Large Angle
Plasmon Scattering in Metals
and Ceramics

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Except where due acknowledgement has been made, the work is that of the said candidate. The work has not been submitted previously, in whole or in part, to qualify for any other academic award. The content of the thesis is the result of work which has been carried out since the official commencement date of the approved research program. Any editorial work carried out by a third party is duly acknowledged,

Signed: Tobias A. Colson 

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Simulations were performed on the Victorian Partnership for Advanced Computing (VPAC) and the Australian Partnership for Advanced Computing (APAC) facilities.

During the procedures of chapter 5, we learned that some years ago experiments of this general type were carried through on Si by Boothroyd and Dunin-Borkowski (private communication) but unfortunately not reported. It was suggested by these authors that this would be corrected, however, to date, a reference of their work cannot be given.

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I. Preface

- Rules are for the obedience of fools,
  and the guidance of wise men.

This investigation is primarily concerned with the low loss, or plasmon region of an electron energy loss spectrum. Specifically, why these spectra have the shape and form that they do; what the significance of the material is in determining the shape and form of these spectra; what can be done with plasmon excited electrons; and how all of this fits in with the current theory of plasmon excitation.

In particular, the concept of plasmon scattering being an energy transfer process of a coupled wave in the material is explored. This gives rise to slightly different explanations of the plasmon scattering process to the status quo. Multiple scattering is typically pictured as a combination of separate and independent, elastic and inelastic scattering events interactively contributing to a final exit wave function. However, this investigation explores the idea of the elastic and inelastic components being a coupled event, and what the consequences of this idea are from a conceptual point of view. The energy transfer process itself, does not deviate from a virtual particle exchange description that is consistent with the standard model. However, the two significant points made throughout the chapters are one: that the elastic and inelastic scattering events are coupled rather than separate, and two: that each successive higher order scattering event in multiple scattering scenarios, are dependant and connected rather than independent.

Chapter 1 gives a brief introduction to the concept of the plasmon. Chapter 2 introduces some theory for the simulation techniques used, as well as introducing some important concepts regarding the scattering models used and referred to throughout the investigation.
Chapter 3 presents some details about the experimental aspects of the investigation and endeavours to present some experimentally acquired plasmon loss spectra, discussing the observed differences between them. The experimental details of spectrum acquisition and sample preparation for the investigation are outlined. The low loss results are discussed both in terms of a ceramic material that was chosen for a case study, and some classic metals for a comparison. The low loss results are considered from the point of view of why they appear different from one material to another.

The questions raised in chapter 3 are further investigated in chapter 4 where a case study material is explored in greater detail. This material, hexagonal ruthenium doped barium titanate is computationally simulated and has its electronic density distribution of states investigated.

Results acquired through the density functional theory technique are shown for hexagonal barium titanate, and ruthenium doped hexagonal titanate. The structures had their atom positions optimised to the lowest potential energy achievable for the fixed geometry and their density of states and electron density maps were subsequently acquired. The results are discussed in terms of the experimental low loss that was acquired for ruthenium doped barium titanate.

Chapter 5 presents a practical use of higher order plasmon scattered electrons through the use of an image filter. This was used to test a simple model describing the dynamical scattering of electrons that have suffered multiple interactions with plasmons. Semi-quantitative agreement is observed in both Si and TiAl under quasi two-beam conditions. In the latter material it is shown that the classical Hirsch, Howie, Whelan analysis of contrast due to dislocations can be carried out in images produced by electrons that have suffered as many as five interactions with plasmons and at thicknesses at which the unfiltered and zero loss images show no contrast.

Chapter 6 then correlates the details explored in the previous chapters to make some assertions regarding exactly what scattering processes occur in the generation of a plasmon spectrum. This chapter is primarily concerned with the theory of plasmon scattering, and ways and means of thinking about plasmon scattering in such a way that makes it easier to utilise and consider in the analysis of materials. The chapter begins with a description of the
conventional way of describing the plasmon, by dielectric formalism. Then, we describe a natural extension of this into the Patterson function. A quantum field theory description is reviewed so as to consider its implications. Finally, a further consequence of the collective description of the wavefield as a whole, that is presented in chapter 5, is considered through the investigation of plasmon scattering through large angles.

Chapter 7 concludes such assertions with a further correlation of the material and its plasmon spectra. This chapter is concerned with two key points concerning plasmon spectra. One: the connection between the concept of a dispersion surface, and the band structure. This elucidates the relation of these concepts to the plasmon spectra. We see that the dispersion surface and the band structure are effectively two alternative representations of effectively the same property of the material. Two: the relationship between those materials that present a plasmon spectrum of what will become known as the ideal form, and those that don’t.

Chapter 8 is a summary of the conclusions presented through the investigation. Here some points of interest for further consideration and study are also reiterated.
CHAPTER 1

Introduction

*Politicians are still the captains of the ship of state, and military men are its deck crew, but now there are scientists and engineers in charge of the engine room, and they propel the ship toward unknown destinations.*

_E. N. Luttwak†._

1.1 Introduction and history of the topic

What is a plasmon? The question at first seems to warrant a quick and simple answer: a correlated excitation of electrons in the Fermi sea. The term has its origins associated with the phenomenon of a plasma. Plasma physics has always been a very broad area of physics, by virtue of the fact that plasmas are to be found in many areas of science. A general definition of a plasma is a conductive assembly of charged particles or fields exhibiting a collective effect. Plasmas can carry electrical currents and generate magnetic fields and because they are found on so many scales, they are associated with disciplines ranging from space science to quantum science. It is under this general description that the term plasmon was coined, referring to a collective excitation of electrons in the conduction band.

Evidence of plasma oscillations was first described by Langmuir and Mott-Smith in 1924 [1] and Dittmer in 1925 [2] attributed these oscillations to plasma electrons. It was Tonks and Langmuir in 1929 [3] that were the first to ascribe an attributable theory to these oscillations.

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and showed a simple relation of the frequency of the oscillation to be \( \nu^2 = \frac{ne^2}{\pi mn} + \frac{c^2}{\lambda^2} \), where \( c \) is the speed of light, \( \lambda \) the electron wavelength, \( e \) the electron charge, \( m \) the mass of the electron and \( n \) the number of electrons concerned [4].

The simple description of a plasmon in an electron scattering experiment is an excitation associated with an incident beam of particles interacting with the outer most electrons of an atom. These electrons, i.e. the valence electrons, and for conductors, conduction electrons, are described as being ‘free’ to transfer between atomic cores. It is under this free electron model, first proposed by Drude in 1900 [5] that a collection of plasmon excitations are described as creating a ripple like wave-packet in the free electron gas of a material.

One way of observing plasmons is by using the technique of Electron Energy Loss Spectroscopy (EELS), where high energy electrons are transmitted through a material. The incident or probe electrons ultimately interact with the material and lose different quantities of energy depending on what part of the material it has interacted with. The majority of electrons will interact with not just one, but a collection of electronic regions of the material, including the valence region, core electrons, electrons confined to the nucleus and those involved in the bonding processes of the material. These are then collected by a spectrometer, and on the resulting spectra those electrons that have been predominately concerned with the valence region of the material, are broadly referred to as plural scattering, assuming the material is not thin enough for only kinematically scattering to occur. Plural scattering really just means ‘uncorrelated scattering’, where the phase and energy loss are a soup of energy loss events.

Those energy loss events that are correlated with each other can reveal useful information about the energy of the electron states involved in bonding, and how this in turn affects the energy of the states that are not directly involved in bonding.

Plasmon excitations have been studied extensively in the past, and in particular, the interesting effects on dispersion that the orientation of the specimen has [6]. Dispersion refers to the effect of how a collective disturbance that possesses some degree of periodicity, will tend to spread out and change its form, either over time, or distance, depending on what domain one chooses to represent the wave packet of disturbance.
These plasmon excitation studies have usually been conducted on metals. Metals are so called for a variety of reasons, but the most important one is, arguably, the extent to which the material possesses ‘free’ electrons. It is these electrons that produce the most well defined plasmon excitations.

A somewhat less intensively studied area of plasmons, has been the utilisation of them for the purpose of imaging. Work on plasmon filtered imaging models in 1974 by Goodman et al. is reported to have originally stemmed from observations of high contrast regions in the inelastically scattered background of convergent beam patterns [7]. The first published evidence was from W. Kossel in 1948 and the first explanation offered by Uyeda, Fukano and Ichinokawa in 1954 [8,9]. In the past, theories of inelastic contrast and of absorption were developed separately. However, since both phenomena have the same physical origin the contrast theory should also explain the absorption. This point was made by Radi (1968) [10] while Cowley, Moodie, Goodman and other coworkers developed N-beam treatments for inelastic scattering and absorption involving the high voltage limit (phase grating approximation) throughout the 1960’s. Howie (1963) [7] observed results for plasmon damping similar to part of those shown here using a different physical model [11]. An approach to dynamical plasmon scattering made by Goodman et al. in 1974 was a reciprocal space method. This approach, which had previously been shown to be more compact and comprehensible than Bloch wave methods, has the advantage of applicability to N-beam situations with the correct boundary conditions.

The Goodman approach was first illustrated at the International Crystallography Conference (ICC), in Melbourne 1974, by Goodman, Johnson, Moodie and Secomb, in the conference proceeding of reference [7]. At the time instrumentation was not sufficient to provide experimental evidence for such a model. However, over the past two decades, TEM high tension stability, and Parallel EELS technology have improved to such a level that we were able to adequately test and verify this theory, and illustrate a potential application for the process (see chapter 6).

At present, the application of plasmon loss electrons for imaging could not be considered a new technique, and the process has been successfully applied to such areas as energy filtered convergent beam electron diffraction and lattice imaging [12,13]. One of the more successful applications has been in increasing phase contrast in alloys, by filtering the respective plasmon loss electrons of various phases in the alloys [13]. However, for one reason or
Chapter 1: Introduction

another, no one it seems has taken advantage of the increased transmission that the multiply scattered, higher order plasmon loss electrons posses.

Nelhiebel et al. [14] noted in 1996 coherent core-loss filtered images, and described the phenomenon in terms of the distorted wave Born approximation. Wang [15] used plasmon-loss filtered electrons to look at lattice images. His main conclusion was that this did not provide any real advantage over zero-loss filtered images. However the benefit of the higher mean free path of higher order plasmon-loss filtered electrons would be difficult to see in a lattice image which is formed incident to a column of atoms where zero-loss electrons would have a higher intensity. Features such as dislocations and stacking faults, whilst not as readily quantifiable, are more easily seen in diffraction contrast. To concur with Wang, loss of intensity is indeed a problem with plasmon loss electrons, as is discussed in Chapter 7.

A good example of the use of zero loss filtered electron is demonstrated by Delille et al. in the imaging of Convergent Beam Electron Diffraction (CBED) discs [16]. Although they are by no means the first to increase the contrast of the disc by filtering out the inelastically scattered beams, i.e. zero-loss filtering, they use the resulting image to determine thickness and extinction distance from such images. However, they completely ignore the plasmons. Their experiments are by their nature, i.e. set up in a two-beam condition, ideal for observing the effects on their measurements by plasmon filtered electrons. Of course the intensity would decrease, and the problem is the lack of correlation in the plasmon excitation in less than ideal samples (see Chapter 6).

The intensity variation of plasmon loss with crystal thickness has certainly been noted in the past. It had also been described previously that thickness fringes might be able to be imaged from plasmon loss events. Howie (1963) endeavoured to do this for n plasmon events, assuming that they were obtained by means of ‘some device’ (we know as an EELS spectrometer) capable of selecting electrons of a given energy loss. It was within the description of how ‘two waves beating together would produce thickness fringes by the action of scattering from one two-beam dispersion surface to another, i.e. from say energy level $E_n$ to $E_m$, by the excitation of a plasmon’. In the absence of interband scattering effects, and the equality of probability amplitudes for each beam scattering from one dispersion surface to another, the waves at each dispersion surface, say the waves at $E_m$, should have the same
amplitude and phase relation as at $E_n$. This suggested that inelastically scattered electrons would also produce thickness fringes [11].

This suggested that the scattered wave should have maintained a degree of coherence. It has been often suggested that any coherence in the wavefield is lost during the transfer from one energy state to another, due to the inelastic energy loss mechanism. However, the very nature of its coupling implies retention of coherence in both the elastic and inelastic scattering processes, as the wave packet transfers through the energy states. This point is evidenced through the fact that we can image pendellösung by inelastically scattered electrons. Indeed this point is evidenced and verified in this investigation. Since there is no direct relationship between the energy of a wave and its phase change incurred during a scattering event, this is to be expected.

Recent investigations by Schattschneider, Lithe and co-workers [17-20] and have been particularly successful at providing evidence for the interference effects and retained coherence in inelastic scattering from core loss electrons.

In contrast to this, a similar experiment to one conducted in this investigation led to the conclusion that coherence is lost in inelastic large angle scattering. However, the present investigation came to the opposite conclusion (see Section 6.9). Hence the idea of observing plasmon filtered images is not new, nor is the question regarding the aspect of coherence in inelastic scattering. As shall be seen though, some alternative conclusions have been reached in the current investigation.
1.2 Barium titanate and other ceramics

In the interest of investigating the process of plasmon excitation with somewhat less than ideal samples, the current investigation has endeavoured to also look at some semi-conductor ceramics. One of particular interest has been barium titanate. Barium titanate has been an important ceramic for over half a century due to its ferroelectric properties and high dielectric constant. Its structure is generally that of a perovskite with an $\text{ABO}_3$ stoichiometry in an octahedral arrangement. This material was discovered during World War II to have high dielectric permittivities with a dielectric constant exceeding 1000. Furthermore, when Von Hippel from the USA and Wul and Goldman from Russia demonstrated ferroelectric switching, it became the first ceramic oxide to demonstrate ferroelectricity [21-27]. Recent interest has been generated by the fact that barium titanate maintains a high dielectric constant at film thicknesses in which materials such as silicon are no longer useful for such purposes.
1.3 References:


[23] A.von Hippel and co-workers, *NDRC Reports* 14-300 (1944), 14-540 (1945);


CHAPTER 2

Theoretical background:
Computational theory and scattering theory

This chapter describes the basic foundations of the theory behind the simulation programs used during the course of the study. It also describes some of the concepts behind the scattering theory that constitutes the foundation of various representations elaborated on in further chapters.
2.1 Introduction

The simulations carried out during this investigation predominately used the simulation technique called Density Functional Theory or DFT. Although there are numerous detailed reviews, books and manuals that describe DFT, this chapter describes the basics behind this technique, from the perspective of correlated excitations. DFT is a very useful and very powerful technique, the predominate virtues of which are endeavoured to be pointed out in this chapter, and are the basis behind why DFT was chosen over other potential simulation techniques. There are a few limitations however, those most important within the scope of this investigation being a fixed basis set (which makes stoichiometric and phase changes extremely computationally expensive) due to the use of planes waves in the computational code (see section 2.4). Also, a zero temperature approximation (i.e. no inclusion of temperature effects) was incorporated due to the computational expense of incorporating a thermal energy factor in the system studied. Somewhat less significant, but nonetheless considered a limitation was the inaccuracy of the exchange-correlation energy (elaborated on within Appendix 2A). The first two prevent many of the current DFT based investigations, particularly on large systems, from being a dynamically based simulation, and all systems in nature can be considered dynamic over relevant time frames. See chapter 4 for further discussion on the parameters used.
2.2 Density Functional Theory

2.2.1 Outline of DFT

Density functional theory is an approach to the electronic structure of atoms and molecules which enjoyed a dramatic surge of interest in the late 1980’s and 1990’s. In all-electron simulation techniques such as that of Hartree-Fock theory, the multi-electron wavefunction has the coulombic interaction between the nuclei and the electron separated, as is consistent with the Born-Oppenheimer approximation, and is expressed as a Slater determinant, which is constructed from a set of N single electron wavefunctions (N being the number of electron in the molecule). DFT also considers single electron functions. However, whereas Hartree-Fock theory does indeed calculate the full N-electron wavefunction, DFT only attempts to calculate the total electronic energy and the overall electronic density distribution.

The basis of density functional theory can be traced back to Hohenberg and Kohn in 1964 [2] and subsequently Kohn with his postdoc Sham in 1965 [3]. Together, these three published 2 papers which were to be the basis of modern DFT and a useful extension of the Thomas-Fermi theory, which had existed since the 1920’s.

As described in Anderson [4] DFT begins with the concept of the electron probability density and takes into account electron correlation. The basic idea is that the energy of an electronic system can be written in terms of the electron probability density, \( \rho \). For a system of \( n \) electrons, \( \rho(\mathbf{r}) \) denotes the total electron density at a particular point in space \( \mathbf{r} \). The electronic energy \( E \) is said to be a functional of the electron density, denoted \( E[\rho] \), in the sense that for a given function \( \rho(\mathbf{r}) \), there is a single corresponding energy.

It is worth remembering that a function can generally be described as an operation that maps numbers into numbers. If an action depends, say, on an entire path, or whole function, it is described as a functional, i.e. it maps functions into numbers. It is a function of \( n \) variables, where \( n \) may tend to infinity.

The concept of a density functional for the energy was the basis of some early and useful approximate models such as the Thomas-Fermi method (which emerged from work done by
the two in the late 1920’s) [5,6] and the Hartree-Fock-Slater method, which emerged from the work of J.C. Slater in the 1950’s [7,8].

It was Hartree [7] who showed that the spherically symmetric part of the electron interaction energy can be included in an unperturbed Hamiltonian, by means of a potential derived from the average charge density of all the electrons but one. That is, a single electron is visualised as moving in an effective potential due to all of the other electrons, as well as the nucleus. The contribution to the potential seen by the $k^{th}$ electron due to all the other electrons is calculated from the spatial average of each unperturbed one-electron wave function $\psi_i^0$, or

$$V_k = \sum_{i \neq k} \int \frac{e^2}{r_{ik}} \tau_i \rho_i \, d\tau_i = \sum_{i \neq k} \left( \frac{e}{r_{ik}} \right) \left( \psi_i^0 \right) \ldots \text{Eqn 2.1}$$

Then this potential is used along with the nuclear potential to solve Schrödinger’s equation self-consistently. That is

$$\left\{ -\frac{\hbar^2}{2m_e} \nabla_k^2 - \sum_{i=1}^{N} \frac{Z_i e^2}{4\pi\epsilon_0 r_{ik}^2} + V_k \right\} \psi_k = E_k \psi_k \ldots \text{Eqn 2.2}$$

is solved for each electron. The new wave function is used in equation 2.1 to calculate an improved potential. The iterations are continued until the potential ceases to change appreciable, i.e. until it becomes self-consistent. However, its short comings include neglecting correlation and the Pauli principle. The Hartree-Fock is so called because Fock [8] improved this model by including exchange by using symmetrised product functions for the initial wave function.

Thomas [5] and Fermi [6] made the first attempts to obtain information about the ground state of atoms using the electron density. The theory developed independently by Thomas and Fermi for the ground state of complex atoms having a large number of electrons is based on statistical and semi-classical considerations. The N electrons are treated as a Fermi electron gas in the ground state confined to a region of space by a central potential. The validity of the Thomas-Fermi model improves as the number of electrons increases. However its description of the electron density is very crude since all of the structure of the radial probability density curves is smoothed out in the statistical averaging process. Thus quantities that rely on the properties of the outer electrons are poorly given.

