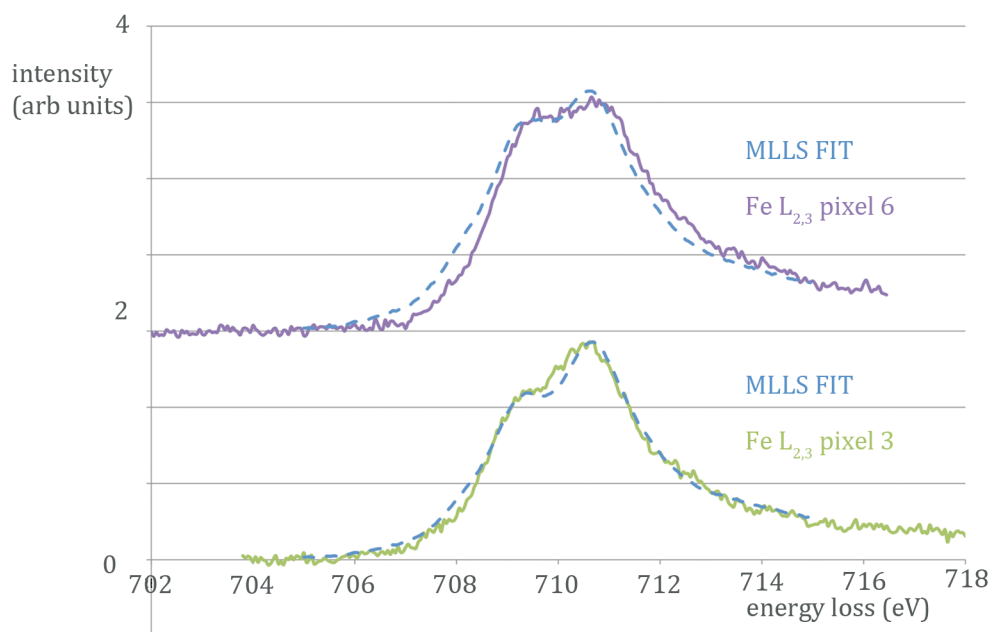


Figure 6.13 - MLLS model functions generated from the fitting of $\text{Fe}^{2+} \text{O}_h$ and $\text{Fe}^{3+} \text{O}_h$ standards to iron $\text{L}_{2,3}$ -spectra for SI region 1, pixels 3 and 6.

It is clear from figure 6.13 that the model functions for pixels 3 and 6 reproduce the experimental fine structure well in comparison to the fitting results for $\text{Fe}^{3+} \text{O}_h$ and $\text{Fe}^{3+} \text{T}_d$ standards. $\text{Fe}^{3+} \text{O}_h$ and $\text{Fe}^{2+} \text{O}_h$ standards are shown in figure 6.14a in comparison to an experimental iron $\text{L}_{2,3}$ -spectrum taken from SI region 1 that was smoothed using a smoothing filter of width 0.2 eV in digital micrograph. A comparison of the fine structure of the $\text{Fe}^{2+} \text{O}_h$ and $\text{Fe}^{3+} \text{T}_d$ standards would suggest that the fine structure of the experimental spectrum would be reproduced well.

Comparing the χ^2 values shown in figure 6.14b with χ^2 values for the $\text{Fe}^{3+} \text{T}_d$ and $\text{Fe}^{3+} \text{O}_h$ fit shown in figure 6.12b, it is clear that χ^2 is significantly reduced by fitting to $\text{Fe}^{2+} \text{O}_h$ and $\text{Fe}^{3+} \text{O}_h$. This clearly indicates a better MLLS fit for $\text{Fe}^{2+} \text{O}_h$ and $\text{Fe}^{3+} \text{O}_h$ than $\text{Fe}^{3+} \text{O}_h$ and $\text{Fe}^{3+} \text{T}_d$. χ^2 values shown in figure 6.14b were high in comparison to the optimised value for bulk CFO ($\chi^2 = 824$). This is possibly due to the poorer signal to noise ratio observed in spectra acquired from the film and might be performing the MLLS fit on smoothed spectra. It is clear from figure 6.14b that χ^2 steadily increases from the bulk of the film (distance = 0 nm) to the interface (distance = 12 - 14 nm), indicating a degrading quality of fit with as the $\text{Fe}^{2+} \text{O}_h$ integrated intensity increased, as seen from figure 6.14d.

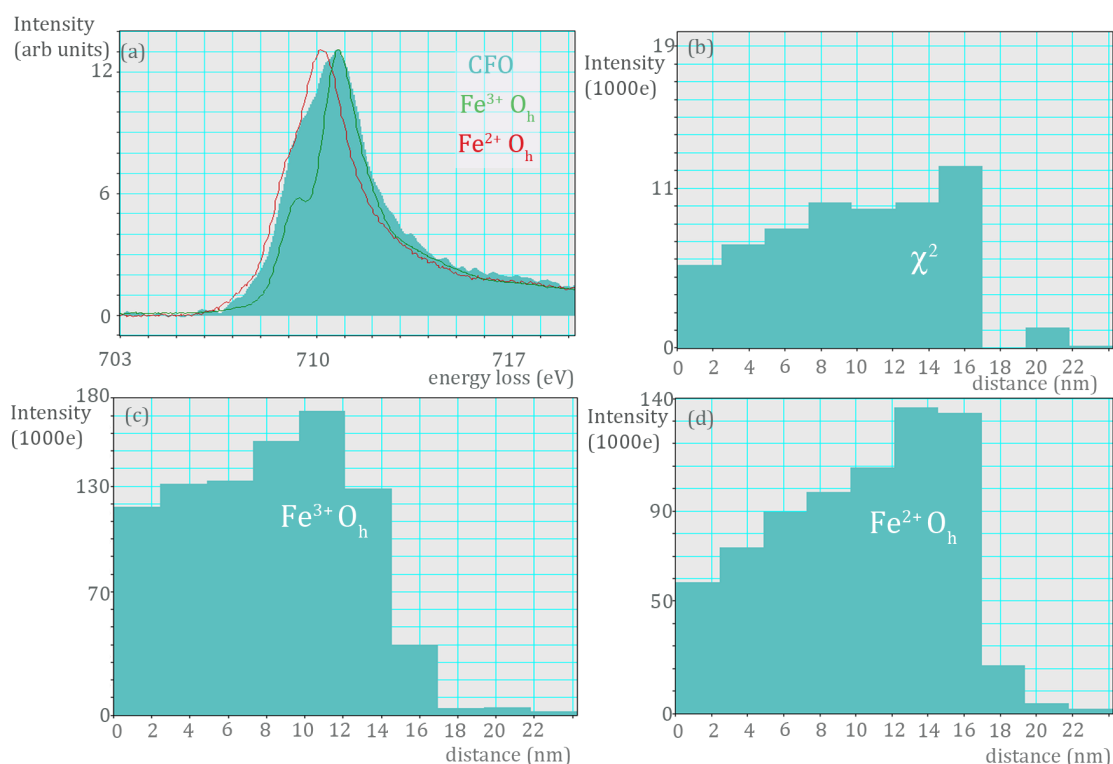


Figure 6.14 – MLLS fitting parameters and results for specimen 4. (a) Standard spectra and iron $L_{2,3}$ -spectrum for STO/CFO, (b) χ^2 vs distance, (c) integrated intensity of $\text{Fe}^{3+} \text{O}_h$ vs distance and (d) integrated intensity of $\text{Fe}^{2+} \text{O}_h$ vs distance.