It was not until 1964 however, that a formal proof was given that the ground-state energy and all other ground-state electronic properties are uniquely determined by the electron density.
Unfortunately, the Hohenberg-Kohn theorem does not tell us the form of the functional dependence of energy on the density, it confirms only that such a functional exists. A major step in the development of DFT came with the derivation of a set of one-electron equations from which in theory, the electron density $\rho$ could be obtained.

These proofs, or theory put forward by Hohenberg and Kohn are as follows:

First theorem: There is a one-to-one correspondence between the ground state density $\rho(r)$ of a many-electron system and the external potential. An immediate consequence is that the ground state expectation value of any observable $\hat{O}$ is a unique functional of the exact ground state electron density:

$$\langle \Psi | \hat{O} | \Psi \rangle = O[\rho] \quad \text{Eqn 2.3}$$

Second theorem: For $\hat{O}$ being the Hamiltonian $\hat{H}$, the ground state total energy functional $H[\rho] \equiv E_{\text{ext}}[\rho]$ is of the form

$$E_{\text{ext}}[\rho] = \langle \Psi | \hat{H} \Psi \rangle = \langle \Psi | \hat{\hat{\rho} + \hat{\rho}} | \Psi \rangle + \langle \Psi | \hat{\rho}_{\text{ext}} | \Psi \rangle \quad \text{Eqn 2.4}$$

where $F_{hk}[\rho] + \rho(\hat{\hat{\rho}} \rho_{\text{ext}}(\hat{\hat{\rho}}) d\hat{\hat{\rho}}$ where $V_{\text{ext}}$ where the Hohenberg-Kohn density functional $F_{hk}[\rho]$ is universal for any many-electron system. $E_{\text{ext}}[\rho]$ reaches its minimal value (equal to the ground-state total energy) for the ground-state density corresponding to $V_{\text{ext}}$.

As shown by Kohn and Sham [3], the exact ground state electronic energy $E$ of an n-electron system, for a system in which paired electrons have the same spatial one-electron orbitals, as in restricted Hartree-Fock theory, can be written as

$$E[\rho] = -\frac{\hbar^2}{2m_e} \sum_{i=1}^{N} \int \psi_i^*(r_i) \nabla_i^2 \psi_i(r_i) dr_i - \sum_{i=1}^{N} \int \frac{Z_i e^2}{4\pi\varepsilon_0 r_{i1}} \rho(r_i) dr_i + \frac{1}{2} \int \frac{\rho(r_1)\rho(r_2) e^2}{4\pi\varepsilon_0 r_{12}} dr_1 dr_2 + E_{\text{xc}}[\rho] \quad \text{Eqn 2.5}$$

where the one-electron spatial orbitals $\psi_i (i=1,2...N)$ are the Kohn-Sham orbitals, the solutions of the equations given below. The exact ground-state charge density $\rho$ at a location $r$ is given by
\[ \rho(r) = \sum_{i=1}^{n} |\psi_i(r)|^2 \quad \text{...Eqn 2.6} \]

where the sum is over all the occupied Kohn-Sham orbitals and is known once these orbitals have been computed. The first term in Eqn 2.5. represents the kinetic energy of the electrons; the second term represents the electron-nucleus attraction with the sum over all N nuclei with the index i and atomic number \( Z_i \); the third term represents the Coulomb interaction between the total charge distribution (summed over all orbitals) at \( \mathbf{r}_1 \) and \( \mathbf{r}_2 \); the last term is the exchange-correlation energy of the system which is also a functional of the density and takes into account all non-classical electron-electron interactions.

Of the four terms, \( E_{XC} \) is the one that is not obtained exactly. Although the Hohenberg-Kohn theorem tells us that \( E \) and therefore \( E_{XC} \) must be functionals of electron density, we do not know the latter’s exact analytical form, and so are forced to use an approximate form of it.

### 2.2.2 The Kohn-Sham equations in DFT

The total energy functionals \( E_e[\rho] \) and \( E_{HF}[\rho] \) corresponding to the exact and Hartree-Fock Hamiltonians respectively are:

\[ E_e[\rho] = T + V \quad \text{...Eqn 2.7} \]
\[ E_{HF}[\rho] = T_0 + (V_H + V_s) \quad \text{...Eqn 2.8} \]

Dropping the brackets for brevity, \( T \) and \( V \) are the exact kinetic and electron-electron potential energy functionals, \( T_0 \) is the functional for the kinetic energy of a non-interacting electron gas, \( V_H \) stands for the Hartree contribution and \( V_s \) for the exchange contribution. By subtracting 1 from 2 the functional for the correlation contribution appears to be:

\[ V_c = T - T_0 \quad \text{...Eqn 2.9} \]

The exchange contribution to the total energy is defined as the part which is present in the Hartree-Fock solution, but absent in the Hartree solution. With the Hartree function given by

\[ E_H = T_0 + V_H \quad \text{...Eqn 2.10} \]

is can be defined as \( V_s = V - V_H \).

With this knowledge, the Hohenberg-Kohn functional can be rewritten in the following way:
$F_{HK} = T + V + T_0 - T_0$
$= T + V + \left( T - T_0 \right)$
$= T_0 + V + V_e + V_H - V_H$
$= T_0 + V_H + V_e + \left( V - V_H \right)$
$= T_0 + V_H + \left( V_e + V \right)$  \quad \ldots \text{Eqn 2.11}

Here $V_{xc}$ is the exchange-correlation energy functional. Whilst the exchange correlation functional is not known, it can be assumed that it is, thereby allowing an explicit energy functional to be written as:

$E_{xc} [\rho] = T_0 [\rho] + V_H [\rho] + V_{xc} [\rho] - V_{xc} [\rho]$ \quad \ldots \text{Eqn 2.12}

At this point the second Hohenberg-Kohn theorem could be used to find the ground state density, but then nothing would have been gained by the transformation. Thus the above expression can be interpreted as the energy functional of a non-interacting classical electron gas, subject to two external potentials, one due to the nuclei, and one due to exchange and correlation effects. The corresponding Kohn-Sham (KS) Hamiltonian is what we calculate to find the electron density of the system. The corresponding KS orbitals are found by solving the Kohn-Sham Hamiltonian. The KS equations for the one-electron orbitals $\psi_i (r)$ have the form

\[
\left\{ -\frac{\hbar^2}{2m_e} \nabla_i^2 - \sum_{i=1}^{N} \frac{Z_i e^2}{4\pi \varepsilon_0 r_{i1}} + \int \frac{\rho (r_2) e^2}{4\pi \varepsilon_0 r_{12}} d^3 r_2 + V_{xc} (r) \right\} \psi_i (r) = \epsilon_i \psi_i (r) \ldots \text{Eqn 2.13}
\]

where $\epsilon_i$ are the KS orbital energies and the exchange-correlation potential, $V_{xc}$, is the functional derivative of the exchange-correlation energy

$V_{xc} [\rho] = \frac{\delta E_{xc} [\rho]}{\delta \rho}$ \quad \ldots \text{Eqn 2.14}

If $E_{xc}$ is known, then $V_{xc}$ is readily obtained. The significance of the KS orbitals is that they allow the density $\rho$ to be computed from equation 2.14.
The KS equations are solved in a self-consistent fashion. Initially, we guess the charge density \( \rho \) (to do so, a superposition of atomic densities for molecular systems is often used). By using some approximate form (which is fixed for all iterations) for the functional dependence of \( E_{\text{XC}} \) on density, we next compute \( V_{\text{XC}} \) as a function of \( r \). The set of KS equations is then solved to obtain an initial set of KS orbitals. This set of orbitals is then used to compute an improved density from Eqn 2.6, and the process is repeated until the density and exchange-correlation energy have converged to some predefined level of accuracy. The electronic energy is then computed from equation 2.5.

The KS orbitals on each iteration can be computed numerically or they can be expressed in terms of a set of basis functions; in the case of the latter, solving the KS equations amounts to finding the coefficients in the basis set expansion. As in HF methods, a variety of basis sets functions can be used and the wealth of experience gained in HF calculations can prove to be useful in the choice of DFT basis sets.

Several different schemes have been developed for obtaining approximate forms of the functional for the exchange-correlation energy. The main source of error in DFT usually arises from the approximate nature of \( E_{\text{XC}} \). In the local density approximation (LDA), it is

\[
E_{\text{xc}} = \int \rho(r) \varepsilon_{\text{xc}}[\rho(r)] dr \quad \text{Eqn 2.15}
\]

where \( \varepsilon_{\text{xc}}[\rho(r)] \) is the exchange-correlation energy per electron in a homogenous electron gas of constant density. The total exchange-correlation functional \( \varepsilon_{\text{xc}}(\rho(r)) \) is obtained by differentiation of the following:

\[
V_{\text{xc}}[\rho] = \rho(r) \frac{d \varepsilon_{\text{xc}}(\rho(r))}{d \rho(r)} + \varepsilon_{\text{xc}}(\rho(r)) \quad \text{Eqn 2.16}
\]

In a hypothetical homogenous electron gas, an infinite number of electrons travel throughout a space of infinite volume in which there is a uniform and continuous distribution of positive charge to retain electroneutrality.

Therefore, it is assumed that at each point \( r \) in the inhomogeneous electron distribution (i.e. the system of interest, say a molecule) where the density is \( \rho(r) \) then \( V_{\text{xc}}(\rho(r)) \) and \( \varepsilon_{\text{xc}}(\rho(r)) \) have the same values as in the homogenous electron gas. In other words, the real electron
density, which surrounds a volume element at a position \( r \), is replaced by a constant electron density with the same value as at \( r \). However, this ‘constant’ electron density is different at each point in space.

The exchange correlation functional is key to the success of the density functional approach. One reason why DFT is so appealing is that even relatively simple approximations to the exchange-correlation functional can give favourable results. The simplest way to obtain this contribution uses the local density approximation LDA.

This expression for the exchange-correlation energy is an approximation because neither positive charge nor electronic charge are uniformly distributed in actual molecules. To account for the inhomogeneity of the electron density, a ‘non-local’ or ‘gradient corrected’ functional involving the gradient of \( \rho(r) \) is often added to the exchange-correlation energy of equation 2.5.

Such a non-local gradient correction to the density correlation is reported to be one of the most accurate and efficient methods for calculations involving d-metal complexes within DFT. The exchange-correlation functional is approximated in terms of the gradient of the local density not just on its value. Hence, these functionals are referred to as a Generalised Gradient Approximation (GGA), rather than the fore-mentioned Local Density Approximation. Good approximations have been achieved by expressing the exchange-correlation energy per electron in terms of a GGA, or non-linear function of the electrons position and probability [9-11]. In this investigation both the LDA and GGA functionals were used to find out which method of electron ground state density correlation approximation was more appropriate for the systems being simulated (see chapter 4).

### 2.2.3 Self consistent field calculations

Achieving a self-consistency for a closed shell ground state molecule may be quite straightforward, in which case the energy will converge after a few cycles. However, in some cases convergence is a problem and the energy may oscillate from one iteration to the next of even diverge rapidly. Various methods have been proposed to deal with such situations. A simple strategy is to use an average set of orbital coefficients rather than the set obtained from
the immediately preceding iteration. The coefficients in this average set can be weighted according to the energies of each iteration. This tends to weed out those coefficients that give rise to higher energies. [12]

2.2.4 Plane-Waves

Bloch’s Theorem states that if the electron potential is periodic with the periodicity of the lattice, the solutions of the standard Schrödinger wave equation can be of the form \( \phi_k(x) = e^{ikr}u_k(x) \). This is the form of a standard plane wave, and as such, each point or wave-vector value \( k \) in the lattice may then be represented in terms of a plane-wave basis set. Because plane waves with small kinetic energies are more important than those with large energies, a truncated plane-wave basis set can be used to cut out the large energies. This introduces that concept of an energy cutoff, which effectively restricts the number of \( k \) points on the lattice array that have a plane-wave expansion set calculated. This therefore makes calculations using plane-wave basis sets feasible, as without the cutoff the expansion would be infinite as it would include an infinite number of plane-waves.

2.2.5 Pseudo-Potentials

The number of plane waves needed to accurately describe core electron effects is very large. The concept of the pseudo-potentials is designed to specifically address this problem and reduce the number of plane waves required for the simulation, hence reducing the computational demand. The pseudo-potentials effectively smooth out the tail of the wave-function by approximating the core electron states of the atom with a whole potential. This then reduces the number of plane-waves required in order for the outer regions of the atom to be accurately described. The pseudo-potentials used are commonly ‘soft’ and/or ‘transferable’. Soft pseudo-potentials only need a small number of plane-waves to describe the atom. Ultra-soft pseudo-potentials need even fewer planewaves, and ultrasoft pseudo-potentials generally need to be tailored to each element in a specific environment. On the other hand, transferable pseudo-potentials are useful in many environments. There is a trade off between the accuracy on one and the versatility of the other. Ultimately the kind of pseudo-potentials being developed are both. Plane-wave basis sets with ultrasoft pseudo-
potentials are the type of basis sets used in all the simulation packages used during the course of this study [13,14].

The advantages gained in DFT, through the use of a plane-wave cutoff and pseudo-potentials, are the primary reason DFT was used to simulate the geometry of this investigation’s case study ceramic. Other techniques such as the all electron methods of Hartree-Fock and Quantum Monte Carlo [15] (see Appendix 2A for a brief discussion) are far too computationally demanding to even be considered for the systems studied here, and classical molecular dynamics approaches are unable to give insight into the electronic structure of the system.

2.3 Scattering theory

The Tonks and Langmuir description of plasmon oscillations [3] showing the relation of the frequency of the oscillation as \( \nu^2 = ne^2/m + c^2/\lambda^2 \), (where \( c \) is the speed of light, \( \lambda \) the electron wave length, \( e \) the electron) is still the foundation of the common formulation used to describe plasmon oscillation. The common formulation, can be derived from Maxwell’s equations using the process of linearization. The resulting formulation results in a dielectric formulism which is essentially a linear response function based on a kinematical single scattering event. Multiple scattering can then be accommodated using Greens functions through the Born approximation series. The consequences of using this formulation are discussed in chapter 6, and the description has been very successful in characterising and explaining results gained in experiments involving plasmon scattering. However, we can explain the same process using a different approach, which has some benefit in explaining certain processes in which the standard dielectric explanation is inadequate.
The following theory is the foundation behind the alternate approach, which is elaborated on in chapter 5 and 6. Whilst the following key points are explained in chapters 5 and 6, it is worth noting here that the essential difference can be summarised as:

1. The wavefield is considered as a single wave function, not the sum of parts.
2. It does not scatter sequentially and elastic and inelastic scattering are not separable in this description.

This investigation will discuss these points further, however, in this chapter, the necessary theory of scattering as a wavefield is outlined. The brevity of this theory warrants further investigation into the referenced texts for those unfamiliar with a quantum field theory concept of scattering.

2.3.3 The propagator and ladder diagrams

The free or ‘bare’ plasmon propagator can be represented by a vertical line, which entails the Feynman diagram expansion of a sequential set of pair bubbles, such as in figure 2.2.

Figure 2.1 Pair bubble Feynman diagram which, in this case, represents a propagator for a plasmon excitation.

Figure 2.1 is a diagrammatic way of saying, within the scheme of the random phase approximation [23], that in the process of a free electron state being excited, there is a virtual polarization taking place between the particle and the hole [23].
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\[ -i\pi(q, \omega) = \begin{bmatrix} k + q \\ \epsilon + \omega \end{bmatrix} \begin{bmatrix} k, \epsilon \end{bmatrix} \]

This has the form of an interaction taking place between two charges in a dielectric, with \( \epsilon_{\text{RPA}}(q, \omega) = 1 + V_q \pi_q(q, \omega) \) being the frequency of the so-called generalised dielectric constant. Dielectric properties arise because of the polarisation of the medium by a field, and thus is an appropriate form for our discussion. Electrons and holes are then represented by higher order terms. This leads to the formation of the collective excitation being the sum of the possible particle hole interaction combinations. It constitutes a collective propagator, not that of a single particle. However, it is still linear in the sense that it is the propagator of a single plasmon quasi-particle.

The correlation energy of a bare electron gas can be shown [22] to be the summation of such propagation terms as;

\[ E_{\text{corr}} = E_r + E_r^b + E_r^c + E_r^d + \ldots \quad \text{Eqn 2.17} \]

which has the pair bubble diagram of figure 2.2.

![Figure 2.2 A Feynman pair bubble diagram shows the interaction between two-particle holes and all of the possible ways of self interaction.](image)

E_r is the effective interaction and the ends are joined by a ‘bare’ interaction, as opposed to an effective interaction where the particle potential takes into account nearest neighbour interactions. So E_r is a bare interaction between two particle hole exchanges. However if we want to represent a higher order interaction, in terms of a higher order plasmon loss, we cannot just use a higher order ring diagram [22].

This is because in the second order for example, two electrons are excited and then de-excited. In third order electrons, 1 and 2 are excited, one of them is de-excited while exciting a third, 3, and then the outstanding electrons are de-excited and so on. So the total energy of
the excitation process, regardless of the order, is conserved i.e. it cannot be regarded as an inelastic.

A ladder diagram on the other hand is an appropriate representation where different energy levels are being accounted for in the system. A two particle propagator, for example, is the sum over the probability amplitudes for all the ways two particles can enter the system, interact with each other and with the particles in the system, then emerge again. The diagram to represent this is the ladder diagram. A partial sum over all ‘ladder’ diagrams for example can be seen in figure 2.3 [22] and is the called the ladder approximation.

Figure 2.3 A two potential propagator, and a two particle propagator with a 1st order interaction, and so on.

Thus a good representation of the plasmon scattering process is therefore, in the scheme of the model presented later (see chapter 6), to combine the two particle propagator, for example, (it could just as well be a n particle propagator), with the particle hole propagator, as a sum of all possible combinations, such as represented by figure 2.4.
How then do we represent this as a ‘two-beam’ interaction, as opposed to a two-particle interaction? We need to represent all the possible combinations of interaction between the two ‘beams’ for each respective energy state. Again a loop is sufficient and we see here that whilst the energy can transfer with a ‘bare’ interaction, a loop allows both energy and momentum to be exchanged. The wiggle, in accordance with convention (see any number of texts, including the references here of Mattuck [23] and Fetter and Walecka [22]) is a sufficient representation however the loop distinguishes the interaction from being one between two independent particles that have entered the system, and a single particle that has entered the system, and interacted with itself, as occurs in diffraction. Thus we will see the model described later on uses a set of loops arranged in a ladder approximation such as figure 2.5.
We see here that the problem of having a multiple scattering process may be viewed from the point of view of an incident flux of superposed plane waves [4], and the scattering can be considered with a partial wave treatment [4] in analogy with classical optics, as with the multi-slice technique. Alternatively the time-dependant perturbation technique could be employed, and Greens’ propagators [23] used to project each scattering plane wave between ‘events’ in an iterative solution such as that used in the Born approximation [24]. There are also numerous matrix formulations, amongst the most common of which is the S matrix [25]. The S matrix describes time independent wave operators for the scattering from free to full states. It is essentially the operator that acts on one state to the next. S is the probability amplitude of this progression from one state to another. The S matrix describes the probability amplitude for scattering between states where the target is stationary.