Given the reasonable fit for $\text{Fe}^{3+} \text{O}_h$ and $\text{Fe}^{2+} \text{O}_h$ in comparison to $\text{Fe}^{3+} \text{O}_h$ and $\text{Fe}^{3+} \text{T}_d$, the relative Fe^{2+} and Fe^{3+} compositions were estimated from the modified integrated intensities of the $\text{Fe}^{2+} \text{O}_h$ and $\text{Fe}^{3+} \text{O}_h$ standards used to form MLLS model functions in SI 1. Shown in figure 6.15 are plots of the variations of the $\text{Fe}^{3+} \text{O}_h$ and $\text{Fe}^{2+} \text{O}_h$ integrated intensity, as fraction of the total model function intensity, against position in the SI. For pixels 9 and 10 noise represents a significant fraction of the total intensity of iron $L_{2,3}$ -spectra acquired at these positions on specimen 4. As a result, the Fe^{2+} and Fe^{3+} fraction calculated by MLLS at these positions is argued to be unreliable and will not be discussed further.

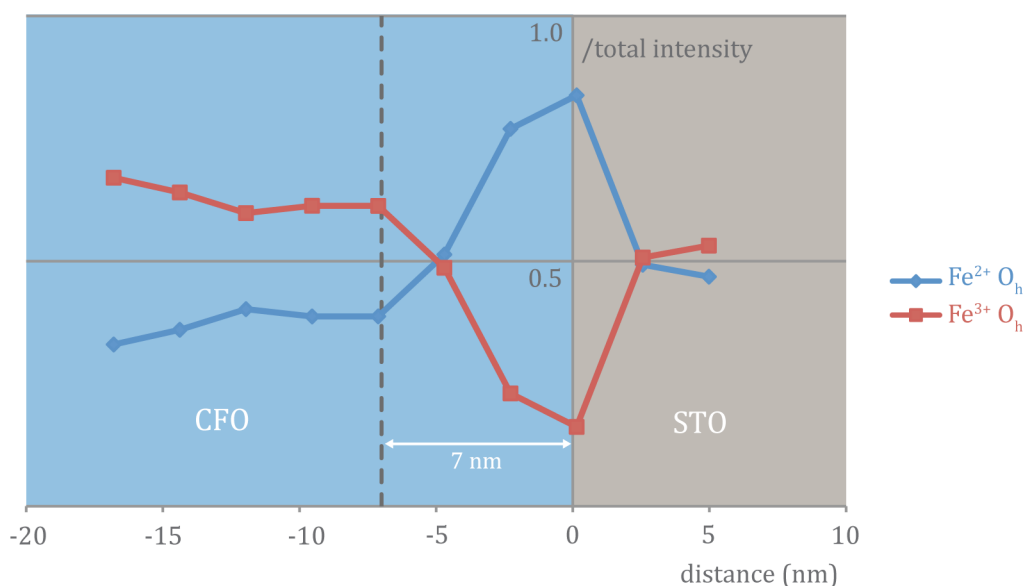


Figure 6.15 - $\text{Fe}^{2+} \text{O}_h$ and $\text{Fe}^{3+} \text{O}_h$ integrated intensity as a fraction of total model function intensity for SI 1 against position in the spectrum image. Data is for the MLLS fitting performed using $\text{Fe}^{2+} \text{O}_h$ and $\text{Fe}^{3+} \text{O}_h$ standards and an iron $L_{2,3}$ spectrum image from SI region 1.

Results shown in figure 6.15 suggest that in the bulk of the film, iron is present mostly as $\text{Fe}^{3+} \text{O}_h$ (70-60%) with a smaller amount of Fe^{2+} (30-40%) also present. At a distance of ~ 7 nm from the STO/CFO interface, the relative Fe^{2+} concentration is seen to increase and the relative Fe^{3+} concentration begins to fall. MLLS fitting results for $\text{Fe}^{2+} \text{O}_h$ and $\text{Fe}^{3+} \text{O}_h$ standards suggest an approximate

iron composition of $\text{Fe}^{2+}_{0.85}\text{Fe}^{3+}_{0.15}$ at the STO/CFO interface. In order to aid interpretation of results from this MLLS fitting, quantification was performed on iron and cobalt $\text{L}_{2,3}$ -edges acquired as part of a non-monochromated spectrum image acquired using the Imperial College FEI Titan in unfiltered mode.

6.5 Quantification

An ADF image of specimen 4 acquired in unfiltered mode is shown in figure 6.16. The region shown in figure 6.16 is not the same region as discussed in previous sections of this chapter. Shown in figure 6.16 are the spatial drift and spectrum image regions used for the acquisition of a 50 pixel 2D spectrum image of pixel length 0.93 nm. From figure 6.16 it is clear that the interface between the film and substrate is sharp. A number of white spots are clearly visible that are likely to be contamination spots from previous imaging and analysis in STEM.

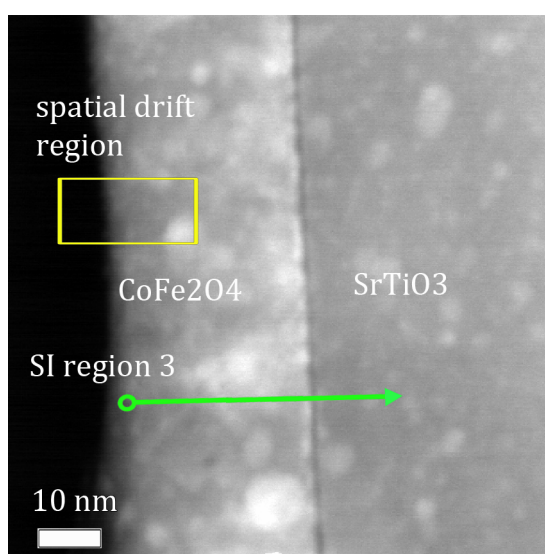


Figure 6.16 – STEM-ADF image of a 50 nm oxygen post-annealed STO/CFO thin film acquired in unfiltered mode. The STO substrate, CFO film, spectrum image region and spatial drift correction region are marked.

Low loss and core loss spectrum images were acquired under the conditions given in section 6.2. Background subtraction was carried out using inverse power model of the form AE^{-r} . Background fitting windows used to extract the iron and cobalt $L_{2,3}$ -edges are shown in figure 6.17a and figure 6.17b respectively. The single scattering distribution was recovered by performing a Fourier ratio deconvolution on the core loss SI with a low loss SI acquired from the same specimen region under the same experimental conditions. The relative iron and cobalt compositions were determined by EELS quantification

performed on the deconvolved core loss spectrum image. EELS quantification parameters used for the iron and cobalt $L_{2,3}$ -edges are shown in figure 6.17. Hartree-Slater models (section 2.12.2) were used for differential energy cross sections used to determine the partial Co and Fe cross sections are shown in figure 6.17

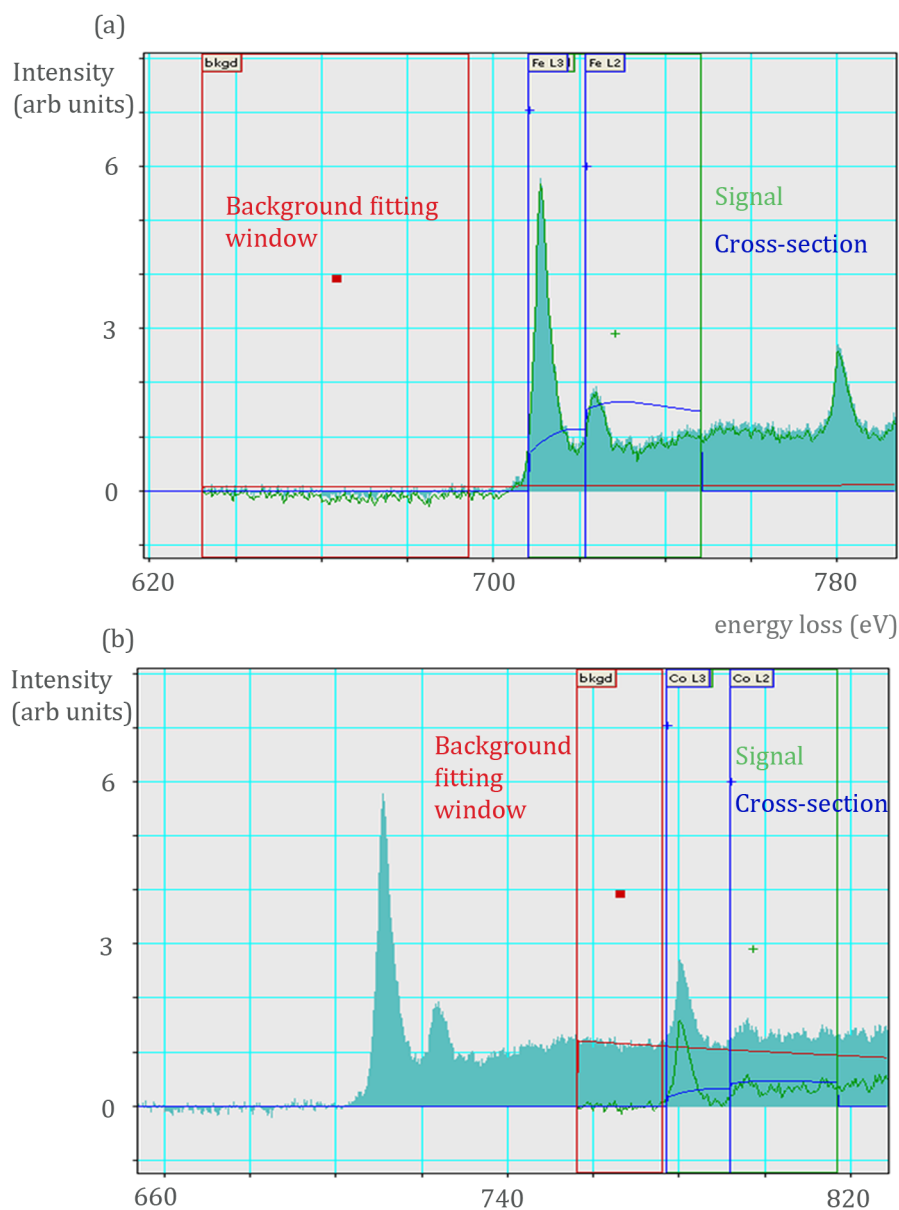


Figure 6.17 – Deconvolved core loss EELS spectra acquired from SI region 3 showing background fitting windows, signal extraction windows and Hartree-Slater cross-sections used to determine the relative: (a)iron and (b)cobalt composition in specimen 4.

Plots of the variation in relative iron and cobalt composition with pixel position in SI region 3 are shown in figure 6.18. From figure 6.18 it is apparent that the relative composition of iron and cobalt does not change significantly over the film. The average relative compositions over the entire SI region were $(71 \pm 1)\%$ for iron and $(27 \pm 4)\%$ for cobalt. Errors were determined from the statistical error in the mean ($\sigma/\sqrt{N}$), where σ is the standard deviation in a data set of N components.

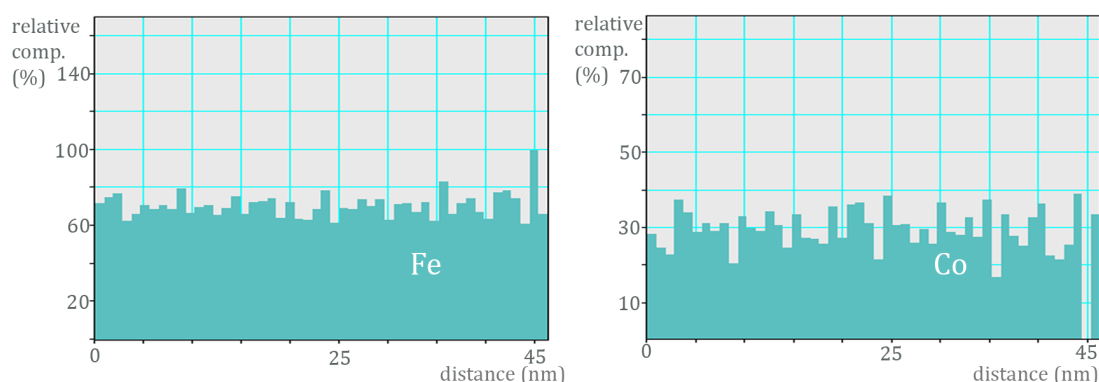


Figure 6.18 – Relative iron and cobalt composition as determined by EELS quantification.