However, there is also the T matrix [25] which describes two particles in motion colliding. In this case the Hamiltonian is invariant over the scattering event and thereby conserves the momentum. In the case of the T matrix, the momentum is a defined variable within the Hamiltonian.

There is even the K matrix, which is effectively the S matrix with imposed unitarity. The K matrix is sometimes called the reactance matrix, or Heitler’s matrix [26,27]. However, whether a set of differential equations, or a matrix formulation is used, they almost all consider each scattering event as being independent, or if coupled, separate the elastic and inelastic components. This leads to the conceptual picture of the elastic and inelastic ‘events’ as occurring in an uncoupled or independent fashion. All of the matrix formulations are different uses of standard perturbation theory where you have an initial state vector, and a final one, and some event, or operator that moves one to the other. Thus, naturally if a second order process is to occur, the operator is just reapplied. However, if an alternative formulation is used, where the elastic and inelastic components are coupled, then it is consistent and acceptable to consider the scattered wave function as containing both elastic and inelastic components and to separate them is not necessary from a conceptual point of view. This is an important distinction as shall be reaffirmed in chapter 6.

The various formulations that describe n beam scattering differ in their approach most significantly in the way the ‘beams’ are coupled (the way in which they couple the multiple scattering.). Figure 2.6 highlights the connection between n beam diffraction formulations.
2.5 APPENDIX

Electron correlation and the exchange energy function in DFT

The most significant drawback of Hartree-Fock theory is that it fails to adequately represent electron correlation. In the self-consistent field method the electrons are assumed to be moving in an average potential of the other electron, and so the instantaneous position of an electron is not influenced by the presence of a neighbouring electron. In fact, the motions of electron are correlated and they end to ‘avoid’ each other more than Hartree-Fock theory would suggest, giving rise to a lower energy. The correlation energy is defined as the difference between the Hartree-Fock energy and the exact energy. Neglecting electron
correlation can lead to some clearly anomalous results, especially as the dissociation limit is approached. For example, an uncorrelated calculation would predict that the electron in \( \text{H}_2 \) spend equal time on both nuclei, even when they are infinitely separated. Hartree-Fock geometries and relative energies for equilibrium structures are often in good agreement with experiment and as many molecular modelling applications are concerned with species at equilibrium it might be considered that correlation effects are not so important. Nevertheless, there is increasing evidence that the inclusion of correlation effects is warranted, especially when quantitative information is required. Moreover, electron correlation is crucial in the study of dispersive effects which play a major role in intermolecular calculations, but it should be noted that the effects of electron correlation are implicitly parametrised. However, specific electron correlation methods have also been developed for use with various levels of semi-emperical calculation; this in turn necessitates the modification of some parameters [12].

In DFT, the approximate nature of the exchange correlation energy presents some interesting problems in the context of electron-electron coupling and the difficulty in accommodating a wave-particle duality in computational algorithms. The approximate nature of the exchange correlation energy can indeed be accommodated through the utilisation of other simulation techniques called the Quantum Monte Carlo (QMC) method and the Hartree-Fock (HF) method. Quantum Monte Carlo (QMC) has been used for some time as it gives a direct wave-function based treatment of quantum many body effects. Based on the regular Monte-Carlo method developed by Neumann, Ulam and Metropolis at the end of World War II [15], the main advantage of QMC of whom a main developer was Ceperley and Alder [28] is that it can calculate directly the exchange-correlation energy of a homogenous system. However, the exchange-correlation energy is determined by calculating the columbic energy difference between the correlation of electrons with parallel spin and anti-parallel spin. This is how it is applied in the functionals used DFT.

In general quantum mechanical methods it is common to express many body wave functions as linear combinations of determinants. However, this proves to be computationally demanding, due to the difficulty in describing the ‘cusps’ that occur whenever two electrons come into contact. The QMC method uses a trial wave function of the Slater-Jastrow type [29]. This Slater-Jastrow wavefunction is one of the key weapons of QMC, however it is also one of its weaknesses. In QMC, the spin variables are often removed from the Slater-Jastrow wave function and the single Slater determinant is replaced with a product of determinants of spin up and spin down orbitals. The function is therefore not anti-symmetric on exchange of
electrons with opposite spins. However, this does not matter because the expectation value for any spin independent operator is the same. This is computationally advantageous and also includes the ‘cusps’. The anti-symmetry of the wave function creates an exchange hole that keeps parallel spin electrons apart, but there is no correlation between the positions of electrons with antiparallel spins. There is a significant probability of finding two antiparallel spin electrons very close to each other and so the electron-electron Coulomb repulsion energy is high. The Jastrow factor has a two body term that reduces the magnitude of the many-electron wave function whenever two electrons approach one another; this reduces the probability of finding two electrons very close together and decreases the electron-electron interaction energy.

Here lies a drawback to this approach. The fact that there is no correlation between the positions of electrons with antiparallel spins, means that highly correlated events, such as those leading to superconductivity are not the type of phenomenon that can be calculated in this scheme. In addition, the way the factor assumes a high Coulombic repulsion between electrons of anti parallel spin ignores anti-parallel spin coupling and bosonic formation between electrons of anti-parallel spin in the same energy state. This electron-electron coupling is key to the concept behind Cooper pairs in superconductivity. However it is also key behind the way plasmon excitations occur, and ultimately, the physical basis behind the electronic properties in materials. The fact that it does not include this is an approximation. QMC and Hartree-Fock take exchange into account in terms of a coulombic repulsion, they ignore symmetry. This is justified on the basis that in terms of energy determination, the contribution is very small. Thus, it is not a bad approximation at all, for homogeneous and ideal materials. Ideal meaning, metals. It does not effect the bonding predictions, and in terms of bonding, spin is accounted for through the implementation of Pauli’s exclusion principle and Hunds rule. However, when complex materials are considered, such as ceramics, semiconductors and insulators, and fundamentally any material that is highly non-homogeneous in terms of electron density distribution, then this very quickly becomes a problem in terms of electronic excitations, as shall be discussed (see Chapter 6 and 7). This argument also applies equally well to DFT, and as is well known, DFT does not perform well when calculating band gaps, and electronic response functions such as the dielectric function for example, which are primarily concerned with correlated valence electron excitations.
2.5 References


CHAPTER 3

The plasmon loss spectrum: Experimental procedure and results

This chapter describes experimental details of spectrum acquisition and sample preparation for this investigation. The low loss or plasmon loss region of an EELS spectrum, are discussed both in terms of a ceramic material, chosen for a case study, and some classic metals for a comparison. The low loss spectrum is considered in the context of why it is different from one material to another.
3.1 Introduction

In an attempt to test certain assertions of the Goodman model described in chapter 2 and examine the plasmon interactions occurring during such tests, a selection of materials needed to be selected. Demonstration of the models assertions could be quickly acquired with certain materials, but not others. Thus, in an attempt to explain why it is, clear plasmon spectra could be analysed in metals, but not ceramics for example, the DOS and crystalline structure of some select materials was conducted. The chosen metals are well understood and materials investigations have been conducted in the past. However, in the case of hexagonal barium ruthenium titanate, little data was available on lattice parameter, space group and DOS. Thus, the hexagonal barium ruthenium titanate was computed and synthesised to ensure assertions made in relation to this material and compared to the metals was correct. In brief terms, it needed to be understood why free electrons was not the only requirement for a good correlation of results with the assertions made by the Goodman model. It was also important to understand that the conclusion made in relation to plasmons and their higher order correlations are not specific to certain materials, even if only a select few materials present ideal examples of what the Goodman model suggests.

3.2 Electron energy loss spectroscopy (EELS)

The EELS apparatus used during the course of this investigation was Parallel EELS or PEELS. This involved the use of a magnetic prism and a combination of octupole and sextupole lenses (see figure 3.1) arranged in a post column format (see figure 3.2). These lenses focus the electrons onto a peltier cooled charge coupled device (CCD) array (see figure 3.3). The magnetic prism splits the electron beam into different energy components, just as an optical prism separates a ray of light into its various colours. Thus, whilst the device is a spectrometer, focusing the beam onto a CCD array, it will also form an image. This, in combination with an energy selecting slit, enables the device to be used as an image filter, where an image can have certain energies ‘filtered’ out. The effect is to reveal features of an image that are formed by electrons with particular energies. Figure 3.2 shows the setup used as supplied by the company Gatan, and their PEELS image filter is commonly referred to as a Gatan Image Filter (GIF). This was attached to a Jeol JEM 2010 200 KeV 1993 Transmission Electron Microscope (TEM) with a LaB$_6$ electron source.
Figure 3.1 *Gatan GIF PEELS system*[1].

Figures 3.2 *a* and *b*, show a schematic and actual photograph of the PEELS post column arrangement used during the investigation, respectively.
In EELS spectra (see figures 3.4, 3.5, 3.6 and 3.7) there is always a large peak sitting on the zero point, which correspond to electrons that have lost zero energy to the material. It is always the case that the majority of probe particles will pass straight through the material, without losing any energy. This does not mean that they have not interacted with, or been scattered by the material. Indeed, it is most likely that they have, they just have not lost any energy in the complete process i.e. they have been elastically scattered.

Figure 3.4 A description for the nomenclature of the various regions of a low loss EELS spectrum is shown.
Immediately following the zero loss energy peak is quite often a flat region ranging anywhere between 0.1 eV and 6 eV in width. The region seems to be predominately void of electron energy states for the probe electron to interact with, and is referred to as the band gap region. It is this region which causes a material to behave like a conductor, semi-conductor or insulator. An insulator should have a large band gap and a conductor no band gap. However, in an EELS spectrum the band gap region can sometimes be arbitrary when distinguishing between the two (figure 3.6 is a classic example). In an insulator, the first energy loss will occur effectively at the Fermi level, and the minimum amount of energy lost to this valence region is greater than the minimum amount of energy required to excite a valence electron. If this is not large, then the apparent band gap can look small. For a conductor this interaction is above the Fermi level and energy loss is from free electrons rather than localised ones. How does one tell the difference then? A conductor will also have plasmon excitation that is typically a lot more localised on the spectra and have multiple plasmon peaks. These are peaks associated with electrons that have lost energy to a plasmon excitation more than once. This is due to a capacity for conduction electrons to excite in a correlated fashion. However, as shall be seen (chapters 6 and 7), these multiple plasmon peaks may not occur, so this feature is not necessarily an ideal feature for identifying a conductor, which further complicates matters. However, in an insulator, it is not the conduction electrons that are being excited, rather the valence electrons, which produces a low loss spectrum that also looks considerably different, as shall be seen.

Figure 3.5 An EELS low loss spectrum of barium phosphate. The vertical scale is intensity in terms of number of electrons counted, and the horizontal scale is energy loss in eV (1.76 relative mean free path thickness).
Chapter 3: The plasmon loss spectrum: Experimental procedure and results

Figure 3.6 An EELS low loss spectrum of copper (probable nickel content of less than 1% wt.). (1.54 relative mean free path thickness).

Figure 3.7 A second EELS low loss spectrum from a pure cold rolled specimen of copper (2.04 relative mean free path thickness).

A semi-conductor is usually identified by a flat, less intense region post-ceding the zero loss peak. However, identifying it is sometimes more complicated than would be expected, as for example when the band gap region is less well defined. Inter- and intra-band transitions can show up in the region making interpretation difficult. However, to have an inter-band transition, one needs a band gap for the transition to occur. Thus, it is not necessarily the case that the observation of an inter-band transition is a direct indication that the band gap no longer exists. Electron states that arise in the band gap are states that are simply less probable. The band gap is that region where states are less likely to occur, they are not forbidden.
In figures 3.4, 3.5, 3.6, and 3.7 the zero loss peak looks as if it has a negative energy associated with it. However, zero is defined as the central point of the zero loss peak, which has a natural width due to the energy resolution limit of the spectrometer. The point spread function, or spread of energy from one pixel to another in the array of photo diodes is not perfect. Also, as is discussed more in chapter 6, to gain a single energy resolution, or an effective delta function of energy is unrealistic, however in this practical case, the monochromaticity of the lanthanum hexaboride source is not going to be better than approximately 1 eV anyway. The intensity scales are treated as arbitrary since, in comparison from one spectrum to another, the absolute intensity is not important, rather it is the relative intensity of one peak to another, in the one spectrum, that is important. Ratios between the zero loss peak to the inelastic component of the spectrum, i.e. the low loss, is typically represented by the relative mean free path (rmfp) (see Appendix 3A for the definition of rmfp).

### 3.3 Sample preparation

#### 3.3.1 Introduction

Ceramic samples were investigated, in addition to the metals, because of their complex structure and in particular because they are comprised of transition elements that contain d electrons. All of the compounds are crystalline and ceramic. The following ceramic crystals were grown precisely for the reason that their plasmon excitation spectra are complex. They are therefore ideal for considering what the low loss region of an EELS spectrum tells us.

This investigation is by no means a complete study of the ceramics or metals, in terms of all the possible information that could be collected, nor compares this data with other established techniques. This is because such properties as the dielectric constant, density of states, and conductivity could all be gained through superior techniques, such as ellipsometry and potentiostat measurements. However, the common limitation to these techniques is the fact that they do not measure properties on the nanoscale. As current pursuits in the materials science domain, circa 2006, are engrossed in so called nano science, the scale limitations are likely to become of increasing relevance. Electron wave devices are pre-eminent when it comes to spatial resolution, both for chemical identification and image acquisition. EELS is one technique that utilises this advantage. It is expected that spherical aberration correctors,
combined with monochromators, and attached to field emission source transmission electron microscopes incorporated with EELS, will become common place. How then can we better utilize the capacity of EELS for electronic property determination on the nano scale? It is hoped that this investigation can be of some use in that consideration.

3.3.2 Solid state synthesis

The history of crystal synthesis is a long and varied one, and as such one finds a plethora of techniques available to the crystallographer. The particular technique chosen usually depends on what material the crystals are to be grown from and the intended use of the resulting crystals.

During the 20\textsuperscript{th} century a common technique was the Czochralski [2] or pulling method where crystals with a high degree of perfection were obtained. This and other related pulling techniques tended to be preferred because they provided a seeding mechanism for the nucleation to take hold.

During the 1970’s however the sol-gel [3] method became popular. This process involves nucleation through the formation of a colloidal suspension and gelation for the solution to seed with a continuous liquid phase. Its main advantage is gained through the lower temperatures required to form glasses and ceramics. It is a technique that tends to be superior in producing a large number of very small homogenous crystallites, or homogenous glasses. The problem with the technique for more generalised crystallographic studies is that crystals tend to be very small.

Chemical vapour deposition and more recently the plasma based deposition techniques such as cathodic arc deposition, are techniques that have become very important in the semiconductor industry due to the requirement of thin layers or films of relatively strain free mono- and poly- crystals and glasses. However, the physics of the interface plays a major role in the product, and the layers will be, for the better part, polycrystalline. This is because whilst the nucleation of a crystal can be achieved with relative ease via the effects of stress reduction, the orientation of that growth is random over short time frames. Indeed chemical vapour deposition is a technique that is poor where single crystals are required. The inhomogeneity of the nucleation is also exacerbated the more the precursor itself is
inhomogeneous, i.e. more than one element is involved such as in the ceramic compounds being studied in the course of this investigation.

As a result the classical technique of solid state synthesis was used. This process of sintering, often in conjunction with annealing, involves holding a polycrystalline rod, or compressed powder at an elevated temperature below the melting point. It is not the most favoured technique as it does not produce macroscopically large crystals like the pulling method or the melt growth method, where a liquid phase is first achieved, and then the crystal ‘frozen’ in from a seed. However, the sinter usually provides well faceted crystals that are reasonably homogenous and well suited to microscopic investigations. In addition, it is a superior in growing single crystals at temperature below temperatures that are typically required for successful crystal growth.

The general technique for all sintering preparations involved mixing and lightly crushing, in ethanol, the precursors in a mortar and pestle. The powders were dried and sintered in a Lenton muffle furnace to 1000°C or in a Gallenhamp muffle furnace to 1100°C in the case of the flux containing powders. The BaCl flux results in a chlorine by-product which can damage the filaments of a furnace, where they are exposed. In all runs the samples were cooled slowly to 500°C and then removed from the furnace and allowed to cool to room temperature (see Appendix 3D for further details).

### 3.3.3 Materials and equipment

Powders used for the preparation included ruthenium powder (99.999%), TiO$_2$ precipitate from a titanium isopropoxide solution, barium carbonate (99.99%) and barium chloride, all from Aldrich chemical company, ruthenium oxide (99.9%) from Stream chemical company. High alumina crucibles were used to minimise contamination. The observations were made on a Jeol JEM 2010 (1993) TEM with a lanthanum hexaboride source. The TEM is fitted with a LINK energy dispersive x-ray spectroscopy (EDS) beryllium window Si-Li detector and a Gatan (2000) GIF PEELS spectrometer. Typical convergence and collection angles for the PEELS were 14 and 4 mrad respectively. All spectra were background and dark count corrected. Scanning electron microscope (SEM) images were acquired on a FEI Quanta 200 SEM with a tungsten source and EDAX EDS detector (Appendix 3D).
Metals samples, considered in chapters 5, 6 and 7, were discs of ultrasonically cut and electropolished copper, aluminium and gold. The copper had a nominal 1% at. wt. addition of nickel and the gold a nominal 1% wt. addition of copper for the practical purpose of enabling them to be handled without bending and/or distorting too much (both metals being extremely soft in their 100% pure form). The copper was electropolished in a solution of orthophosphoric acid (87% w/w) and the gold in a solution of 3 parts HCl acid (37% w/w), 1 part glycerol and 2 parts ethanol. The aluminium foil was supplied courtesy of Dr. T. Peterson and was in the form of strips mounted on a bare copper grid. Silicon, which is considered in chapters 5, 6, and 7 was in the form of a wedge of chemically etched pure silicon, and an aerospace alloy of TiAl was also accordingly cut and electropolished as were the other metal samples. In chapter 7, the properties of graphite, PbRuO$_3$, YBaCuO$_3$(123) and SiO$_2$ (quartz) were also briefly considered. The ceramics were sintered according to the solid state synthesis described in the previous section. The YBaCuO$_3$(123) had been sintered by Prof. H.J. Whitfield of RMIT University Applied Physics.

3.4 The low loss spectrum
3.4.1 Introduction

Analysis of the low loss spectra is primarily concerned with the band gap. However attempting to correlate the features with simulated data such as the density of electronic states for example (see chapter 4), is a far from straightforward exercise. The low loss spectra include the plural scattering, conduction band scattering and core excitations. In this investigation, no clear band gap was evident in the ceramic spectra, nor is the plasmon excitation peak relatively clear. With simpler materials, theoretical models should work better since they are typically based on the free electron approximation, and the free electron approximation ignores the appreciable structure in the cores. In simple metals for example, this contribution is generally small anyway. However, the barium ruthenium titanates are far form ideal metals, and one should expect them to have a lot of core state contribution to the conduction band, particularly where such ‘large’ elements as barium are included.
3.4.2 Barium ruthenium titanate

A number of experimental and theoretical studies have examined the structures of the perovskite and hexagonal phases of BaTiO$_3$. The experimental studies [4-8] have employed X-ray diffraction (XRD) to determine the geometry of the different phases. The theoretical studies have employed density functional theory [9-11], as described in chapter 2 and ab-initio Hatree-Fock [12] and other empirical [13,14] computer simulation methods. While a large amount of attention has been paid to the perovskite phases, particularly due to the ferroelectric properties of the tetragonal phase, its high temperature polymorph, and the accompanying cubic/hexagonal phase transition have only more recently attracted interest [20,21]. Unlike the lower temperature transitions, which are displacive, the cubic to hexagonal phase transition has traditionally been looked upon as reconstructive and thus a much more energetic event. This high temperature phase is known to also be able to displace into two low temperature hettotypes of monoclinic and orthorhombic symmetry, however the phase is difficult to produce [8,22,23].

Over a range of temperatures, BaTiO$_3$ undergoes a number of phase changes, including a cubic/tetragonal transition around 120°C, a tetragonal/orthorhombic transition around 0°C, and an orthorhombic/rhombohedral transition at around -90°C [4]. The perovskite (cubic) phase undergoes a high temperature transition into an accompanying polymorph with a hexagonal stacking (see figure 3.8).

There have been a number of investigations on the nature of the cubic/hexagonal transition [20,24] and it is reported that oxygen vacancies are thought to induce instability into the hexagonal structure [20,25,26]. Recent studies [20,25,27] suggest that reduction is accompanied by the formation of the O(1) vacancies in the hexagonal h-BaO$_3$ layers (see figure 4.1), and changes in unit cell dimensions are dominated by an increase in the Ti(2)-Ti(2) separation. Such changes are consistent with an increasing Coulombic repulsion between adjacent Ti(2) ions as oxygen ions are removed from the shared octahedral faces.

Doping BaTiO$_3$ with transition metals has been shown to stabilize the high temperature hexagonal phase [26]. Substitution of the Ti 4-fold ion, for a transition metal with more d electrons, for example, is known to have this effect [20,25].
h-Hexagonal- BaTiO$_3$ $\xleftarrow{1300\, ^\circ C}$ h-Hexagonal- BaTiO$_3$

↑↓$1280\, ^\circ C$

↑↓$51\, ^\circ C$

c-Cubic- BaTiO$_3$

↑↓$120\, ^\circ C$

↑↓$-51\, ^\circ C$

c-Tetragonal- BaTiO$_3$

↑↓$0\, ^\circ C$

c-Orthorhombic- BaTiO$_3$

↑↓$-90\, ^\circ C$

c-Rhombohedral- BaTiO$_3$

h-Orthorhombic- BaTiO$_3$

↑↓$199\, ^\circ C$

c-Tetragonal- BaTiO$_3$

↑↓$0\, ^\circ C$

c-Orthorhombic- BaTiO$_3$

↑↓$-90\, ^\circ C$

c-Rhombohedral- BaTiO$_3$

Figure 3.8 The polymorphism process of BaTiO$_3$ has 3 displacive transitions in the perovskite phases and 2 displacive transitions in the hexagonal phases. c- and h- represent cubic and hexagonal stacking respectively [4,8,18,23].

3.4.3 The low loss EELS of hexagonal Ba$_3$RuTi$_2$O$_9$ and Ba$_3$Ru$_2$TiO$_9$

The low loss of hexagonal Ba$_3$RuTi$_2$O$_9$ and Ba$_3$Ru$_2$TiO$_9$ are studied since the hexagonal phase of barium titanate ceramic was focused on in the investigation. Doping barium titanate with a transition element such as ruthenium makes the crystallisation of the hexagonal phase significantly easier, as discussed in the previous section.

The effect of the different dopant position is charge balance (see figure 4.1 for an example of the arrangement of the octahedra). In the case of the one third ruthenium doped barium titanate, Ba$_3$RuTi$_2$O$_9$, if the two Ru atoms are on the same A$_2$O$_9$ octahedral group, then the electrons will be paired with the Ru atoms both positioned in face sharing octahedra. However if they are not, then no such paring will occur. If there is a band gap difference present when Ba$_3$RuTi$_2$O$_9$ has a pairing of spin, then theoretically this can provide a mechanism for experimentally determining how the dopant is arranged in a given material. It could be conjectured that high resolution EELS should have the potential to determine this. However, in this particular study, no such band gap difference could be observed. A problem that occurred was that it was impossible to determine whether a band gap of 1 eV or less was present or not. Such an energy resolution is greater than the resolution of the EELS apparatus used. An attempt was made to observe such a difference in a high resolution EELS system.
These higher resolution spectra were acquired on a VG HB601 100KeV cold FEG STEM, fitted with a Gatan ENFINA PEELS spectrometer. The VG STEM is based at Sydney University, Australia, and was used with the assistance of V.J.Keast. The STEM’s cold Field Emission Gun (FEG) is a coherent source which leads to a higher brightness allowing smaller probes and greater spatial resolution. The higher resolution results, as can be observed in figures 3.10, 3.12 and 3.13 show the detail in the low loss region around the band gap and preceding the plasmon excitation. However, unfortunately, due to the zero loss peak tail, as well as the large number of occupied states suspected to be above the Fermi level, the question regarding the band gap difference for the different ruthenium stoichiometries could not be resolved. The large asymmetric tail on the zero loss peak is a problem that possibly the new (circa. 2006) monochromators, in conjunction with aberration correctors are able to resolve.

An important point to make, with regards to the low loss spectra of ruthenium doped barium titanate, is a variability in the precise stoichiometry of these crystallites. The stoichiometry of the materials studied is nominal which means that whilst the material has been sintered to contain the nominated stoichiometry, the stoichiometry of each individual crystal can vary and this is evident in the low loss spectra of this material. The stoichiometric variability in $\text{Ba}_3\text{RuTi}_2\text{O}_9$ is why three spectra are shown for this material, where as $\text{Ba}_3\text{Ru}_2\text{TiO}_9$ had a constant form. This stoichiometric variation is seen in the preparation. Therefore no quantitative assertion is made from these results, the purpose of which is not to determine a definitive stoichiometry, but to highlight the form or shape of the low loss in these materials. The form or shape does not determine the difference between two stoichiometries such as $\text{Ba}_3\text{RuTi}_2\text{O}_9$ and $\text{Ba}_3\text{Ru}_2\text{Ti}_2\text{O}_9$, but then core loss EELS is used for this. Indeed energy dispersive X-ray spectroscopy is also superior in this sense. It should be pointed out that at no stage is the potential to make a quantitative measurement of the band gap by EELS being disputed, although in this case, most of the materials are metallic conductors anyway, as we shall discover (see Appendix 3D for details).

### 3.4.3.1 $\text{Ba}_3\text{RuTi}_2\text{O}_9$ results

The three spectra in figure 3.9 are all taken from different crystals in the same sample. In the band gap region of figure 3.9, only 3.9a is relatively flat, where as 3.9b and 3.9c show a form...
suggesting significant interaction over the band gap and if there is indeed a band gap, that it must be very small. This spectrum in figure 3.10 has been acquired with much higher resolution than those in figure 3.9. Here the band gap appears to be completely filled. However the presence of a small band gap, on the order of 1 eV cannot be ruled out, since the resolution is not sufficient to distinguish such a small band gap amongst a wide zero loss peak and the electrons occupying the conduction band states.

Figure 3.9 The low loss region of hexagonal $\text{Ba}_3\text{RuTi}_2\text{O}_9$ with a 0.05 eV/channel dispersion. The form is identical apart from the band gap region, which looks quite different.
Figure 3.10 The low loss region of a EELS spectra acquired from hexagonal Ba$_3$RuTi$_2$O$_9$. Acquired on a VG STEM, the resolution is greater, thus finer detail is evident, particularly in the 12-22 eV region.

The low loss spectra reveal little about the size of the band gap. This could be due to two reasons. Firstly, there might be no band gap, but past studies on related materials suggest that this material should be a semi conductor indicating that the band gap must be very small [4-8,28,29]. Two, occupied states above the Fermi level may be creating low loss peaks immediately following the zero loss peak making it difficult resolve where such a small band gap would begin. The full width of the peak at half of its maximum height in intensity, (FWHM), of the zero loss peaks are typically between 0.3 and 0.4 eV. However, the peak still has a large tail. It is thought that a monochromator on future EELS systems could contribute greatly to reducing not so much the FWHM of the zero loss peak, but rather the tail which would also contribute greatly to resolving band gaps from EELS spectra.

3.3.3.2 Ba$_3$Ru$_2$TiO$_9$ results

In just about every low loss EELS spectra acquired from hexagonal barium titanate doped with 2/3 ruthenium (figure 3.11), the band gap region is consistently flat for approximately 4 eV post ceding the zero loss tail suggesting less electronic states around the Fermi level. The
sinter for Ba$_3$Ru$_2$TiO$_9$ was much more homogenous than the Ba$_3$RuTi$_2$O$_9$ sinter which contributed to the more consistent stoichiometry and thus low loss spectrum. Figure 3.12 and 3.13 (following page) is taken with a greater resolution in the VG STEM.

![Graph](image1)

**Figure 3.11** The low loss region of hexagonal Ba$_3$Ru$_2$TiO$_9$ with a 0.05eV/channel dispersion. The form is consistent, and the band gap region does not have the variability that the Ba$_3$RuTi$_2$O$_9$ preparation did, due to a much more consistent sinter.

![Graph](image2)

**Figure 3.12** Low loss of hexagonal Ba$_3$Ru$_2$TiO$_9$, taken on a VG STEM. The form, whilst consistent with figure 3.11, has much more detail.
Figure 3.13 Low loss spectrum of hexagonal $\text{Ba}_3\text{RuTi}_2\text{O}_9$. The form is consistent with figure 3.12, peaks at 5.5 eV, 13 eV, 17.5 eV, and 18.5 eV, for example, however again the band gap is different, it is much more sensitive to stoichiometric differences.

Two thirds doping is analogous with the ruthenium paring or both occupying the same $\text{A}_2\text{O}_9$ octahedral group. Some of the spectra, e.g. figures 3.12 show a small peak in the band gap region. It is likely to be due to an excitation from the s and d orbitals of the unit cell. It is such an inference that leads to some investigation of the density of electronic states in the next chapter (chapter 4).

3.4.4 $\text{BaRuO}_3$

The low loss spectrum of the barium ruthenate (figure 3.14) shows the material to be a conductor and this correlates well with previous reports [30]. The spectra’s shape, form and peak positions have considerable similarity with the spectra of barium ruthenium titanate.
Figure 3.14 Low loss spectra of barium ruthenate with 0.1 eV/channel dispersion. The main characteristics being a filled band gap with a noticeable tail on the zero loss peak and a large plasmon excitation peak at approximately 27 eV. It shows a full or occupied band gap region strongly suggesting the material to be a good conductor.

3.3.5 Barium titanate

Figure 3.15 Low loss spectrum of BaTiO$_3$ which shows a form dominated by the 27eV plasmon peak. There is also quite a degree of fine structure evident both pre and post ceding the plasmon peak and the band gap region is a lot wider and flatter than ruthenium containing samples.
There is a general similarity in the low loss features of the BaXO$_3$ materials, where X is equal to ruthenium, titanium or a mixture of both. In BaTi$_{x}$Ru$_{y}$O$_{3}$ (figure 3.9 and 3.11) and BaRuO$_3$ (figure 3.14), with the inclusion of plural scattering, the plasmon peak and the peak at 14 eV, and its multiple at 54 eV are all present. Barium titanate (figure 3.15) is the only one that shows significant differences. It is a bona-fide semi-conductor [2,31] and the flat, broad band gap feature supports this. It is none the less difficult to correlate the low loss features of barium titanate for example with all the influencing factors that make its low loss spectrum quite different to the ruthenium doped samples. These include a smaller unit cell, a smaller extinction distance, no ruthenium means no extra d electrons, and because the unit cell is of a higher symmetry there is no superlattice present [30, Appendix D].

3.5 Discussion

The materials investigated in this chapter were quite different in terms of structure and it is not a simple process to find a pattern from the structure alone. The barium ruthenium titanates are hexagonal, whereas the barium titanate is cubic. However, the low loss spectra alone suggest a considerable similarity between materials. They all have a dominant plasmon peak around 27 eV, a zero loss that tails into the band gap region and a filled band gap highlighting semi-conducting properties being near that of an ideal conductor. The elements are the basis of this similarity. They are all closely related in terms of their elemental constituents, i.e. barium, ruthenium and oxygen. So whilst the structure may be different, the electron density in the valence region, and the bonding characteristics are, not surprisingly, the more dominant factor influencing the properties of the material and the form of the low loss spectrum. This is, in the context of other more quantitative techniques, a rather empirical statement, and of course valence electron density is not the only determining factor. Particularly when considering that whilst electron density and EELS fine structure of the material may be determined quantitatively, subtle differences can have a large effect on the material.

Both empirically and quantitatively, the low loss spectrum in EELS, appears capable of providing insight into the potential macroscopic properties of a nano-scaled specimen through a comparative analysis, even when the materials are complex ceramic materials such as these.
As will be discussed in the following chapters, the spectra are far from ideal. The reason for this and what it means is elucidated in chapter 6 and 7. Particularly since the plural scattering has been included. It is common to remove the plural scattering for the purpose of identification of bonding energies in the core loss fine structure. However, the collective plural scattering is a result of an interaction with that region that is the most strongly affected by crystal morphology and elemental constituents, namely, the valence region. Thus it is worth considering what the spectra tell us, when the scattering is through a realistic cross section of the material and where multiple scattering is expected to take place.

3.6 Conclusion

In all the low loss spectra, the loss of energy due to the occupied states above the Fermi level can be seen. It is expected then that these states are involved in ionic/metallic type bonding, being less localised, and making the material more ‘metallic’. As a result, band gap sizes are impossible to determine accurately from the initial spectra, particularly given energy loss to the states above the Fermi level overlaps with the ‘tail’ of the zero loss peak. However, the spectra do have an identifiable shape or form which is consistent in all these ceramics. The question then is why is the band gap so difficult to resolve and why do these ceramics all have a low loss spectrum that looks so similar? Why are the plasmon peaks, located at 27 eV so poorly defined and broad? These are questions we attempt to answer in the following chapters.
3.6 Appendix

Appendix 3A: Scattering Mean Free Path Length

The Relative Mean Free Path (RMFP) is a comparative way to refer to the thickness of a material. The intensity of the low loss spectrum is dependant on the amount of energy lost to the material. This in turn is dependant on the electron density of the material and the mean free path is an indirect means of measuring this. However, the thicker the material, the more scattering that occurs and the higher the intensity of the low loss spectrum. Thus, if we take the difference of the thickness and the intensity, we find the relative mean free path. This can be done by integrating under the area of the elastic scattering and the inelastic scattering peaks, and calculating the difference.

The equation relating thickness and intensity is as follows:

\[ e^{\frac{t}{\lambda}} = \frac{I_I}{I_0} \]

where \( I_I \) is the intensity of the inelastic part, and \( I_0 \) is the area under the zero loss peak [33].

Appendix 3B: Diffraction Techniques

3B.1 Selected Area Diffraction

The most common electron diffraction technique, and one that was dominant in this investigation, is that of Selected Area Electron Diffraction (SAED or SAD) [34]. The technique focuses a parallel beam of high energy electrons, typically between 100 and 300 KeV, onto a small selected area of a specimen. This is useful in the determination of crystal structure, lattice parameters and orientation of the crystal growth, particularly owing to the fact that single crystals can be readily selected for examination. Whilst the selected area is comparatively large, of the order of 1µm, a great amount of information can be acquired through the d spacing (spacing between the crystal stacking planes) (see Appendix 3D for examples).
3B.2 Convergent Beam Electron Diffraction

Another useful electron diffraction method is Convergent Beam Electron Diffraction (CBED) [35]. Whereas in SAD, the electron beam on the specimen is parallel and relatively large, typically of the order of 1 μm in diameter, CBED has a converging beam of electrons which is quite small in diameter, usually 1-10 nm. In CBED, a pattern of disks is produced and a consequence of the TEM being capable of forming an electron probe smaller than 20nm in diameter, is that in such a small area, it is easier to find a region of crystal free of defects. Thus CBED can be applied to determine the symmetry of the crystal, a detail almost impossible to determine fully using SAD. A significant advantage of CBED, is that the intensity variation for a single Bragg diffraction angle can be acquired. This gives data on dynamical diffraction and absorption.

Two drawbacks of working on such a small area, however, are that there is an increased risk of local contamination and the convergent beam may heat or damage the specimen, particularly if a field emission source is used owing to the high current density. As a consequence, it needs to be noted that an undisturbed CBED pattern can only be expected if there is no strong lattice distortion or crystal bending inside the irradiated area. Both the specimen and the microscope need to be clean and free of hydrocarbon contamination. This means that in order for the crystals to be stable in the electron beam, they cannot have an abundance of protons in or on them through hydroxyl or hydrocarbon contamination. The discs of a CBED pattern may, for example, contain pendellösung, which can provide information about specimen thickness through the subsidiary minima, or kikuchi lines, which can be used to determine misorientation relationships between small grains in deformed materials.

Also, the Laue zone pattern of a large aperture, of the order of 10°, can be used for 3-D reconstruction of the lattice. This is because the Ewald sphere intersects higher order Laue zones (HOLZ) in circles of large diameter. Thus, while the absence of defects requires careful crystal preparation and TEM ‘driving’, the technique can be superior in determining specimen thickness, unit cells and lattice parameters (see Appendix 3D for examples).
3B.3 The Laue condition

The Laue conditions, \( q \cdot a_i = h_i \) integers, which result from the Fourier transform of the crystal lattice, guarantee that the scattered plane waves with wave vector \( k \) do indeed overlap and interfere constructively so that their amplitudes sum. With \( q = k - k_o \) and \( q = g \), the foregoing Laue conditions can be solved for \( q = k - k_o \) using \( a_i \cdot g = h \) and \( g = ha^{*}_1 + ka^{*}_2 + la^{*}_3 \) gives \( k - k_o = g(l) \). This is the Bragg condition in vector notation and results in the well known Bragg condition \( 2d_{hl} \sin \theta_B = \lambda \). This formula can be used to generate a construction first used by Ewald. Diffraction will only be observed if the Ewald sphere intersects one or more points, \( g \), of the reciprocal lattice. In electron diffraction, the radius of the Ewald sphere is much larger than the distances between the reciprocal-lattice points, and thus an approximation of a near flat Ewald curvature can be made.

Appendix 3C: The low loss spectrum of metals

Standard simple metals were chosen for comparison of their low loss spectra and included Cu, Au, and Al. Silicon was chosen as it is a simple, extensively studied material, which is face centered cubic in crystal structure and relatively easy to visualise from a crystallographic point of view. Copper and gold were also extensively studied, cubic and both well known to be very good conductors. TiAl was chosen (in chapter 5) as a ‘real world’ example of an alloy that is also a very good conductor. In accordance with all this, aluminium is an obvious addition, also being a very good electrical conductor. These examples all exhibited properties that made them useful in studying the significance of the form of the low loss spectrum in identifying the varies properties of ceramics. The low loss spectra for the materials mentioned above are presented in figures 3C.1 – 3C.4.
3C.1 Aluminium

![Graph of aluminium spectrum](image)

Figure 3C.1 Low loss spectrum of polycrystalline aluminium foil (Sample courtesy of Dr. T. Petersen, 1.75rmfp 0.1eV/channel dispersion).