The expected Fe:Co ratio in stoichiometric CFO is 2:1. As the Fe:Co ratio determined from 50 nm STO/CFO was approximately 7:3, it is likely that the CFO is non-stoichiometric and iron rich ($\text{CoFe}_{2.33}$). Cheng and Downing^[150] previously suggest that Co^{2+} ions on O_h sites are replaced with Fe^{2+} ions in non-stoichiometric iron rich CFO.

Quantification of core loss edges that are closely spaced in the EELS spectrum is often problematic as the tail of a preceding edge can give a background for the following core loss edge that cannot be modelled using a conventional inverse power law^[56,151]. From figure 6.17 it is clear that if the background window used to generate the background model for cobalt were increased in width, the background model function would become unphysical due to the tail of the preceding iron $\text{L}_{2,3}$ -edge. Given the proximity of the iron and cobalt $\text{L}_{2,3}$ -edges in the EELS spectrum, relative composition might be determined more accurately by MLLS fitting^[151].

6.6 Discussion

A schematic of post-annealing processes previously shown in chapter 1 is shown in figure 6.19 to aid discussion. Oxidation and cation ordering layers are shown.

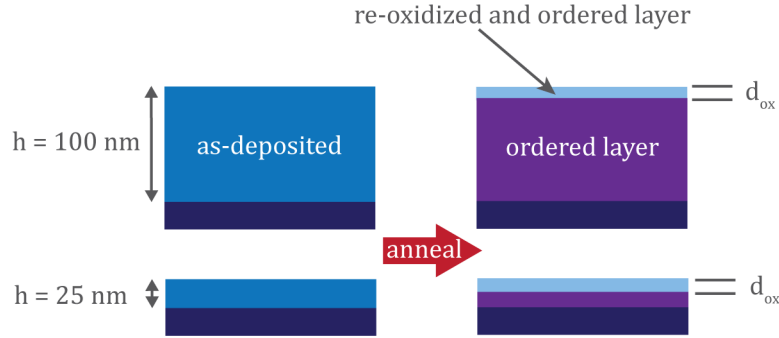


Figure 6.19 Illustration of the relationship between thickness of reoxidized layer (d_{ox}) after annealing and the total film thickness (h) and ordered layers predicted to arise from oxygen post-annealing [3].

Axelsson *et al.* [3] previously proposed a formula for as-deposited CFO as,

$$\text{Co}^{2+}\text{Fe}_{2w}^{2+}\text{Fe}_{2(1-w)}^{3+}\text{O}_{4-w}\square_w \quad (6.1)$$

where $\square$ represents a vacancy. Cations were assumed to be randomly distributed between A and B sites to account for structural disorder expected from the PLD growth conditions [3,26].

During post-annealing, cation ordering is argued to take place by short-range diffusion, simultaneously over the film volume. Axelsson *et al.* [3] predict that this short range diffusion leads to a modification to the perfect inverse CFO structure as shown in equation 6.2.

$$\left(\text{Fe}_{2w}^{2+}\text{Fe}_{1-w}^{3+}\right)\left[\text{Co}^{2+}\text{Fe}_w^{2+}\text{Fe}_{1-w}^{3+}\right]\text{O}_{4-w}\square_w \quad (6.2)$$

Axelsson *et al.* [3] also predict oxidation to occur during post-annealing, by long-range diffusion of oxygen and/or cation vacancies. Vacancy diffusion was argued

to be dominant, leading to a modification to the perfect inverse structure as shown in equation 6.3.

$$\left(\text{Fe}_{1-y/4}^{3+}\square_{y/4}\right)\left[\text{Co}_{1-y/4}^{2+}\text{Fe}_{1-y/4}^{3+}\square_{y/2}\right]\text{O}_{4-y}\square_y \quad (6.3)$$

where $w = 4y/(4-y)$. Stoichiometric inverse CFO is then thought to form by vacancy annihilation [3].

In order to validate the chemical model proposed by Axelsson *et al.* [3] differences in the chemical formulae of: as-deposited, cation ordered and post-annealed CFO (equations 6.1 – 6.3) were identified and compared to the iron and cobalt EELS fine structural analysis performed previously in this chapter.

6.6.1. Cation Reordering

From equation 6.1 it is clear that for an AD CFO film, Axelsson *et al.* [3] expect CFO that is oxygen deficient, with Co^{2+} , Fe^{2+} and Fe^{3+} cations occupying both T_d and O_h sites. If cation ordering occurs during post-annealing as predicted, the short-range diffusion of cations in the CFO is expected to affect the O_h and T_d site occupancy leaving the oxygen stoichiometry unaffected. From equation 6.2, Co^{2+} cations are expected to occupy O_h sites only. Fe^{2+} and Fe^{3+} are predicted to occupy both O_h and T_d sites in cation ordered CFO.

As previously discussed in section 6.3.1, the fine structure of cobalt $L_{2,3}$ -spectra acquired from the bulk of specimen 4 is in close agreement with the fine structure of a cobalt $L_{2,3}$ -spectrum acquired from bulk CFO by Docherty [15]. Docherty [15] also reports a degree of inversion in bulk CFO of $\lambda = 0.82$. As the fine structure in a transition metal $L_{2,3}$ -edge reflects both the metal valence and coordination, it is likely that in the bulk of specimen 4, CFO has an approximate degree of inversion of $\lambda \sim 0.8$. It is apparent that the chemical model proposed is immediately limited as a fully inverse structure is predicted for CFO. It is clear from fine structural analysis of Co $L_{2,3}$ -spectra acquired from

specimen 4 that CFO is not fully inverse, in agreement with Docherty ^[15], Vaingankar ^[20], Rieck and Thijssen ^[21] and Sawatzky *et al.* ^[22].

For post-annealed CFO, Axelsson *et al.* ^[3] predict a change from a random cation arrangement as predicted for as-deposited CFO, to a cation arrangement in which cobalt is present as Co^{2+} O_h only. In a random spinel, the cation distribution over A and B sites is such that the T_d sites are occupied by 1/3A and 2/3B cations ^[12]. This random distribution would lead to CFO of chemical formula $(\text{Co}_{0.33}\text{Fe}_{1.33})[\text{Co}_{0.66}\text{Fe}_{0.66}]\text{O}_4$. Given the close agreement in cobalt ELNES acquired from specimen 4 and that previously acquired by Docherty ^[15], it is argued that the ideal inversion parameter for CFO can be approximated to be $\lambda = 0.8$, lowering the constraints of the chemical model. In this case, cation diffusion as predicted by Axelsson *et al.* ^[3] would give rise to an approximate change in cobalt stoichiometry in CFO from $(\text{Co}_{0.33})[\text{Co}_{0.66}]$ to $(\text{Co}_{0.2})[\text{Co}_{0.8}]$.