3C.2 Gold

![Graph of gold spectrum](image)

Figure 3C.2 Low loss spectrum of electropolished Gold foil (0.71rmfp 0.1eV/channel dispersion).
3C.3 Copper

Figure 3C.3 Low loss spectrum of cold rolled copper sample. (2.04rmfp 0.1eV/channel dispersion)

3C.4 Silicon

Figure 3C.4 Low loss spectrum of silicon (2.16rmfp 0.2eV/channel dispersion)
The aluminium and silicon samples (figures 3C.1 and 3C.4) are remarkably different to the ceramics that have been discussed so far. They have a readily identifiable band gap region and clearly defined multiple plasmon peaks. There is no core loss activity in the entire low loss region of the spectrum, and in addition there is no Landau distribution i.e. background which is dominant in the ceramic materials. However, gold (figure 3C.2) and copper (figure 3C.3) don’t share the same spectrum ‘form’ or shape that aluminium and silicon do. They don’t have clearly defined multiple plasmon peaks, but do have a significant low loss EELS background.
Appendix 3D: Sintering results

3D.1 Barium titanate

A 1 to 1 mol ratio of BaCO$_3$ to TiO$_2$ was mixed, stirred and placed in a high alumina crucible. This powder was slowly heated to 1000°C stepwise and left to nucleate over several days. The rough sinter was cooled to 400°C and removed from the furnace.

The sinter, in ethanol, was ground in a mortar and pestle and placed back into the furnace, heated rapidly to 500°C, allowed to stabilise, then further heated to 1000°C for approximately 48 hours. The sample was cooled to 500°C in the furnace where it was finally removed and allowed to cool to room temperature.

The resulting sinter was a collection of well faceted white crystals, which were broken and lightly crushed under ethanol. A 20% mol by weight BaCl flux was added and further lightly crushed and stirred. This preparation was placed in the muffle furnace and heated to 1000°C stepwise. The sinter was again left at 1000°C for several days before being removed from the furnace and cooled. The resulting crystals remained cubic (figure 3D.1) and were still rather inhomogeneous.

Figure 3D.1 Cubic SAD pattern in the [310] zone-axis orientation and a Scanning TEM (STEM) image of the initial sinter of cubic barium titanate. This sample was heated to 1000°C over several days and resulted in cubic white crystals.
Thus, a pre flux preparation was alternatively placed into a furnace and heated up to 1350°C for half a day. This preparation proved to be more homogenous. The sinter was a white/cream colour consisting of larger chunks of which were themselves made of small clear/yellow crystals (see figure 3D.2) and were a combination of tetragonal and hexagonal phases.

As figure 3D.2 shows, the sinter had not nucleated well, and a partial melt was evident through the globular appearance of the sample. As a result the crystals that are present are very small, less that 1 µm, and are not ideal in terms of easily identifiable grains.

Figure 3D.2 SEM images of barium titanate prepared at 1350°C, which has a more globular appearance than the initial sinter suggesting it has undergone a partial melting.

Figure 3D.3 Two SAD TEM patterns of crystals that are hexagonal and tetragonal (cubic), respectively. They are from the second preparation sintered at 1350°C.

The reaction that was expected to occur was:

\[ BaCO_3 + TiO_2 \rightarrow BaTiO_3 + CO_2 \]
However, what seems to occur is a combination of the following reactions:

\[ \text{BaCO}_3 + \text{TiO}_2 \rightarrow \text{BaTiO}_3 + \text{CO}_2 \]

\[ 3\text{BaTiO}_3 + \text{CO}_2 \rightarrow \text{Ba}_{3-x}\text{Ti}_x\text{O}_{9-y} + \text{Ba}_y\text{O}_y + \text{CO}_2 \]

\[ \text{BaCO}_3 + \text{TiO}_2 \rightarrow \text{BaO} + \text{TiO}_2 + \text{CO}_2 \]

### 3D.2 Ruthenium doped barium titanate

A stoichiometric %mol ratio of BaCO\(_3\) and (TiO\(_2\).xH\(_2\)O and Ru or RuO\(_2\)) were weighed, mixed, stirred, and lightly crushed in a mortar and pestle under ethanol. This preparation was then placed in the muffle furnace and slowly heated to 1000°C, as in previous preparations. The sinter was left a 1000°C for several days and then removed.

The addition of ruthenium stabilized the hexagonal phase at a sintering temperature of approximately 1000°C. The general symmetry of P6\(_3\)mm was found in all hexagonal/trigonal crystals. An increased concentration of the ruthenium dopant above 1/3 had the effect of promoting faceted growth in the [0001] direction. This is the main difference with the 1/6 Ru\(^4+\) doped crystal, which neither had faceted growth in the [0001] direction, nor displayed evidence of having undergone a complete reaction. There was by-product present in both the optical images, and in the TEM as evidenced by an abundance of polycrystalline samples. By comparison, the BaRuO\(_3\) crystal (see section 3.6) whilst being similar geometrically, differed in the heavy domaining of the crystals and the 9R stacking which gave a longer c axis.

The unit cell parameters (Å), as determined by selected area electron diffraction using the Jeol 200 KeV 2010 TEM, are seen in Table 3D.1:

<table>
<thead>
<tr>
<th>Ceramic</th>
<th>Lattice parameter a (Å)</th>
<th>Lattice parameter c (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaTi(<em>{1/3})Ru(</em>{2/3})O(_3)</td>
<td>5.62</td>
<td>13.45</td>
</tr>
<tr>
<td>BaTi(<em>{2/3})Ru(</em>{1/3})O(_3)</td>
<td>5.81</td>
<td>14.62</td>
</tr>
<tr>
<td>BaTi(<em>{4/5})Ru(</em>{1/5})O(_3)</td>
<td>5.40</td>
<td>13.23</td>
</tr>
<tr>
<td>BaRuO(_3)</td>
<td>5.51</td>
<td>21.83</td>
</tr>
<tr>
<td>BaTiO(_3)</td>
<td>5.20</td>
<td>-</td>
</tr>
</tbody>
</table>
Selected area electron diffraction (SAD) and convergent beam electron diffraction (CBED) showed that preparations of ruthenium doped barium titanate (BaTiO_3) consisted of hexagonal crystallites. Solid state sinters of BaCO_3 + RuO_2 + TiO_2 were prepared to produce BaTiRuO_3 powder with either a 1/3 or 2/3 Ru:Ti ratio. By resintering with a flux, small relatively strain free crystals were produced. The 2/3 Ru^{4+} doped crystallites were thin and strain free enough for the electron diffraction to show the Fourier transform of a shape function. Standard integration of the zero loss peak over the plasmon loss peaks in the respective low loss electron energy loss spectroscopy (EELS) spectrum gives a thickness of approximately 1.03 relative mean free path (see appendix 3A for the definition of relative mean free path).

3D.3 BaTi_{5/6}Ru_{1/6}O_3

The presence of extra d electrons in BaTi_{5/6}Ru_{1/6}O_3 locks in the hexagonal phase, although it favoured the [1-10] orientation (figure 3D.4).

![Figure 3D.4. SAD pattern of BaTi_{5/6}Ru_{1/6}O_3 in the [1-10] orientation.](image)

The resulting sinter consisted of small yellow rocks with a yellow and black char type speckle throughout. The sinter had not seeded properly and pink flakes of RuO_2 and yellow crystals of barium titanate had not diffused into the sample properly (figure 3D.5).
Chapter 3: The plasmon loss spectrum: Experimental procedure and results

Figure 3D.5 Optical photos of BaTi$_{5/6}$Ru$_{1/6}$O$_3$ sinter showing unreacted pink and yellow crystals amongst the black barium ruthenium titanate. 3D.5a) is at a lower magnification showing the macroscopic powder; 3D.5b) at a higher magnification and 3D.5c) is at an arbitrarily large magnification showing the black crystals set amongst the yellow semi-reacted powder.

Figure 3D.6 SEM images of the BaTi$_{5/6}$Ru$_{1/6}$O$_3$ sinter shows the morphology of this sinter to be in the form of flakes rather than the chunks or globular appearance that the barium titanate showed.

The sinter was reground under ethanol, dried and returned to the furnace to be left at 1000°C for several days. As this run had only partially reacted, the sample was reground, and reheated to 1100°C for several days. This sinter had reacted better with large clumps of small black shiny crystals and small clumps of red crystals. The pure Ru (99.999%) had partially reacted with the O$_2$ atmosphere, which seemed to act as an inhibitor to further reaction with the BaCO$_3$ and TiO$_2$. If the sinter preparation could be heated to a higher temperature, better faceted and homogenous crystals may have formed.
The resulting sinter had crystals that were well faceted nonetheless and as can be seen in the optical and SEM images (figures 3D.5 and 3D.6), had two distinctive habits associated with the two forms of crystallites barium ruthenate and RuO₂.

A second preparation was subsequently carried out with a RuO₂ precursor rather than the pure ruthenium. The optical images (figure 3D.7) show lots of small shiny black crystals. There remains in the optical image some yellow barium titanate and large pinkish crystals of RuO₂. However, SEM images (figure 3D.8) also showed a more homogenous sinter, and with crystals which were larger and better faceted.

![Image](image1.png)

Figure 3D.7 Optical photos showing the powder from the second preparation using a RuO₂ precursor rather than pure ruthenium. Again the yellow brown sinter of barium ruthenate sintered with pure ruthenium can be seen. However, in contrast to figure 3D.5, it shows how the sinter is much more homogenous and black indicating better incorporation of ruthenium into the sample.

![Image](image2.png)

Figure 3D.8 SEM image of the sinter incorporating a 1/6 ratio of ruthenium from RuO₂ without the presence of flakes which occurred when using pure ruthenium.
3D.4 $\text{BaTi}_{2/3}\text{Ru}_{1/3}\text{O}_3$

A 1/3 mol or greater addition of ruthenium was found to grow hexagonal crystals that are typically faceted in the [000z] orientation, with a 6H, P63mmc symmetry (figures 3D.9, 3D.10, and 3D.11). Unlike the partial hexagonal morphology that occurred with a 1/6 ratio of Ru/Ti, the incorporation of a 1/3 ruthenium to titanium locked in the hexagonal phase. There was no combination of phases, nor a partial melt; it had completely reacted and undergone a transition to the high temperature hexagonal phase.

Figure 3D.9 Optical photo showing the powder from the preparation of $\text{BaTi}_{2/3}\text{Ru}_{1/3}\text{O}_3$ using $\text{RuO}_2$. The sinter is homogenous and a charcoal black.

Figure 3D.10 SEM image of $\text{BaTi}_{2/3}\text{Ru}_{1/3}\text{O}_3$ shows the hexagonal crystallite faceted in the [0001] zone-axis orientation. Some surrounding white coloured $\text{BaCl}_2$ flux that was not properly removed is also evident.
Figure 3D.11  

a) TEM bright field image of thin strain free crystals of BaTi$_{2/3}$Ru$_{1/3}$O$_3$, b) corresponding CBED pattern and c) SAD pattern can be seen in the [0001] zone-axis orientation and showing the 6-fold symmetry of the P6$_3$mmc space group.

3D5 BaTi$_{1/3}$Ru$_{2/3}$O$_3$

The synthesised macro crystals of BaTi$_{1/3}$Ru$_{2/3}$O$_3$ tended to be slightly distorted and as a result first appeared to have a 3-fold rather than 6-fold symmetry. But they maintained the general features that the addition Ru$^{4+}$ had on the structure (figures 3D.12, 3D.13 and 3D.14) i.e. a 6H stacking sequence and P6$_3$/mmc symmetry. It is interesting to note that the SEM images (figure 3D.13) of the larger, 1 – 5 µm thick crystals, showed that the crystals had grown in two layers and appeared to have a twin along the c axis. This growth is likely to be the cause of the morphology of the crystals which appear to be of a trigonal character rather than a hexagonal one. However, the CBED patterns (figure 3D.14), acquired from smaller and thinner crystals than those seen in the SEM images, do not reveal any identifiable deviation from the 6-fold symmetry that is analogous with the barium ruthenates. The crystallites were a lot smaller than those in the BaTi$_{2/3}$Ru$_{1/3}$O$_3$ preparation (average of 5µm in diameter as opposed to >10µm), and as a result the sinter was more homogeneous.
Figure 3D.12. Optical photos of the \( \text{BaTi}_{1/3}\text{Ru}_{2/3}\text{O}_3 \) sinter. They both show a homogeneous sinter. b) taken without a camera flash, gives a better indication of how black the sample is.

Figure 3D.13 a)-d) SEM images of different crystals of the synthesised \( \text{BaTi}_{1/3}\text{Ru}_{2/3}\text{O}_3 \). These crystals were much smaller than those of the \( \text{BaTi}_{2/3}\text{Ru}_{1/3}\text{O}_3 \) preparation. The morphology of these crystals shows clearly defined facets. The twinning in the layered growth formation can be seen in c).
Figure 3D.14 STEM image of a BaTi$_{1/3}$Ru$_{2/3}$O$_3$ crystal, and its associated b) CBED and c) SAD patterns. Both patterns are in the [0001] orientation and the CBED pattern indicates a crystal with the standard P6$_3$/mmc symmetry.

3D5.2 A transform function

The selected area diffraction pattern for the synthesised BaTi$_{1/3}$Ru$_{2/3}$O$_3$ (figure 3D.15) shows reflections that exhibit transforms approximating a $\sin^2(ax)/x^2$ function. Whilst difficult to see in figure 3D.15, each of the six small arms that surround a reflection are the result of simple Fraunhofer type diffraction through a hexagonal aperture. The bands of zero intensity can actually be seen! Figure 3D.15b shows a plot of the above function.
Figure 3D.15 a) selected area diffraction pattern of BaTi$_{1/3}$Ru$_{2/3}$O$_3$, showing reflections that exhibit transforms approximating a $\sin^2(ax)/x^2$ function.

Figure 3D.15 b) A sinc function
Since the sinc function is descriptive of Fraunhoffer diffraction, it may be said that this spectrum is just another scattering distribution function, or Patterson. A generalised Patterson for example is usually described in terms of atoms and the scattering interaction of atomic cores.

3D.6 BaRuO$_3$

Barium ruthenate was first reported by Randall and Ward [37] in 1959. It has a nine layered hexagonal structure that retains the P6$_3$mmc symmetry of its sister, the Ru doped hexagonal barium titanate. However, the unit cell possesses an extra octahedral group giving it nine layers of hcc configuration. It therefore has a longer $c^*$ axis, but with a shorter $a^*$ axis due to the tighter binding of the Ti-O bond.

There have been a variety of reported stoichiometries of the barium ruthenate compound [37-39]. However the most common stoichiometry is BaRuO$_3$, whilst one of the most common forms of BaRuO$_3$ is the 9R nine layer structure.

The synthesised crystals of barium ruthenate, unlike the titanates, were heavily domained (figure 3D.16), however, the symmetry and structure (figure 3D.17) remained fundamentally the same with the 9R stacking sequence possessing the face sharing octahedra arrangement. The low loss spectrum was seen to also be very similar to the barium titanates (section 3.6.6), although it lacked some of the fine structure.
Figure 3D.16 TEM bright field image of barium ruthenate which is heavily domain; b) shows a different crystal which is thin and layered showing a diffraction contrast effect, which is called a moiré pattern.
Figure 3D.17. a) and b) are the SAD and CBED pattern of BaRuO$_3$ in the [0001] orientation, respectively. The CBED has a 6-fold rotation symmetry like the barium ruthenium titanate. The a and b axis are smaller making the unit cell thinner and longer than the barium ruthenium titanate; c) SAD pattern of a twin taken in the field of view seen in the moire’ pattern of figure 3D.16b.

3.7 References:

CHAPTER 4

Computational evidence of complex ceramic electronic distribution

The density functional theory (DFT) results are presented for hexagonal barium titanate, and ruthenium doped hexagonal titanate. The structures were geometry optimised and their density of states and electron density maps acquired. The results are discussed in terms of the experimental low loss spectrum that was acquired for ruthenium doped barium titanate.
4.1 Introduction

A DFT study is conducted on the case study ceramics to confirm a direct conclusion of chapter 3, i.e. that the low loss form and features were dictated by the coulombic or charge distribution and in particular the electronic states at and near the Fermi level.

To this end, a geometry optimization of the hexagonal phase of BaTiO$_3$ has been conducted using Density Functional Theory (DFT) within the Local Density Approximation (LDA) and Generalized Gradient Approximation (GGA) schemes. The effect of different ruthenium doping concentrations on the structure and stability of the hexagonal phase has also been investigated. Since this investigation was also conducted on a doped structure of BaTiO$_3$ (Ba$_3$Ti$_x$Ru$_y$O$_3$), it was also simulated.

In previous theoretical studies, the atomic positions are often relaxed while keeping the cell volume fixed [1-4]. In some studies where the cell volume is relaxed [5-7], the optimised lattice parameters are not reported [6], which can be important from the point of view of experimental conference; where they are reported [5,7], it was only the cubic phase that was examined.

We employed density functional theory to determine the geometry of the hexagonal phase of BaTiO$_3$. To account for the lack of computational study on the hexagonal phase, the four perovskite phase hettotypes of barium titanate were also simulated to gain a reasonable assessment of the accuracy of DFT in geometry optimisation for these materials. A full geometry optimisation is conducted allowing both the ionic positions and the cell volume to relax. The results obtained using the LDA and GGA schemes are also compared.
4.2 Method

4.2.1 Computational details

All calculations were performed using the Vienna Ab-initio Simulation Package (VASP) code, which performs fully self-consistent DFT based plane-wave pseudopotential (PW PP) calculations [8-11]. The Kohn-Sham equations are solved using the functional of Perdew and Zunger [12] for the Local Density Approximation (LDA) scheme, and Perdew and Wang [13] for the Generalized Gradient Approximation (GGA) scheme. A plane wave cut-off energy of 395.994 eV and 395.700 eV was employed for the GGA and LDA schemes, respectively. The ultrasoft pseudopotentials, as supplied by VASP for Ba, Ti, O and Ru were used. K-space sampling was performed using a 6x6x6 Monkhorst Pack scheme for all of the perovskite phases and a 4x4x3 Gamma point mesh for the hexagonal phase. Several kpoint meshes were tested and the energy was found to converge to 0.0001eV for these meshes. The structures were relaxed using a Gaussian smearing width of 0.1 eV for the determination of partial occupancies for each wavefunction. The tetrahedron method with Blochl corrections [14] was used for the energy determination and calculation of the density of electronic states, during which the relaxed structure was fixed.

4.2.2 Structure models and geometry optimisation protocols

Five unit cells were constructed comprising the cubic, tetragonal, orthorhombic, rhombohedral and hexagonal phases of BaTiO₃. The initial atomic positions corresponded to those obtained experimentally [15-17]. The unit cells for the perovskite computations were based on a B centred octahedra in the ABO₃ structure. During the calculation, the atomic positions, as well as the cell angles and volume were allowed to relax. The orthorhombic phase did have its Ba(2) position fixed as this was found to give a lattice parameter closer to experimental results than the calculation where all atoms were allowed to relax.