Given the close agreement in the fine structure of Co $\text{L}_{2,3}$ -spectra acquired by Docherty ^[15] with Co $\text{L}_{2,3}$ -spectra acquired from the bulk of specimen 4 it seems likely that the cobalt stoichiometry in the bulk of specimen 4 is close to $(\text{Co}_{0.2})[\text{Co}_{0.8}]$. The increase in Co concentration on O_h sites is in support of the chemical model and the concept of oxygen post-annealing induced cation diffusion.

As previously discussed in section 6.3.1, the fine structure in Co $\text{L}_{2,3}$ -spectra acquired from specimen 4 suggests that at a distance of approximately 0 – 2.4 nm from the STO/CFO interface, cobalt was present in majority as Co^{2+} T_d cobalt composition of Co^{2+} T_d . The chemical model proposed cannot describe this change.

As formulae for as-deposited and cation ordered CFO contain both Fe^{2+} and Fe^{3+} on O_h and T_d sites it is not possible to support these predictions with analysis of the iron $\text{L}_{2,3}$ -spectrum ELNES from specimen. Taking into consideration the effects of crystal field symmetry, the high Fe^{2+} concentration at the interface is possibly a contributing factor to the change in Co^{2+} coordination at the STO/CFO

interface, as Fe^{2+} would preferentially occupy O_h sites though further work is needed for this to be confirmed.

6.6.2. Oxidation

Axelsson *et al.* [3] propose oxygen deficiency in as-deposited CFO films is reduced during oxygen post-annealing by oxidation. It is argued that the oxidation will occur by long-range diffusion of oxygen and/or cation vacancy diffusion. Chen and Downing [150] previously report the dominance of cation vacancy migration in CFO compared to oxygen diffusion which also agrees with Giletti and Hess [152] who report a generally slow oxygen exchange rate in a similar spinel material, magnetite, even at high temperature. It was previously argued by Axelsson *et al.* [3] that with increased annealing time diffusion of oxygen and cation vacancies through the oxidation layer would become increasingly difficult, limiting the thickness of oxidized layer (d_{ox}) as shown in figure 6.19.

A CFO structure containing oxygen deficiencies and cation deficiencies on both O_h and T_d sites was predicted as consequence of oxygen and cation vacancy diffusion. O_h sites were predicted to be occupied by Co^{2+} and Fe^{3+} cations with T_d sites predicted to be occupied by Fe^{3+} . Comparing to the cation ordered CFO (equation 6.2), it is clear that there is an absence of Fe^{2+} in the oxidized and cation ordered structure (equation 6.3). Fe^{2+} is also not present in ordered stoichiometric CFO.

It is clear from equation 6.3 and the chemical model, that the cation distribution over O_h and T_d sites is not expected to be affected by oxidation of the CFO. As a result the cobalt chemistry observed in specimen 4 and discussed in section 6.6.1 does not contradict the possibility of further oxygen and cation vacancy diffusion. However, as for the cation ordering model, the oxygen and cation vacancy diffusion model is not sufficiently robust to directly explain the change in cobalt coordination (and therefore change in degree of inversion) observed at the STO/CFO interface in specimen 4.

A key aspect of the oxygen and cation vacancy diffusion model is the existence of a thickness limited oxidation layer. If present, this layer would be observable as a transition from the structure shown in equation 6.3 to structure more like that shown in equation 6.2 or, stoichiometric CFO of $\lambda = 0.8$; $(\text{Co}^{2+}_{0.2}\text{Fe}^{3+}_{0.4})[\text{Co}^{2+}_{0.8}\text{Fe}^{3+}_{1.6}]\text{O}_4$.

As discussed in section 6.4, iron was found to be present in the bulk of specimen 4 in mixed valence (70-60% Fe^{3+} O_h , Fe^{2+} O_h 30-40%). The Fe^{2+} O_h concentration was found to increase as the Fe^{3+} O_h concentration decreased so that at the interface the approximate iron stoichiometry was $\text{Fe}^{2+}_{0.85}\text{Fe}^{3+}_{0.15}$. This increase in Fe^{2+} concentration with increasing distance from the free surface of the CFO film is consistent with the chemical model proposed by Axelsson *et al.* [3] for oxidation mediated by oxygen and cation vacancy diffusion.

Axelsson *et al.* [3] predict final ordering in CFO to occur by vacancy annihilation. The presence of a significant Fe^{2+} concentration in the bulk of specimen 4 would either suggest that either this vacancy annihilation process is incomplete or stoichiometric CFO does not form under the PLD deposition conditions applied. This is further supported by quantification results indicating that the 50 nm oxygen post-annealed STO/CFO under investigation was iron rich. Such stoichiometry might provide charge compensation for the predicted Fe^{2+} content, though the quantification data available is insufficient for any firm conclusions to be made. A further consequence of the presence of Fe^{2+} would be a decrease in M_s with respect to stoichiometric CFO as the spin moment for Fe^{2+} is less than Fe^{3+} .

6.7 Conclusion

Analysis of the fine structure of cobalt $L_{2,3}$ -spectra acquired from an oxygen post-annealed 50 nm STO/CFO thin film showed that in the bulk of the film, the majority of cobalt was present in divalent form and octahedral coordination. A discrete change in fine structure was observed at the interface, possibly attributed to strain observed in previous microstructural investigations by HRTEM or an increase in the Fe^{2+} concentration at the interface. The near edge fine structure of cobalt $L_{2,3}$ -spectra acquired at the STO/CFO interface suggested a majority local cobalt environment of $Co^{2+} T_d$.

Fine structural analysis of iron and cobalt $L_{2,3}$ -spectra acquired by monochromated STEM-EELS has provided some confirmation of the validity of the chemical model previously proposed by Axelsson *et al.* [3] to explain variations in the magnetic hysteresis loops of (001) STO/CFO thin films associated with post-processing conditions (section 1.6.2). Majority cobalt coordination was identified in the bulk of a 50 nm oxygen post-annealed (001) STO/CFO film consistent with that expected to result from annealing induced cation diffusion. Variations in iron valence were identified that were consistent with predictions of annealing induced vacancy driven oxidation. A number of limitations of the chemical model were also identified.

In the chemical model, ordered CFO was predicted to be fully inverse which was found to be inconsistent with monochromated STEM-EELS results in addition to previous investigations found in the literature [15,20-22]. A local change in cobalt coordination observed at the STO/CFO interface in the 50 nm oxygen post-annealed (001) STO/CFO film could not be explained by the model.

Further work is needed to provide full validation of the chemical model. This would be in the form of the same set of monochromated EELS experiments on an as-deposited (001) STO / CFO film of thickness 50 nm, and analysis of the oxygen stoichiometry in both the AD and OA films.

Chapter 7 – Conclusions and Future Work

7.1 Introduction

In this thesis, the structure-property-processing relationship in STO/CFO has been investigated for as-deposited and oxygen annealed films of thickness less than 200 nm. Structural relaxation mechanisms were investigated by aberration corrected HRTEM, which provided new and useful information about misfit accommodation in perovskite/spinel thin film systems. Monochromated STEM-EELS results for a post-annealed STO/CFO enabled bulk magnetic properties to be correlated with local chemistry, providing a some verification of the chemical model for the relationship between M_s and CFO chemistry previously reported by Axelsson *et al.* [3].

7.2 Conclusions

7.2.1. Specimen Preparation

High quality TEM specimens that are representative of bulk material are essential for meaningful and accurate (S)TEM analysis of a material. XTEM specimens were prepared from STO/CFO and LAO/CFO thin films by INLO using a dual beam FIB system and conventional argon ion milling. Low energy argon milling was also performed on FIB prepared specimens. Carbon coating was investigated as a method for the prevention of specimen charging. XTEM preparation methods were assessed based on XTEM specimen properties that included: relative specimen thickness and lattice image quality (HRTEM, HRSTEM). XTEM specimen quality was found to vary with the preparation technique and preparation parameters such as milling energy. Differences in reproducibility were also identified.

7.2.1.1. Dual beam FIB

Dual beam FIB performed using a Nova nanolab system (FEI, NL) was found to yield high quality STO/CFO XTEM specimens and gave high sample throughput compared to conventional argon milling by the method reported by Scott *et al.* [96]. High reproducibility was observed; 100% of the XTEM specimens prepared were suitable for TEM and STEM imaging. TEM and STEM imaging performed on FIB prepared STO/CFO specimens showed regions of STO/CFO that were electron transparent with the substrate/film interface region visible over areas of over $\sim 0.01 \mu\text{m}^2$. While dual beam FIB produced XTEM specimens that were suitable for low magnification imaging, thickness mapping showed that the relative thickness variation over the electron transparent regions was too great for meaningful EELS analysis.

High quality HRTEM images were acquired from an XTEM specimen prepared from an STO/CFO film of thin film thickness 50 nm, suggesting low kV cleanup at 5 kV was effective in removing amorphous damage. However, considerable differences were observed in STO lattice images acquired from further XTEM specimens prepared by INLO under the same conditions. While dual beam FIB was shown to produce XTEM specimens consistently, that were suitable for low magnification imaging in TEM and STEM, specimens could not be produced reproducibly that were suitable for good HRTEM or EELS analysis.

7.2.1.1. Argon Ion Milling

Conventional argon milling [96] was found to produce high quality XTEM specimens suitable for TEM and STEM imaging that were also suitable for HRTEM and EELS analysis. In comparison to dual beam FIB, specimen throughput and reproducibility was poor as the argon ion beam easily removed regions of interest. Reproducibility was improved by performing high energy milling (5 kV) perpendicular to the substrate/film interface until perforation, followed by low energy milling (1 kV – 0.2 kV) parallel to the substrate interface. This was found to reduce specimen thickness controllably and allowed specimen regions to be prepared that were suitable for HRTEM analysis, that were typically much larger ($\sim 0.1 \mu\text{m}^2$) than equivalent regions for FIB prepared

specimens. Results showed that low energy argon milling produced regions that were thinner than FIB prepared specimens. In general, amorphous damage was reduced with greater success by low energy ion milling than low kV cleanup in FIB. As a result, XTEM specimens prepared by argon ion milling were more suitable for HRTEM and HRSTEM imaging and EELS analysis.

In contrast to FIB prepared specimens, XTEM specimens prepared by argon ion milling suffered from severe hydrocarbon contamination during STEM imaging and EELS analysis. The effect of contamination was effectively eliminated by plasma cleaning XTEM specimens for 30 minutes in Ar/O₂ plasma with a 50% rest period, before argon milling.

Results showed that low temperature milling performed at 1 kV caused less sputtering damage than 1 kV milling at room temperature. No differences in specimen quality were observed between specimens milled at 0.5 kV at room and low temperature. Results showed that low temperature argon milling performed at 0.2 kV produced the best XTEM specimen sample though the effect of low energy and low temperature could not be separated in this case.

7.2.1.1. Dual beam FIB and Argon Ion Milling

FIB prepared specimens were subjected to low energy ion milling using a PIPS (Gatan, UK) to reduce specimen thickness and remove amorphous damage. Relative thickness results showed that the FIB specimen thickness could be successfully reduced by argon milling at 1 kV using a single ion gun and no specimen rotation. However, after argon milling under these conditions thickness change of $0.3 < t/\lambda < 1.0$ was observed over the electron transparent region of the FIB specimen which was too high for EELS analysis. Double-sided 1kV thinning performed on another FIB specimen did not lead to any measurable reduction in thickness of a second FIB specimen. The limited success of argon milling performed on FIB specimens using a PIPS (Gatan, UK) was attributed to difficulty in ensuring the argon beam was incident on the FIB lamella surface.

7.2.1.1. Carbon Coating

Insulating specimens are subject to charging effects in the TEM due to exposure to the electron beam. During HRTEM imaging performed on STO/CFO specimens, charging effects were apparent in the form of beam deflection or specimen drift of a TEM specimen. Results showed that the spatial drift originating from charging effects was unpredictable and impossible to compensate by manually adjusting the specimen position. A carbon layer of approximate thickness 10 nm deposited on the exit surface of a TEM specimen was found to completely eliminate successfully reduce charging in STO/CFO specimens whilst also affecting TEM image contrast negligibly.

7.2.2. Microstructure of SrTiO₃/CoFe₂O₄ Thin Films

Selected area diffraction performed on as-deposited and oxygen post-annealed STO/CFO specimens confirmed an epitaxial growth relationship for CFO films grown on (001) STO, confirming the (001)_{STO}//(001)_{CFO} orientation relationship previously reported by Axelsson *et al.*, Xie *et al.* and Huang *et al.* [3,34,35].