The hexagonal phase of BaTiO₃ was constructed with initial atomic positions corresponding to those obtained experimentally [15-17]. During the calculation, the atomic positions, as well as the cell angles and volume were allowed to relax. The hexagonal phases presented a difficult case for the geometry optimisation routine. The initial unit cell for the hexagonal GGA calculation had to be enlarged by 1.5 times so convergence could be reached. The LDA
hexagonal calculation was started from the GGA hexagonal optimized results, as it would not converge from the experimentally supplied data.

During the relaxation of the unit cell, the routine fixes the plane wave basis set. To correct for this, the relaxation routine was continually restarted with the optimised basis set until there was no change in basis set between iterations. This is important, as whilst the routine will converge according to a set criterion, 0.001eV in this case, it is always for a fixed plane wave basis set, and thus gives an incorrect convergence. It is true that relaxing the structure in this way will result in a discontinuity in the energy, however such a protocol produces an absolute convergence in terms of lattice parameters and does not affect the final static energy calculation on an optimised geometry [14,18,19].

Figure 4.1. Structure of the cubic A-centered (left) and hexagonal (right) unit cells of BaTiO$_3$, indicating the types of atoms present, and highlighting the A$_2$O$_9$ octahedral group

Four models were used to examine Ru doped hexagonal BaTiO$_3$ at 1/6, 1/3 and 2/3 concentrations. The Ru atoms were substituted for the Ti(2) atoms at the 4-fold B cation site.
of the hexagonal structure (figure 4.1), giving rise to structures with the following stoichiometry: BaTi$_{5/6}$Ru$_{1/6}$O$_3$, BaTi$_{2/3}$Ru$_{1/3}$O$_3$ and BaTi$_{1/3}$Ru$_{2/3}$O$_3$. For the 1/3 Ru doped structure, two models were examined. One, where the 2 Ru atoms in the Ba$_6$(Ti/Ru)$_6$O$_{18}$ stoichiometry were placed within the same Ti$_2$O$_9$ group, and the other where the 2 atoms were placed in separate Ti$_2$O$_9$ groups (Table 4.3). A geometry optimisation was performed for each model using the Local Spin Density Approximation (LSDA).

4.3 Results and discussion
4.3.1 Energetics and Geometry

Previous studies using theoretical [1,2,20-23] techniques to investigate barium titanate have all concentrated on the perovskite phases. To the best of our knowledge, there have been no previous computational studies of the optimised hexagonal structure. The optimised latticed parameters for the cubic, tetragonal, rhombohedral, orthorhombic and hexagonal phases of BaTiO$_3$ are presented in Table 4.1. The values determined previously using theoretical [1,2,20-23] and experimental [15-17,24,25] techniques are shown for comparison. The displacement of atomic coordinates from experimental values after geometry optimisation using GGA and LDA are also discussed.
Table 4.1  
Calculated lattice parameters (a, b, c) in angstroms of the perovskite and hexagonal phases of BaTiO$_3$ using the generalized gradient and local density approximations. Experimental and calculated values determined by previous studies are shown for comparison. No previous studies had performed a total geometric optimisation of this phase for comparison.

<table>
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<th>Tetragonal a=b</th>
<th>Orthorhombic a b c</th>
<th>Rhombohedral$^a$ A=b=c</th>
<th>Hexagonal a=b c</th>
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<td>-</td>
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</table>

$^a$ Rhombohedral angles of un-optimized and GGA optimized phases were 89.87° and a=b=89.87° and g=90.00° degrees respectively; rhombohedral angles of LDA optimized phase were a=b= 89.95° and g= 90.00°
4.3.1.1 The perovskite phases

For all the perovskite phases it was found that GGA tended to overestimate the lattice parameters, while LDA underestimated them, as can be seen in Table 4.1. The cubic and tetragonal phases both retained their symmetry using both the LDA and GGA schemes and gave lattice parameters close to experiment and comparable with other theoretical calculations. The fractional positions of the atoms (Table 4.2) remained unchanged for the cubic phase. For the tetrahedral phase, there were no atomic displacements in the x-, y- directions. In the z-direction, the atomic displacements were larger for the GGA scheme but were still less than 0.072 Å, and less than 0.048 Å using LDA.

The rhombohedral unit cell only exhibited small atomic relaxations (less than 0.008 Å), giving rise to slightly different a(=b) and c lattice parameters and also a small change in the c-axis angle (see Table 4.1).

The orthorhombic unit cell resulted in a larger volume than experiment [15,16]. While there was no change in the fractional atomic positions in the x-direction for either LDA or GGA, there was a considerable change in the yz plane, particularly for the O atoms, which moved by up to 0.77 Å and 0.95 Å for GGA and LDA, respectively. The oxygen ions seemed to favour grouping around the Ti(1) atoms for GGA or Ti(2) atoms for LDA.

The resulting optimized lattice parameters for the orthorhombic phase were larger for both schemes. Previous investigations have fixed the unit cell volume during the simulation in order to avoid the so called ferroelectric instability associated with error in the lattice parameter determination [6,30]. This is a problem, particularly given the inherent overestimation and underestimation of the lattice parameters by GGA and LDA functionals, respectively. This instability seemed to have played a more significant role in this phase, however, although the LDA achieved a better geometry than the GGA, neither method produced a good agreement with experimental data for the lattice parameters. Fixing the cell, as previous studies have done, may help avoid this problem, but this would be counterproductive to the aim of this study. It should therefore be concluded that the zero temperature lattice relaxation performed within either the LDA or GGA approximation in
VASP, using the afore-mentioned pseudopotentials, is not capable of predicting the correct structure for the orthorhombic phase.

4.3.1.2 The Ti₂O₉ octahedral group

It is interesting to compare the stability of the corner-shared octahedral arrangement (of the perovskite phases) to the face-shared arrangement (of the hexagonal phase). The face shared arrangement is the Ti₂O₉, or more general A₂O₉ octahedral arrangement referred to throughout this investigation. The two octahedra groups were built with a Ti₂O₉ stoichiometry and arranged in the two different ways. For one model, the two octahedra were arranged so that they shared a corner, representing the common perovskite geometries. For the second model, the octahedra were aligned so that they shared a face, as is found in the hexagonal phases studies in this investigation. An LDA geometry optimization was then performed on these two hypothetical structures.

According to Pauling’s third rule, a corner shared arrangement should be more stable than a face-shared arrangement, because the cations are brought closer together in the face shared arrangement and the increased repulsion between the cations leads to a reduction in stability. This result was reflected in our calculations which showed the face-shared octahedral groups to have a higher energy (by 18.249eV) than the corner shared octahedra. In addition, the Ti-Ti cation separation was 1.09Å shorter in the face shared arrangement. Therefore, our modelling experiment supports the idea that the hexagonal phase is less stable because of a decreased stability of the face sharing octahedra.
4.3.2 The Hexagonal Phase

Relaxation of the hexagonal phase of BaTiO$_3$ using LDA and GGA kept the P6$_3$/mmc symmetry. The lattice parameters (Table 4.1) were found to be slightly larger than experiment using GGA by 1.94% and 1.54% and slightly smaller using LDA by 0.70% and 0.85% for the a and c axis, respectively. Hence, LDA proves to give better structural parameters than GGA for the high temperature hexagonal phase. Comparison of the fractional atomic displacements indicates there is little difference between LDA and GGA (Table 4.2). For both schemes the Ti atoms appear to displace the most from the experimental position, however, the displacements are not as large as seen for the orthorhombic phase, being less than 0.075 Å in the x- and y- directions. The next largest displacements were seen for the Ba atoms, which displaced by approximately 0.049 Å. The movements of the O atoms were less than 0.018 Å. All atomic displacements in the z-direction were less than 0.008 Å.

As seen from Table 4.1, there is a natural variation in the experimentally obtained lattice parameters, and whilst our LDA results appear to be quite good, the variation is greater than 0.1 Å. How much of this variation is due to the unsuitability of the pseudopotential, and how much is due to the temperature T = 0 K condition of the optimisation procedure is not easily resolved. This is a problem, also found for the perovskite phases, that the structural optimisation of the lattice parameters still faces, as this investigation has highlighted. To the best of our knowledge there have not been any previous DFT geometry optimizations of the high temperature P6$_3$/mmc hexagonal phase to compare.
Table 4.2

The change in optimised (fractional) positions of the atoms in the primitive unit cell of the different perovskite and hexagonal phases of BaTiO₃, calculated using LDA and GGA.

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<td>-0.018</td>
</tr>
<tr>
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<td>0.001</td>
</tr>
<tr>
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<td>0.002</td>
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<tr>
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<td>0.018</td>
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<td>0.028</td>
</tr>
<tr>
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</tr>
<tr>
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<td>0.005</td>
</tr>
<tr>
<td>O</td>
<td>0.028</td>
<td>-0.028</td>
</tr>
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4.3.3 Ruthenium doped hexagonal phase

The optimised structural parameters and total energy values for the 4 different Ru doped hexagonal BaTiO$_3$ structures are presented in Table 4.3. The relative energy for the two 1/3 Ru doped structures is also show, with the most stable structure having a value of 0 and the less stable structure having a positive value.

Depending on the Ru dopant concentration there are different cation B(2)-B(2) interactions present within the two octahedra of each structure. For the 1/6 doped model there is a Ti(2)-Ru(2) interaction in one octahedra and a Ti(2)-Ti(2) interaction in the other; for the 2/3 Ru model there are only Ru(2)-Ru(2) interactions; while for the two 1/3 models, there are either two Ti(2)-Ru(2) interactions or one Ru(2)-Ru(2) interaction plus one Ti(2)-Ti(2) interaction. The different B(2)-B(2) separation distances are displayed in Table 4.3 for the different doped models.

For the spin polarised 1/6 Ru doped model, the $\gamma$ angle was found to deviate by 0.02$^\circ$ from the ideal hexagonal structure. The Ti(2)-Ti(2) separation and Ti(2)-Ru(2) separations of the doped structure calculation are essentially equal to each other and are $\sim$4 % larger than the Ti(2)-Ti(2) separation of the undoped hexagonal phase. The volume is also slightly larger than the undoped phase due to the increase in the c axis length.

A comparison of the total energies for the two 1/3 Ru doped models suggests that the structure is more stable when the Ru atoms are located within the same A$_2$O$_9$ octahedral group. For the more stable structure, the Ti(2)-Ti(2) separation is only less than 0.4% smaller than in the 1/6 doped phase and similarly is $\sim$4 % Å larger than in the undoped hexagonal structure. The Ru(2)-Ru(2) separation is shorter than the Ti(2)-Ti(2) separation by $\sim$6 %.
Table 4.3
Structural parameters calculated for Ru doped hexagonal BaTiO$_3$ optimised using LDA.

<table>
<thead>
<tr>
<th>Ru Doped Concentration</th>
<th>#Ti atoms substituted with Ru</th>
<th>Ti(2)-Ru(2) distance (Å)</th>
<th>Ru(2)-Ru(2) (Ti(2)–Ti(2)) distance (Å)</th>
<th>A axis length (Å)</th>
<th>C axis length (Å)</th>
<th>c/a</th>
<th>Volume (Å$^3$)</th>
<th>Total Energy relative energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1/6$^c$</td>
<td>1</td>
<td>2.671</td>
<td>2.670</td>
<td>5.679</td>
<td>13.886</td>
<td>2.445</td>
<td>387.89</td>
<td>-259.493</td>
</tr>
<tr>
<td>1/3</td>
<td>2 (in same octahedra)</td>
<td>-</td>
<td>2.488 (2.663)</td>
<td>5.665</td>
<td>13.878</td>
<td>2.450</td>
<td>385.66</td>
<td>-254.960</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.186</td>
</tr>
<tr>
<td>1/3</td>
<td>2 (in different octahedra)</td>
<td>2.673</td>
<td>-</td>
<td>5.675</td>
<td>13.901</td>
<td>2.450</td>
<td>387.67</td>
<td>-254.774</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.673</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.186</td>
</tr>
<tr>
<td>2/3</td>
<td>4</td>
<td>-</td>
<td>2.504</td>
<td>5.655</td>
<td>13.898</td>
<td>2.458</td>
<td>384.82</td>
<td>-245.690</td>
</tr>
</tbody>
</table>

$^c$ $\gamma = 119.98^\circ$
For the 2/3 Ru doped phase, the structure is not spin polarised, as is the case for the most stable 1/3 phase. The Ru(2)-Ru(2) separation is also similar. This is not surprising as both models have a Ru(2)-Ru(2) interaction.

The volume of the unit cell of the different Ru doped structures is found to decrease from that of the undoped structure only in those models where there is a Ru(2)-Ru(2) interaction. There is however, a consistent increase in the c/a ratio with increasing dopant concentration.

In general the size of the Ru(2)-Ru(2) separation, which is smaller than Ti(2)-Ti(2) or Ti(2)-Ru(2), gives rise to a reduction in the a lattice parameter and hence volume. The volume of the 2/3 Ru doped model is therefore smaller than the 1/3 model as there are two Ru(2)-Ru(2) interactions.

It could therefore, based on this evidence, be suggested that when there is a Ru(2)-Ru(2) interaction present in the octahedra there is pairing of electrons, likely due to a d-orbital overlap between the two Ru atoms. However, the interatomic distance between the O(2) atoms and the 4-fold atoms is still less than that of the B(2)-B(2) distance. Thus, to what extent such d orbital overlap plays in stabilising the $A_2O_9$ octahedra cannot be qualified from this evidence alone.

In contrast, when Ru(2)-Ti(2) interactions are present, the energy of the structure is not reduced as much as it is with the Ru(2)-Ru(2) interactions. The reduction is most probably through the spin polarisation of the unpaired electrons, which are found to induce a spin magnetic moment on the Ru atoms only. The Ru atom in both the 1/6 Ru doped model and the 1/3 Ru doped model was calculated to have a magnetic moment of 1.3 $\mu_B$. These results highlight the influence that the position and concentration of the dopant has on the resulting magnetic properties of the system. It is also particularly curious that there is no spin induced on the titanium atom because it suggests that there is little interaction between the 4-fold atoms.
4.3.4 Density of States

4.3.4.1 Introduction

The DFT calculations have shown such a small energy difference between the two octahedral group configurations, that it seems intuitively natural that a variation in this configuration i.e. whether the two 4-fold atoms in the octahedral group are the same or different, should be found experimentally. Indeed, on the macro scale, the energy difference between individual unit cells would not be a relevant property, and the DFT calculations do not account for non-local effects in the material. Thus issue comes of concern when dealing with individual unit cells, in which case calorimetric measurements, the magnetic properties of whole crystal and diffraction techniques that probe ranges greater than a single unit cell would not show this difference in the octahedral configuration. The fine structure in EELS could reveal which configuration we had, through identification of whether we had a Ru(2)-Ru(2) or Ru(2)-Ti(2) bond. However there is a catch in that if the configuration was random, and the crystal is more than a single unit cell in dimension, then the fine structure would actually reveal detail from the combined effect of the two configurations. To gain a specimen 1 unit cell in thickness is far from trivial. Another possible region of interest in EELS would then be the band gap. Again this would be a combined effect. So then which would be more easily identified in terms of combined difference? Identification of the Density Of electronic States (DOS) of the two configurations should then be considered and the graphs below attempt to provide some insight into this.

4.3.4.2 Electron density distribution in $\text{Ba}_3\text{RuTi}_2\text{O}_9$

In figure 4.3, the electron density map of $\text{Ba}_3\text{RuTi}_2\text{O}_9$ is taken from a slice perpendicular to the $b$ axis, in the $a$ and $c$ plane (see figure 4.2). The interesting feature of figure 4.3 is the apparent lack of electron density between the Ti(2) and Ru(2) atoms that share the octahedral group. It is almost all between the oxygen atoms and these 4-fold atoms.
Chapter 4: Computational of complex ceramic electronic distribution

Figure 4.2 Structure of the hexagonal unit cell of $\text{Ba}_3\text{Ti}_x\text{Ru}_y\text{O}_{9-x}$, indicating the types of atoms present. The two thick lines indicate the position of the slices taken for the density distribution plots.

Figure 4.3. This electron density map is of a slice taken down the $b$ axis where we see the $A_2O_9$ octahedral group with a different arrangement of two face sharing octahedra containing a Ti(2) and Ru(2) atom. The slice cuts through the 4-fold atoms which are located at the fractional position of 0.407 along the $b$ axis (see figure 4.2).
Figure 4.4 is similar to 4.3 in the sense that there is also little evidence of significant interaction between the 4-fold atoms. However figure 4.4a does suggest more interaction between the Ru(2) atoms than between Ti(2)-Ti(2) or Ti(2)-Ru(2), (figure 4.4b and 4.3) as is expected from the shorter bond length (see Table 4.4) between the two 4-fold ruthenium atoms.

The electron density maps for the 1/3 and 2/3 ruthenium doped unit cells of Ba$_3$Ti$_{x/3}$Ru$_{y/3}$O$_9$ suggest the more dominant interaction is between the oxygen ions and the 4-fold site transition elements. As previously commented on (section 1.3), it has been suggested that the ruthenium induces stability into the high temperature hexagonal phase due to the greater interaction between the d orbitals of these ions [15-17,24]. However, if these electron density maps (figures 4.3, and 4.4) are to be considered alone, then the increased interaction between the transition element, ruthenium, and the neighbouring oxygen ions, would appear to be just as important.

These pictures support the view that there is more interaction between the Ru(2)-Ru(2) (figure 4.4a) than there is between Ru(2)-Ti(2) (figure 4.3) or Ti(2)-Ti(2) (figure 4.4b). The data in section 4.3.3 also led to this conclusion. However, to conclude that the most likely position of two Ru(2) atoms in this stoichiometry, i.e. Ba$_3$RuTi$_2$O$_9$, is in the same octahedral group, would be contradictory to previously published considerations of this stoichiometry [19,24,26]. A recent article by Maunders et. al.[26] also suggested that the Ti(2) and Ru(2)
atoms alternate in position. The results in this investigation cannot be said to testify as to the likely position of the Ru(2) dopant, rather only indicate which is most energetically favourable. This is because the DFT calculations are based on energetics, not kinetics. Thus the experimental data of Maunders et. al. is not directly comparable because it is from a crystal which is subject to the kinetics of the system. An ideal analogy is again diamond and graphite, where graphite is a more energetically stable configuration, however the kinetics of the system, where the carbon is exposed to the required pressures and temperatures, results in a structure, which whilst energetically might be ‘metastable’ is certainly not a material which one expects to ‘fall apart’.

The two Ru(2) atoms in the same octahedra appear to be energetically favourable, particularly given that this configuration enables all the electrons to be paired. Thus, given that most of the bonding interaction appears to be between the 4-fold atom and its surrounding oxygen atoms, neither configuration can be ruled out.

4.3.4.3 Density of States in Ba₃RuTi₂O₉ and Ba₃Ru₂TiO₉

A more quantitative interpretation can generally be gained through the difference of two or more electron density maps. However, it is difficult to compare two unit cells where the atoms are not identically located. Thus, for this case it is more appropriate to compare the electron density distribution in a more qualitative manner, and more informative to compare the total density of states, which is shown in the present section.