Aberration corrected HRTEM performed on as-deposited and oxygen post-annealed STO/CFO has enabled the interface structure to be investigated at a spatial resolution not previously seen in the literature. This investigation has enabled the direct imaging and characterization of structural defects responsible for mismatch accommodation in addition to identifying clear differences in the microstructure that were attributed to post-processing conditions. HRTEM imaging performed on 50 nm and 200 nm OA STO/CFO, identified misfit dislocations of Burgers vector $\mathbf{b} = a_0/4[100]$ were identified in a band approximately 3 nm from the substrate/film interface. The normalized sum of the Burgers vectors for the region of interest analysed was found to be $0.83\mathbf{b}$, suggesting the majority of the mismatch strain in 50 nm OA/STO was accommodated by misfit dislocation formation.

Optimised XTEM preparation parameters allowed HRTEM analysis over large areas which enabled elastic strain and defect strain to be quantified in STO/CFO

specimens and correlated with lattice strain and microstrain previously calculated by Axelsson *et al.*^[32]. For 25 nm AD STO/CFO specimens, a small compressive elastic strain was identified that was similar in agreement with lattice strain determined by Axelsson *et al.* No variation was observed at increased distance from the interface. The defect was found to be in close agreement with the lattice mismatch and did not vary with distance from the interface, suggesting the majority of misfit strain in as-deposited 25 nm was by misfit dislocation formation. Disagreements between defect strain determined from HRTEM and microstrain determined by XRD suggested the mismatch strain was accommodated by dislocations at the interface and not distributed isotropically in the 25 nm AD STO/CFO films.

Results showed that the misfit strain in OA STO/CFO was accommodated by a combination of elastic relaxation and misfit dislocation formation. In the case of a 50 nm OA STO/CFO film, a semi-coherent layer approximately 3 nm thick was observed at the interface in which the majority of the misfit strain was accommodated elastically. As the distance to the interface increased, the defect strain was found to rise while the defect strain increased. At a distance of 8 nm from the interface, the elastic relaxation measured by HRTEM was in close agreement with the lattice strain determined by XRD. The defect strain was in close agreement with the mismatch strain indicating relaxation by dislocation formation after the coherent layer at the interface. Results showed that for both AD and OA STO/CFO films, the sum of the lattice strain and defect strain determined by HRTEM was in reasonable agreement with the mismatch strain.

7.2.3. EELS of Standards

7.2.3.1. Near-Edge Fine Structural Analysis

Oxygen K-spectra and metal L_{2,3}-spectra were acquired from iron and cobalt oxides by monochromated STEM-EELS and a systematic investigation of near-edge fine structure performed. Model spectra were calculated using the full multiple scattering code FEFF 8 to aid interpretation of the fine structure of oxygen K-spectra

The oxygen K-edge was found to consist of five major peaks over energy loss range 532 – 570 eV. The fine structure of oxygen K-spectra acquired from the iron oxides and cobalt monoxide was in good agreement with the literature [63,115], with the exception of the relative intensity of the onset peak for FeO. The FeO onset peak was found to be higher in intensity than previously reported by Colliex *et al.* [115]. Variations in fine structure were attributed to partial covalency and oxygen 2p and metal 3d hybridization in the low energy loss region of the oxygen K-spectrum and oxygen 2p metal 4sp hybridization at higher energy loss. Peak positions and relative peak intensities in oxygen-K spectra acquired from Co₃O₄ and ZnCo₂O₄ were not in agreement with spectra acquired from the iron oxides and CoO. This disagreement was attributed to the large number of d electron density in Co₃O₄ and ZnCo₂O₄ leading to the possibility of fine structure determined by electron correlation effects. The oxygen K-edge fine structure was well reproduced by FEFF 8 for the iron oxides and CoO after correction of the Fermi energy, though poor agreement was observed for Co₃O₄ and ZnCo₂O₄.

Iron L_{2,3}-spectra were observed to consist of two white lines, the L₃ line at around 709 eV and the L₂ line at around 722 eV. Each white line was split into two satellite peaks, in agreement with the literature. The peak splitting was attributed to the crystal field splitting energy of the O_h field in the oxides investigated. The relative peak intensity was found to vary with iron valence, corresponding to a change in occupancy of the t_{2g} and e_g states. Cobalt L_{2,3}-spectra were also observed to consist of two white lines with superimposed fine structure in the form of multiplet satellite peaks, in agreement with literature

XAS and CI model spectra. In contrast to the iron $L_{2,3}$ -spectra, abrupt changes in the multiplet structure of cobalt $L_{2,3}$ -spectra were observed across the oxide series investigated. The changes in fine structure could not be attributed to the t_{2g} and e_g occupancy as observed in the iron oxides.

7.2.3.2. Multiple Linear Least Squares Fitting

A $Fe^{3+} T_d$ standard was determined empirically from standard spectra acquired from Fe_3O_4 , FeO and $\alpha-Fe_2O_3$ powders. By iteratively introducing energy shifts between the iron $L_{2,3}$ -spectra acquired from the iron oxide powders, conditions were identified that produced a $Fe^{3+} T_d$ with near edge fine structure in good agreement with a reference $Fe^{3+} T_d$ spectrum published by Crocombette *et al.* [138]. MLLS fitting was performed on an iron $L_{2,3}$ -spectrum that had been previously acquired by Docherty [15] from bulk CFO powder in which the degree of inversion was well defined ($\lambda = 0.82$). Under optimised fitting conditions λ was calculated from $Fe^{3+} T_d$ and $Fe^{3+} O_h$ EELS standards to be $\lambda = 0.65$. The optimised χ^2 value was found to be ~ 800 .

A $Co^{2+} T_d$ standard was also determined empirically from standard spectra acquired from $ZnCo_2O_4$ and Co_3O_4 . Poor agreement was observed between the $Co^{2+} T_d$ standard and a reference spectrum published by Bazin *et al.* [116]. An artefact was observed in the $Co^{2+} T_d$ cobalt $L_{2,3}$ -spectrum that was attributed to the subtractive method used to calculate the $Co^{2+} T_d$ standard. This artefact could not be removed by optimisation of the calculation parameters. MLLS fitting was performed on a cobalt $L_{2,3}$ -spectrum previously acquired by Docherty. λ could not be calculated reliably from $Co^{2+} T_d$ and $Co^{2+} O_h$ (CoO) standards. This was due to the calculation artefact in the $Co^{2+} T_d$ cobalt $L_{2,3}$ -spectrum and the presence of satellite peaks in the fine structure of the $Co^{2+} O_h$ cobalt $L_{2,3}$ -spectrum not observed in CFO.

It was concluded that an estimate of λ could be determined with confidence by MLLS fitting to iron L_{2,3}-spectra but λ could not be determined with any confidence from cobalt L_{2,3}-spectra.

7.2.4. Local Chemistry of SrTiO₃/CoFe₂O₄ Thin Films

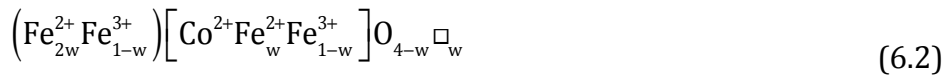
Metal L_{2,3}-spectra were acquired from 50 nm OA STO/CFO by monochromated STEM-EELS. Fine structural analysis of the cobalt and iron L_{2,3}-edges enabled correlation of the local chemistry with the magnetic properties and provided experimental verification of the oxidation and cation ordering processes reported to occur during oxygen post-annealing by Axelsson *et al.* [3].

Fine structural analysis of cobalt L_{2,3}-spectra showed that the cobalt was mostly present as Co²⁺ in octahedral coordination in the bulk of the STO/CFO film. A sharp change in fine structure was observed at the interface that was likely to correspond to a change in film structure in which Co²⁺ was present mostly in tetrahedral coordination. It is possible that the change in Co²⁺ majority coordination is associated with elastic strain the CFO layer, as the fine structural change in the cobalt L_{2,3} fine structure was observed at a similar spatial position to the strained region in 50 nm OA STO/CFO previously identified by HRTEM. It is also possible that this change in coordination may be associated with an increase in Fe²⁺ concentration at the STO/CFO interface.

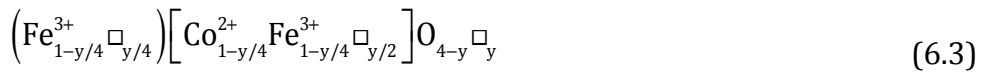
A gradual change in the fine structure of iron L_{2,3}-spectra acquired from 50 nm OA STO/CFO was observed that was not limited to the interface as previously observed for cobalt L_{2,3}-spectra. MLLS fitting performed on iron L_{2,3}-spectra acquired from 50 nm OA STO/CFO using optimised fitting parameters for Fe³⁺ T_d and Fe³⁺ O_h standards gave large values of χ^2 (50x10³ – 240x10³). MLLS fit functions formed from Fe³⁺ O_h and Fe³⁺ T_d could not reproduce the near edge fine structure of iron L_{2,3}-spectra acquired from 50 nm OA STO/CFO, as was expected from the large χ^2 values.

By fitting with Fe²⁺ O_h and Fe³⁺ O_h standards, the fine structure of experimental iron L_{2,3}-spectra was well reproduced suggesting mixed iron valence in the 50 nm OA STO/CFO film. MLLS results suggested that in the bulk of the film, approximately 30-40% of the iron was present as Fe²⁺ and 60-70% was present as Fe³⁺. The fractional Fe²⁺ composition was seen to increase from the bulk to the interface, as the fractional Fe³⁺ composition decreased.

Axelsson *et al.* [3] suggest the presence of a reoxidized and ordered layer close to the surface of a post-annealed CFO thin film and an ordered layer close to substrate/film interface. Cation ordering is reported [3] to give rise to the structure shown in equation 6.2.



Reoxidation by vacancy diffusion leads to the structure,



where $\square$ represents a vacancy.

Fine structural analysis of Co and Fe L_{2,3} spectra provided some confirmation of the chemical model reported by Axelsson *et al.* [3] but also showed some a number of limitations. CFO was predicted to be fully inverse in the model that was found to be inconsistent with EELS results and the wider literature [15,20-22]. The model was also unable to explain the sharp change in cobalt coordination observed at the STO/CFO interface in a 50 nm oxygen post-annealed (001) STO/CFO film.

However, the majority Co²⁺ O_h cobalt environment observed in the bulk of the 50 nm oxygen post-annealed (001) STO/CFO film was in support of predictions made by Axelsson *et al.* [3] of annealing induced cation ordering. The increase in

Fe^{2+} concentration observed toward the interface in this film supported predictions of vacancy diffusion and surface oxidation thought to occur during post-annealing by Axelsson *et al.* [3]. In order to fully validate this model, further EELS analysis must be performed on as-deposited (001) STO / CFO films of thickness ~ 50 nm, and analysis of the oxygen stoichiometry in both the AD and OA films undertaken.

It is clear from the chemical formulae shown in equation 6.2 and equation 6.3, that some Fe^{2+} is expected in the cation ordered layer but not in the reoxidized layer. MLLS fitting performed on iron $\text{L}_{2,3}$ -spectra acquired from post-annealed 50 nm showed a gradual increase in Fe^{2+} content from the bulk of the film toward the interface. This confirms predictions made by Axelsson *et al.* of a transition from a reoxidized surface layer, to a cation ordered layer with increasing depth into oxygen post-annealed CFO films [3].

7.3 Future Work

An investigation of the structure-property-processing relationships in as deposited and oxygen post-annealed $\text{SrTiO}_3/\text{CoFe}_2\text{O}_4$ has been carried out by aberration corrected TEM and monochromated STEM-EELS. This investigation has provided useful information regarding the preparation of XTEM specimens from oxide thin films of thickness < 200 nm that will allow higher quality XTEM specimens to be prepared in the future. This will benefit future research of oxide thin films by (S)TEM and EELS. Useful information about the interface structure was provided by aberration corrected TEM and film chemistry by monochromated STEM-EELS. This thesis has presented a number of points that would benefit from further investigation.

A high quality XTEM specimen was produced by low temperature milling at 0.2 kV though it was not clear if the surface quality of the benefit of low temperature or low energy as a room temperature milling at 0.2 kV was not performed. Investigations of variation in specimen quality with milling energy and temperature would be more complete if an additional experiment was carried out at 0.2 kV at room temperature. Further specimen preparation experiments that would be of benefit would be an investigation of the effect of plasma cleaning on crystalline specimens. While H_2/O_2 plasma cleaning was not found to be damaging for carbon films, a similar investigation was not performed of insulating oxide materials, which would potentially be more susceptible to heating effects than commercially available carbon films.

Both microstructural and chemical investigations would benefit from an increased number of specimens. A limited number of as-deposited specimens was available making it impossible to link microstructural features to film thickness, for as-deposited films. STEM-EELS investigations performed on as-deposited specimens would be of great benefit, as this would enable further correlation between local chemistry and post-processing conditions.

Further EELS investigations of the interface structure that would be of benefit would be to perform quantification or MLLS fitting on Ti $L_{2,3}$ and O K-spectra in addition to investigating Fe $L_{2,3}$ and Co $L_{2,3}$ -spectra. Investigation of possible interdiffusion would be of interest as well as a study of the near-edge fine structure of the Ti $L_{2,3}$ -edge at the interface.

Metal $L_{2,3}$ -spectra acquired in this project were compared to model spectra found in the literature that were calculated using CI models. It would be of benefit to calculate $L_{2,3}$ -spectra and investigate the effect of varying bond lengths within a coordination shell or introducing strain and structural distortion.

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