Figures 4.5 and 4.6 show total DOS plots of the 4-fold Ti(2) and Ru(2) atoms that sit in the A₂O₉ octahedral group of the Ba₃RuTi₂O₉ unit cell. The Ru(2)-Ru(2) or ‘same’ and Ru(2)-Ti(2) or ‘different’ octahedral arrangements, seem to have little difference in their DOS spectra. The Ru(2) atom (figure 4.6) has a higher number of states around the Fermi level. There is no particular evidence of a preferential interaction between the 4-fold atoms when the Ru(2)-Ru(2) arrangement exists, in either figure. Thus whilst the geometry of the unit cell is such that when both A atoms of the group are Ru(2), the 4-fold separation distance is shorter (see section 4.3.5), according to figures 4.5 and 4.6, the DOS does not seem to be affected.
Figure 4.5 Total DOS for the 4-fold Ti(2) atom in the optimised unit cell of Ba$_3$RuTi$_2$O$_9$ in which the 4-fold atoms are arranged in the same or different arrangement.

Figure 4.6 Total DOS for the 4-fold Ru(2) atom in the optimised unit cell of Ba$_3$RuTi$_2$O$_9$ in which the 4-fold atoms are arranged in the same or different arrangement.
However, the unit cells total DOS for the Ru(2)-Ru(2) arrangement has an equal spin up/spin down contribution. Therefore is has no measurable, or observable difference in the spectrum, because of this paired electron configuration. The Ru(2)-Ti(2) arrangement on the other hand, shown here (figure 4.7), does show an energy difference between the spin up/spin down contribution. Particularly around the Fermi level, where between 0 and 1.5 eV there are only spin down electron states.

![Total DOS for different arrangements](image)

**Figure 4.7 Total DOS for the unit cell for the Ru(2)-Ti(2) octahedral arrangement of the VASP optimised hexagonal Ba$_3$RuTi$_2$O$_9$ showing spin up/spin down energy difference.**

This is theoretically a potential source of identification via the EELS spectroscopy technique. If the spectrometer could separate the two spins, much like a Stern-Gerlach experiment, it could potentially distinguish between the two dopant configurations. Testing for a non-zero magnetic moment on the macrocrystal is also a possible method. However this would run into difficulty if the unit cells did not all have the same dopant configurations in the crystal. This spin dependant EELS (SDEELS) would enable a ‘local’ micro or nano range means of identification. This apparatus is yet to be realised, although SPEELS (spin polarized EELS) is a technique of, arguably, similar approach. SPEELS involves polarizing the incident electron wave, which then allows a linearly or circular polarized exit wave to be analysed. This is an insightful technique as the polarized wave can be referenced to the incident wave to determine the polarizing effect of the material [27-29].
If one was to differentiate, or filter the two spin components of a high energy exit wavefunction from an unpolarised beam, each localised wavefunction, i.e. electron, will have a different spin dependence on it. Therefore, if the electron has passed through a region of coupled electron pairs, i.e. a symmetrised wavefunction region, such as a coherent plasmon packet, or field of Cooper-pairs, or a region of the band gap, where all of the electron spins are correlated to a single value, then there could be a spin differential in each collected exit wavefunction. This could then be potentially imaged using a PEELS arrangement.

Another difference between the two octahedral arrangements that can be seen in the unit cell DOS (figure 4.8) is the difference in band gap. Whilst figure 4.8 shows little difference in the total DOS for the two arrangements, figure 4.9, plotted with a resolution of \( \pm 0.005 \) eV, versus \( \pm 0.0915 \) eV for the previous DOS plots, shows a small change in the band gap width. This is also a possible source of distinguishing between the two octahedral arrangements. The ‘same’ arrangement would appear to have a smaller band gap, of the order of \( 0.2 \pm 0.005 \) eV (figure 4.9). This trend seems logical since the ‘same’ configuration is energetically favourable.

![Graph showing DOS for total unit cell for same and different arrangements](image)

Figure 4.8 The DOS for the total unit cell for the same and different arrangements. There is little difference with the exception of the greater contribution form the ‘different’ arrangement at the -18eV and 13 eV levels.
Figure 4.9 The DOS for the total hexagonal $\text{Ba}_3\text{RuTi}_2\text{O}_9$ unit cell for the same and different arrangements. The scale is expanded to better see the band gap region.

4.4 Conclusion

Structural optimisation of all perovskite and hexagonal $\text{BaTiO}_3$ have shown that GGA overestimates the unit cell parameters, while the LDA scheme presents lattice parameters that are smaller than experimental results. Whilst this is consistent with previous studies, the LDA scheme presented more experiment consistent geometries than the GGA with respect to the hexagonal phase.

Analysis of 4 different Ru doped models indicated that for the 1/3 Ru doped model the more stable structure exists when the two Ru atoms are placed within the same octahedral group in the unit cell as opposed having one in each octahedra. In the Ru doped structures that contain a Ru(2)-Ti(2) interaction a magnetic moment is induced on the Ru atoms.

The DOS confirmed extensive occupation above the Fermi level which explains the intensity in the low loss spectrum around the Fermi level. It also showed that there is almost no difference between the two octahedral arrangements of ruthenium doping. Whilst it confirmed
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that there is indeed a band gap difference between the two octahedral arrangements, this
difference is so small that attempting to identify which octahedral arrangement we have
through EELS would at first seem a fruitless exercise. Particularly with the kind of resolution
we saw in the chapter 3 results, and given the questionable accuracy of the pseudo-potentials
used in the LDA scheme used for energy determination.

There were two differences noted however that could feasibly be used for identification. One,
the B(2)-B(2) bond length which a consistent selected area diffraction study might reveal, if it
was conducted with a quantitatively assured stoichiometry. Two, the spin difference approach
would seem to be, potentially, the more reliable as the difference is greater and its effect
would be less influenced by long range coulombic effects. We just need to build the
equipment to test it.

4.5 References

Chapter 4: Computational of complex ceramic electronic distribution


CHAPTER 5

Coherent Inelastic Scattering in Si and TiAl

An image filter was used to test a simple model describing the dynamical scattering of electrons that have suffered multiple interactions with plasmons. Semi-quantitative agreement is observed in both Si and TiAl under quasi two-beam conditions. In the latter material it is shown that the classical Hirsch, Howie, Whelan analysis of contrast due to dislocations can be carried out in images produced by electrons that have suffered as many as five interactions with plasmons and at thicknesses at which the unfiltered and zero loss images show no contrast. This work in this chapter was carried out collaboratively with Prof. H.W. Whitfield, and Prof. A.F. Moodie. It was the model of Goodman et. al. that was the catalyst for the experimental work (see section 5.5 for an explanation of the model that was presented in Goodman et. al. [3]).
5.1 Introduction

So we see the DOS of the barium titanates indicated electron state occupation above the Fermi level. In chapter 3 we also found that this material, whilst been a conductor or semi-conductor, and whilst containing so called free electrons, presented low loss spectra that was particularly different to the metals. Thus, as a result we can see that the ideal sample to use in chapter 5 will be Si and perhaps Al. As will be shown in chapter 5, we actually used an alloy, TiAl for the purpose of using a ‘real world’ sample. But, looking at the Cu and Au, and the ceramic barium ruthenium titanate, it was not just a matter of selecting a good conductor, or a material with free electron content, it was the kind of spectra that the material generated that was important. We touched on why these materials produced these kind of spectra in chapters 3 and 4. We shall return to this issue in chapter 6 and 7. However, in this chapter we shall confirm the assertions made by the Goodman model and draw some additional conclusions about the plasmon interaction.

5.2 Theory

Yoshioka's equation [1], describing the inelastic scattering of fast electrons in solids belongs to the class of multi-channel formulations of quantum mechanics that have been intensively studied for many years. Despite this, some relatively straightforward and apparently simple questions remain unanswered. Two of the more important reasons for this stem directly from the Coulombic interaction, namely the large cross section for many-body interactions and the prevalence of many beam scattering.

This latter point is well illustrated in the Borrman effect [2] (see figure 5.2 where the central beam is non-centrosymmetric and the first order diffraction beam is symmetric in intensity distribution), which, at the outset appeared to offer a direct method of estimating inelastic interactions. The effect is most conveniently observed in convergent beam diffraction mode by setting up a “two-beam” orientation and noting the asymmetry of the central beam about the Bragg angle; the diffracted beam remaining symmetric. A Bloch wave calculation with only two
beams and a phenomenological absorption coefficient can then usually be fitted to the intensity
distribution in the central beam, often to considerable accuracy, by using the structure amplitude
of the diffracted beam and the phenomenological coefficient as adjustable parameters. However,
as is well known, if a purely elastic n-beam calculation is carried through for the same system the
central beam is usually still found to be asymmetric and further the asymmetry changes as the
crystal is rotated about the diffraction vector. The reasons for this are well understood and derive
from the circumstance that many-beam interactions can rarely be neglected in obtaining a
quantitative estimate of processes involving the exchange of energy with the specimen.

All of these considerations apply with equal weight on the image plane so that the quantitative
interpretation of lattice images from a thick crystal is likely to involve substantial computation.
At lower resolution fewer problems are likely to accrue since frequently, for instance in the
classical techniques for the determination of the Burger's vector of defects, only the form of the
intensity distribution is significant. Examples of this are evident later in the chapter.

In an attempt to gain a qualitative grasp of some of the simpler aspects of the solutions to
Yoshioka's equation [1] a grossly simplified but soluble model was set up many years ago [3].
The essence of the approximate description is that electrons suffering successive plasmon losses
couple into the elastic dynamically scattered beams, retaining phase relationships. If this model
had any validity, it would provide a mechanism for the scattering of electrons by plasmons
through angles very much larger than those that are often estimated kinematically. With the
further simplification that the wavelength differences are ignored and that an effective two-beam
interaction can be established the total scattering process is described by the ladder of figure 5.1.
Here horizontal loops represent two-beam scattering at one energy and vertical loops coupling of
electrons that have interacted with a plasmon. All loops are summed to infinity. Here it has been
guessed that the form of the solution depends principally on the topology of the scattering
diagram, in effect that a very rough approximation to the complete scattering diagram summed to
infinity will give a better indication of the nature of the experimental results than a sum over the
first few accurately calculated terms in the Born series.
Figure 5.1. A scattering diagram displaying elastic and inelastic scattering. The horizontal lines represent scattering at a fixed energy and the vertical lines represent scattering between different energies. The wave-packet transfers rapidly through the energy states ($\epsilon_n$) when all excitation errors ($\zeta_n$) are small and equal. 0 and h refer to the zeroth order and diffracted beams respectively [3].

The solution to the ladder approximation (Appendix 5A gives an outline) takes the form of a wave packet that “moves” through the crystal with each successive plasmon loss. With increasing many-beam interaction, this form is progressively degraded. The form of the solution is sufficiently distinctive that it seemed superficially that a qualitative experimental check would prove possible but meticulous work by Alan Spargo [private communication] showed that the experiment imposed stringent demands on both mechanical and electronic stability which could not be met at the time. Now, those demands can be met and qualitative aspects of the model were verified during the course of this investigation. An attempt to describe one practical application and to mention some implications for quantitative work are also mentioned. This application was suggested by A.F.Moodie [private communication].

5.2.2 Theoretical Considerations

Two significant points that were mentioned in the summary are key to a proper understanding in the processes being discussed in the next two chapters. This is a good place to reiterate these
points and they shall be re-enforced a number of times as they are key to comprehending some of the conclusions and statements being made.

One: that the elastic and inelastic scattering events are coupled rather than separate. This is a point of distinction with respect to Yoshioka’s formalism [1] and is true where the maths does not separate out the two processes i.e. elastic and inelastic scattering. This is important because it means one does not need to think of scattering as being a time dependent sequential process. Questions such as ‘does it undergo elastic and then inelastic scattering, or the other way around?’ are simply not valid. However, it also means questions relating to the step-by-step process of scattering are also not valid. In virtual energy exchange for example, there is no time dependency in a virtual energy exchange process in the sense of a virtual particle moving from time \( t = 0 \) to time \( t=1 \), the energy exchange takes place in a single time frame. This is consistent with the standard model of the universe and thus such discussions do not break any currently accepted laws and concepts in quantum mechanics, nor does Yoshioka’s equations.

The problem is it is sometimes difficult to think in this way because of the dominance of the Born series and Perturbation theory in the construction of the mathematics in scattering theory. True, the mathematics works! But it forces a particular way of thinking about the scattering that is not always necessary.

Two: that each successive higher order scattering event in multiple scattering scenarios, are dependant and connected rather than independent.

This is a consequence of the collective description of the wavefield as a whole, that is presented in chapter 5. It is important to continue to think in terms of wave-particle duality. Since the solution and these discussions refer to the wave-field as a whole, it is instructive to consider the consequence of this as follows. If a wave function was made up from a single electron, it would contain all the information that one associates with elastic and inelastic scattering.
Thus, the two points to remember are:

1. *The wavefield is considered as single wavefunction, not the sum of parts.*
2. *It does not scatter sequentially and elastic and inelastic scattering are not separable in this description.*

### 5.3 Experimental Setup

Using convergent-beam diffraction techniques wedge shaped crystals were oriented in an optimum two-beam configuration (see figure 5.2), that is, one with the minimum number of non-systematic interactions; then a field of thickness fringes (pendellösung) which started from the edge of the specimen was imaged, first unfiltered, then filtered for zero loss and successive plasmon losses. Finally, convergent-beam mode was reinstated in order to determine whether any change in orientation could be detected.

Even with current equipment this series of operations lasted for more than an hour and hence imposed severe demands on stability. It was found that these demands could be met provided that:
- (a) at least one hour was allowed to pass after switching on the entire instrument before a detailed line up was attempted,
- (b) the specimen and instrument were sufficiently clean so that no contamination could be detected throughout the experiments,
- (c) specimens were securely mounted on a bare grid.

The materials chosen for the experiments, Si and TiAl have small unit cells so that orientations could be found at which the two beam approximation has as great a range of validity at 200KeV as it ever can have.

The plasmon loss spectra, of the type analysed by Howie [4] and Hirsch and Humphrey [5] were measured in the usual way and it was checked that the secondary contribution i.e. contribution from sources other than that of the plasmon excitation process, was sufficiently small in both materials as to have a negligible effect on the model.
Images were accordingly recorded on the GIF with an exposure of two seconds and at successive offsets of 16.6 eV for Si and 16.8 eV for TiAl. A slit width of typically 5.0 eV was used. The form of the wave packet was found to be insensitive to the width of the slit and to the precise value of the offset. Gross changes in the slit width, say to 10eV however, by allowing more background to contribute to the image, whilst not degrading the form of the wave packet, did degraded the visibility of the thickness fringes. Tanaka has pointed out [6] that using a slit with width less than that of the loss peak does not improve the visibility of plasmon loss filtered convergent-beam diffraction patterns but simply reduces the signal to noise ratio. This was consistent with what was found in this investigation. Finally, whether the forward scattered or the diffracted beam was selected with the objective aperture made no appreciable difference to the observations. Figures 5.4 and 5.7 are a good example of this, where figure 5.4 is a set of bright field images and 5.7 is a set of dark field images.

Figure 5.2 Example of a two-beam setup, which also shows the Bormann effect [2].

5.4 Results and Discussion.

In two beam orientation, with the 004 reflection satisfied, the plasmon loss spectrum of the Si wedge shows a zero loss peak and five plasmon loss peaks detectable above the background (figure 5.2). Images and line scans formed from the various loss peaks are shown in figure 5.3 and figure 5.4. Here the maximum intensity of the thickness fringes can be seen to move into
thicker parts of the specimen with successive plasmon losses in qualitative agreement with the model.

Figure 5.3. The plasmon loss spectrum of the Silicon wedge in two-beam orientation showing the zero loss peak and 5 plasmon loss peaks. The 5th plasmon loss, as evidenced in the images below, being the last that will contribute to an image that is resolvable above the background.

Figure 5.4. The pendelloesung from a silicon wedge move to the right, up into the wedge of the specimen, as the wave packet transfers through the energy states. Image a) is a zero loss filtered image, b) is imaged from the 1st plasmon loss filtered electrons, c) the 2nd plasmon loss, d) the 3rd plasmon loss, e) the 4th plasmon loss, and f) the 5th plasmon loss.
Figure 5.5. Line scans of the pendellosung exhibit the progression of the wave packet as it transfers through the energy states. The peak amplitude moves to the right until it is dispersed in the weak background (relative scale that is arbitrary in units).

Thus to reiterate what we see: The low loss spectrum is taken from a specific region of the silicon wedge that shows pendellosung. When an image is formed from those electrons that are involved in losing defined amounts of energy in the generation of a plasmon, the resulting image will still display pendellosung. However the pendellosung will be visible in the thicker part of the material.

A similar series of observations was made on a specimen of lower wedge angle (figures 5.6, 5.7 and 5.8) and dark field images were recorded at successive plasmon loss peaks. Again the results show at least semi-quantitative agreement with the model.
Figure 5.6. The plasmon loss spectrum from the second Si wedge. This is a much thinner wedge resulting in only two resolvable plasmon loss peaks. Here, as is clear in figures 5.7 and 5.8, the excitation error is very small as evidenced by the low background. Images from the 3rd and 4th plasmon losses are still evident even though they are scarcely visible in the spectrum. It is noticeable that the maximum intensity of the pendellosung moves to the thicker part of the wedge.

Figure 5.7. Image of a different region of the silicon specimen. The objective aperture has been centred on the diffracted beam so that dark-field images are produced. It is noted that the maximum intensity of the pendellosung moves to the thicker portion of the wedge. Image a) is an unfiltered dark field image, b) is a zero loss filtered image, c) the 1st plasmon loss, d), e), and f) the 2nd, 3rd and 4th plasmon losses respectively.
Figure 5.8. The unfiltered line scan of figure 5.7, profile a) is over a more even wedge, and shows the near exponential apparent absorption of the pendulum solution. Profile b) is the zero loss filtered image line scan showing reduced background and intensity c) and d) again show the wave packet progression with increasing thickness. In e) and f) the peaks are scarcely detectable and degradation of the signal-to-noise ratio is apparent (relative scale that is arbitrary in units).

Although Si proved convenient in establishing that the model had some degree of plausibility it seemed desirable to determine whether the approximation retained some validity in describing the scattering from a material of quite different type, namely one of metallic character. To this end the experiments were repeated using the alloy TiAl which has a low-energy loss spectrum of similar general character to Si (figure 5.9). The results are shown in figures 5.10 to 5.14. Clear evidence of the progression of the predicted ‘wave -packet’ into the specimen is again apparent.

With respect to the observed pendellösung in figures 5.10 and 5.13, for higher order plasmon losses, the peak intensity moves to greater thicknesses, however, due to a reasonably high inelastic scattering factor, the ‘straggling’ in each of the n scattering events increases and thus we still get electrons contributing to an image in the thinner part of the specimen. i.e. the pendellösung tend to begin at zero thickness, even when being imaged from a higher order plasmon loss.
Figure 5.9. The plasmon loss spectrum from the TiAl sample. The well defined plasmon loss peaks and low background have the form that is necessary for the validity of our theory.

Figure 5.10. Filtered images of TiAl specimen in two beam orientation at a) zero loss, and b, c, d, e, f, at 1\textsuperscript{st}, 2\textsuperscript{nd}, 3\textsuperscript{rd}, 4\textsuperscript{th}, 5\textsuperscript{th} plasmon losses respectively showing the wave-packet image resulting from coupling in the ladder approximation. Images derived from successive plasmon losses derive from increasingly thick portions of the specimen. Surface defects disappear and details from thicker portions of the specimen become visible.
Figure 5.11. The profiles of the pendellösung of figure 9 showing the wave packet progression through the specimen. Where a) is the zero loss profile, and b), c), d), e), and f) are the 1\textsuperscript{st}, 2\textsuperscript{nd}, 3\textsuperscript{rd}, 4\textsuperscript{th}, and 5\textsuperscript{th} plasmon losses respectively (relative scale that is arbitrary in units).
Figure 5.12. Unfiltered image a), and 6th plasmon loss image b) of TiAl alloy. The arrows highlight the appearance of dislocations and increased contrast around the stacking fault. The grain boundary and pendellösung show greatly enhanced visibility when filtered for higher order plasmon loss electrons. 5.12c is the zero loss filtered image showing the effect of excluding any plasmon scattered electrons. 5.12d has had the contrast brightness and gamma artificially adjusted to achieve a maximum possible intensity. It clearly shows even with the grey scale altered, it cannot match the unaltered plasmon filtered image in intensity over the thicker region of the wedge i.e. you can not see the dislocations that run deep into the specimen unless you are filtering the higher order plasmon peak and excluding the zero loss energy.
Figure 5.13. The successive images of a) unfiltered, b) zero loss and c), d), e), f), g) and h) are the 1st, 2nd, 3rd, 4th, 5th and 6th plasmon losses respectively, show the wave packet nature resulting from the ladder model. Images, taken at the same exposure, and derived from successive plasmon loss peaks reveal the presence of dislocations in thicker parts of the spectrum.

From these observations we conclude that, despite its crudeness, the simple ladder process provides a good description of the process which generates the form of the intensity distribution resulting from the coupling of plasmon loss with ‘two-beam’ scattering, at least for some of the less complicated types of materials. It would appear that this can assume significance in several apparently disparate applications.

The first relates to the observation of defects. Imaging the zero loss peak is a standard technique, bringing obvious benefits particularly at high resolution. However the formation of a ‘wave-packet’ generated by vertical coupling on the ladder and the consequent movement of the maximum into thicker parts of the specimen with successive plasmon losses means that filtering in thickness becomes possible. This is illustrated in figures 5.10, 5.11, 5.12, 5.13 and 5.14. In particular it becomes possible, by the selection of the appropriate plasmon loss peak, not only to detect but to analyse the strain fields of defects, using the classical techniques of Hirsch, Howie and Whelan, at thicknesses where no contrast is observed in the unfiltered or the zero loss beam.
(figure 5.12). It is, of course, one of the great strengths of the classical two beam technique that the \( g_b \) criterion depends only on the form rather than on the quantitative aspect of the wave-function, and this is preserved in the ladder approximation.

Figure 5.14. The profiles of the pendellösung of figure 12. Where a) is the unfiltered profile b) is the zero loss profile, and c), d), e), f) and g) are the 1\(^{\text{st}}\) 2\(^{\text{nd}}\) 3\(^{\text{rd}}\) 4\(^{\text{th}}\) and 5\(^{\text{th}}\) plasmon losses respectively. The dip at 53 nm is from the stacking fault evident in the associated images (relative scale that is arbitrary in units).

The second concerns the quantitative description of the Bormann effect. For electrons the localised losses, that is, core transitions, have relatively low cross sections and dynamical scattering is always significant. These factors make the quantitative analysis of the convergent beam diffraction pattern obtained from a crystal, say, some 1,000Å in thickness a matter of some difficulty and this is nowhere more apparent than in attempts to calculate the asymmetry in the
disc of the forward scattered beam when a low index reflection is satisfied, without recourse to
phenomenological coefficients, assumptions about two beam approximations or the model, valid
only for the scattering of X-rays, still to be found in many standard texts. By establishing an a
priori estimate of the parameter $b$ (see appendix A referring to the equation with parameter $b$) in
the ladder approximation it is hoped that a more realistic description can be devised.

At this point, before we summarise a conclusion, it would be instructive to reconsider figure 5.12.
To reiterate the point, figure 5.12a is an unfiltered image, so it includes zero loss and plasmon
loss electrons. Figure 5.12b is a plasmon loss filtered image. The screw dislocations on the thick
side of the stacking fault can only be made out when filtering for the plasmon loss electrons. The
zero loss image, figure 5.12c, sharpens the image up and makes it clearer, but it does not show
the dislocations on the thick side of the stacking fault. The ‘enhanced image’ makes that region
already illuminated, brighter, but only serves to highlight the fact that it is not a question of
intensity in the zero loss image, it is because electrons from the thick regions are simply not
involved in the construction of the zero loss image.

![Figure 5.15 Unfiltered (figure 12a) Vs. plasmon filtered image (figure 12b). The same parameters
are set. The figure reinforces the fact that irrespective of how you look the picture of how much
manipulating you do, the only way to see the dislocations that run deep into the thick portion of
the specimen is to image the specimen thought plasmon filtered electrons.](image)

Figure 5.15 Unfiltered (figure 12a) Vs. plasmon filtered image (figure 12b). The same parameters
are set. The figure reinforces the fact that irrespective of how you look the picture of how much
manipulating you do, the only way to see the dislocations that run deep into the thick portion of
the specimen is to image the specimen thought plasmon filtered electrons.
5.4 Conclusion.

It is concluded that for materials, and in orientations, in which the two-beam approximation can be expected to have some validity the ladder approximation described in this chapter will have comparable validity, provided that the low-energy-loss spectrum is of similar simple type to that of Si or TiAl. When those conditions are satisfied the technique of imaging from successive plasmon loss peaks will enhance the contrast of defects at increasing depths in the crystal, thereby enabling Hirsch-Howie-Whelan analysis to be carried through at thicknesses otherwise inaccessible at the operating voltage.

The approximation can be extended to describe many-beam interactions but, beyond the effective three-beam approximation it becomes complicated, and in particular loses the simple ‘wave-packet’ form.

As has been noted previously this type of ladder approximation also provides a mechanism for extended convergent-beam contrast.
5.5 Appendix


INELASTIC CONTRAST AND ABSORPTION FOR A PARALLEL-PLATE CRYSTAL

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Observations have been made recently of high contrast regions in the inelastically scattered background of convergent-beam patterns. Strictly speaking, the first published evidence was from Kossel (1948) and the first explanation offered by Uyeda and co-workers (1954). In the past, theories of inelastic contrast and of absorption have been developed separately. However, since both phenomena have the same physical origin the contrast theory should also explain the absorption. This point was made by Radi (1968) while Cowley and coworkers (1966-69) developed N-beam treatments for inelastic scattering and absorption involving the high-voltage limit (phase grating approximation). Howie (1963) obtained results for plasmon damping similar to part of those shown here using a different physical model. Our approach to dynamical plasmon scattering is a reciprocal space method, which we believe is more compact and comprehensible than Bloch wave methods, and has the advantage of applicability to N-beam situations with the correct boundary conditions.

A scattering diagram applicable to plasmon plus elastic scattering is shown in Figure 1. Horizontal loops represent elastic and vertical loops inelastic scattering. Energy states are $E_0$, $E_1$, etc. Results for a 6-rung calculation (Figure 2) show the non-exponential damping and emergence of a ‘wave-packet’ which transfers rapidly through energy states when all excitation errors are small and equal, i.e. for forward or symmetrically equivalent scattering. The model also explains multiple scattering contrast at high angles.

A derivation is given with 2-beam elastic scattering. Extension to N beams alters the details but not the emergence of a wave packet. Differential equations for the nth amplitude are

$$q_n' = iaPq_n + ib(q_{n-1} + q_{n+1}) + iC_n Lq_n$$

where $a$ and $b$ are elastic and inelastic scattering factors, $q$ is a matrix of the form $\begin{pmatrix} \varphi_0 \\ \varphi_n \end{pmatrix}$ and

$$L = \begin{pmatrix} r_n & 0 \\ 0 & \xi_n \end{pmatrix}$$

contains the excitation errors.

More compactly, using scattering matrices (Sturkey 1962),

$$S' = iaE(P)S + ibGS$$

leading to the separable and diagonalizable solution

$$S = \exp iaE(P)z \cdot \exp ibGzl$$

with $l = \begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \end{pmatrix}$ and where $E(P)$, $G$ are commuting matrices of diagonal, and circulant character.
Since in practice $b \ll a$ this solution has the form of a carrier and a modulation wavefield. The carrier is the 2-beam solution with finite (excitation error) while the modulating part forms a wave packet. This can be discussed in terms of quasi-particle theory. When the $\zeta_n$ are unequal, the form is still valid, but individual rungs will have damped envelopes. When all $\zeta$ differ appreciably form $\zeta_0$ the wave packet is lost.

The $r_n$ in the above L matrix become appreciably non-zero only for a crystal with highly tilted boundaries. This is the only case when upper-layer effects are appreciable in plasmon scattering in the ‘free-electron’ approximation. Finite $r_n$ introduces an orientation dependence into plasmon scattering due to the crystal surfaces, in addition to that due to the lattice.

Experimental evidence for the above model to be discussed is (i) extended convergent-beam contrast (ii) asymmetric absorption function for a highly tilted crystal. In addition, evidence for the sensitivity of plasmon excitation to excitation error has appeared, but this work should be extended. It is noted that the present diffraction theory gives many results parallel to those from channelling theory based on classical scattering. However, the latter cannot apply to diffraction contrast in the energy range 80 to 100eV from crystals up to 1000Å thick.

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Appendix 5A2: Further Outline of the Approximation

We see in the above equations that if $b$, was to equal 0, then we would effectively have a two beam solution, where by $a$ is effectively $\sigma$, $P$ is effectively $V_{hkl}$, L contain the excitation errors, and because in this case we are perpendicular to the specimen, i.e. no large angles, $r_n$ is 0. $C_n$ constant of the nth excitation error.
It was Ewald who first derived the two-beam approximation, thereby revealing new aspects, not only of crystallography, but also of physics. The diagrammatic methods established more than a quarter of a century later display in graphic form the radical nature of the approximation which, in this language, selects one type of diagram and sums to infinity all diagrams of this type. Ewald, of course, used the approximation to describe the scattering of X-rays by a perfect crystal, a physical system in which the approximation is extremely good. Because the interaction is Coulombic and the rest mass is finite the approximation is never more than qualitative when applied to the scattering of electrons. Nevertheless the approximation finds wide and important application since, for instance, it constitutes the basis for the most extensively used method for the analysis of defects. The factor of importance here is that the form, that of a two level system, is all important.

The set of equations describing the ladder model for the system considered here is,

\[ \frac{d}{dz} \Psi_n = iM \Psi_n + ib(\Psi_{n-1} + \Psi_{n+1}), \]

with \( M \equiv \begin{pmatrix} 0 & \sigma V_g & \\
\sigma V_g & \zeta_g & \\
\zeta_g & \end{pmatrix} \), the two-beam matrix for the reflection \( V_g \) having the excitation error \( \zeta_g \) and the interaction constant \( \sigma \). \( b \) is the scattering factor for the vertical couplers in the ladder. This is a less general system than that considered in [2] since the experiments are carried through at nearly normal incidence and since all excitation errors are taken to be equal, that is, that only two-beam interactions are allowed.

Defining \( |S\rangle \equiv \begin{pmatrix} |\Psi_1\rangle \\
|\Psi_2\rangle \\
\vdots \\
|\Psi_{n-1}\rangle \\
|\Psi_n\rangle \\
\vdots \end{pmatrix} \), the set of equations can be written in scattering matrix form as,

\[ \frac{d}{dz} |S\rangle = i(M \otimes E)|S\rangle + iC|S\rangle, \]

where \( E \) is the unit matrix for the entire system and \( C \) is a matrix which selects the appropriate kets. Since the matrices commute the solution can be written formally as,

\[ |S\rangle = \exp\{iMz\} \exp\{ibCz\} |0\rangle. \]
Now whatever the details of the calculation, $b \angle \angle \sigma V'$, so that the intensity distribution as a function of $z$ will take the form of a ‘wave-packet’, the ‘carrier’ being thickness fringes. The simplicity of this result, unsurprisingly, diminishes progressively as the approximations are relaxed. What is perhaps surprising is that such a crude model can describe severely circumscribed but attainable experimental situations sufficiently well for it to be used as a basis for devising and implementing applications.

### Appendix 5B: Yoshioka’s equation


\[
\left(-\frac{\hbar^2}{2m} \nabla^2 + H_e + H'\right) \phi = E \phi
\]

Where $-\frac{\hbar^2}{2m} \nabla^2$ is the kinetic energy of the electron, $H_e$ the energy of the crystal and $H'$ the interaction energy between the interaction energy and the crystal. The prime represents the term which separates the inelastic energy exchange from the rest of the interaction. (See the reference for full details).

### 5.6 References

CHAPTER 6

Correlations in Plasmon Scattering of Electrons

This chapter is primarily concerned with the theory of plasmon scattering, and the ways and means of thinking about plasmon scattering such that it is easier to utilise and consider in the analysis of a material. The chapter begins with a conventional approach of describing a plasmon through the dielectric formalism. A natural extension of this formalism utilising the Patterson function is then proposed. A quantum field theory description is discussed along with its implications, and finally a further consequence of the collective description of the wavefield as a whole is considered in the investigation of plasmon scattering through large angles.
6.1 Introduction

It was shown in chapter 5 that through the filtering of electrons that have undergone inelastic scattering, images can be formed from regions that are many mean free path lengths into a specimen. However, in order for this to occur we must have the scattering process involving primarily the conduction electrons. When the second, third, and higher order processes become involved with bound valence electrons (no longer unbound, near-free or ‘bare’), we lose what we call the form of the plasmon response that is associated with an interaction predominately concerned with these ‘bare’ electrons. The form literally just refers to the shape and appearance of the spectrum. As was found in chapter 5 when this form is lost, filtering higher energies in the low loss region of the spectrum does not provide any advantage in terms of image creation. Indeed, the images are blurry and lack distinguishable features which leads to the conclusion that when our desired form, what we call the ideal form, is lost, so to does the desired coherence in the image.

A characteristic of materials that contain this ‘bare’ plasmon response is that they are conductors or semi-conductors. B, Al, Si, P, Ga, Ge, As, Sn, and compounds such as GaAs, TiAl, for example, all have a bare plasmon character (see chapter 7 and ref. [1]).

When comparing Si, Al, and TiAl, for example, they all share the ‘simple’ metal form of electron correlation and as such, have a characteristic ‘bare’ plasmon spectrum (see figure 6.1). Thus, the kind of material where an image can be formed with these bare electrons must depend on the characteristics of its conduction band.

A characteristic pattern of this ‘bare’ plasmon loss spectrum, is the multiple, or higher order plasmon loss excitation peaks. It is well known, that if a specimen is too thin, such higher order losses will not be excited. However, simply making a specimen thicker will not automatically result in well defined higher order excitation peaks because there is also the necessity for there to be a homogeneity in the coulombic field that forms the conduction band. It is evident that when this homogeneity is not found, the simple type of plasmon loss spectrum, as seen in figure 6.1, will not be obtained.
Figure 6.1. *Simple type or ‘bare’ low loss plasmon EELS spectrum showing the desired form, from the point of view of plasmon imaging.*

6.2 The Form Factor and the Patterson

6.2.1 The dielectric formalism

It is well known [3-5] that the plasmon loss spectrum is directly related to the imaginary component of the dielectric function of the material through the relationship of

\[
\text{Im} \left( \frac{1}{\varepsilon(\omega, q)} \right) = \frac{4\pi e^2}{q^2} \left[ S(-\omega, q) - S(\omega, q) \right] \quad \text{Eqn 6.1}
\]

where \( q \) is the vector of \( \theta \) rad \( k \), \( \varepsilon \) is the dielectric response function, \( \omega \) angular frequency, and \( S \) the form factor, which describes the scattering distribution of the material and is related to both the mean free path of the material and the degree of order, or lack there of, in the material. The form factor and its interpretation is found across all scattering techniques, including x-ray scattering, neutron and light scattering, and electron scattering where it is commonly referred to as the scattering factor. The form factor is a measure of the degree of scattering for a given angle i.e. the amplitude as a function of \( k \), and the structure factor, is a measure of the form factor averaged over all orientations for a given structure, because the scattering itself is a function of angle.
It is this dielectric function that is commonly referred to as a potential source of utilization of the low loss spectrum.

Where dielectric function is written as:

$$\text{Im}\left(\frac{1}{\varepsilon(\omega,q)}\right) = \frac{4\pi e^2}{q^2}\left[S(-\omega,q) - S(\omega,q)\right] \quad \text{Eqn 6.2}$$

so that

$$S(\omega,q) = \frac{N}{2\pi} \int d^3x e^{iqr}G(x,t)$$

where $G$ is a pair distribution function in both space and time. …Eqn 6.3 \cite{3,6}

The form factor is, in simple terms, the Fourier transform of the charge distribution, which is called the Van Hove correlation function, or the time dependant radial distribution function. This is why it is eluded that by performing an inverse Fourier transform, the electron density distribution of the material can be obtained.

In this case the inverse Fourier transform of equation 6.2, will give the distribution function of the density distribution. The reason for this is that, whereas for x-ray, light and neutron scattering, multiple scattering can be reasonably ignored, this is not the case for electrons. So the distribution function $G(x,t)$ becomes the distribution of a distribution, and so on, depending on how many scattering events take place.
Figure 6.2 Diagram of the scattering vectors referred to in the formula throughout the chapter. $k$ is the incident beam, $k'$ the scattered beam and $q$ the vector of $\theta$ rad.

The low loss is directly representative of the electron density distribution of the material. Thus, where we have a fermion-fermion interaction, we see a direct analogy with inelastic neutron scattering.

6.2.1.1 The neutron analogy

This section presents background theory that is relevant to the neutron analogy presented in the previous section. The neutron analogy is presented because it explains how a correlation function is used to describe a property from the momentum and energy exchange, which occurs during a scattering event. This helps understand why a Patterson function can be used in the case of plasmon scattering, because, as will be explained, the Patterson function is a
correlation function. Therefore, regardless of the fact that in the analogy, atomic positions of, in this case neutrons, are the subject of correlation with plasmons, we are still presented with a correlation function. However, it is a correlation of electron densities in the case of plasmon electron scattering.

The van Hove function, used in neutron scattering, is generally complex since the position operators \( r_i(0) \) and \( r_j(0) \) do not commute. The integration over \( dr' \), of the Van Hove correlation function \( G(r,t) = \frac{1}{N} \sum_{i=1}^{N} \sum_{j=1}^{N} \left\{ \delta[r' + r(t)] \right\} \delta[r - r_j(0)] dt \) is not trivial since the position operators \( r_i(0) \) and \( r_j(t) \) remain non-commutating, except in the classical case, or where \( t = 0 \) in the quantum case. This is because in the quantum mechanical case, the position operator is \( r_i(t) = \exp(iHt/\hbar)r_i\exp(-iHt/\hbar) \), using Heisenberg’s representation. As such, the van Hove function is generally complex [7].

It therefore follows that \( G(-r,-t) = G^*(r,t) \) and importantly, since for fluids \( S(k,\omega) \) is invariant under a change of sign of \( k \), hence \( S(-k,\omega) = S(k,\omega) \). Significantly, this is for a classical case, or where \( t = 0 \), which is a subtle point, which will be commented on again in section 6.3.3. However, if we assume for the moment, as is typically done, that the coulombic field can be approximated as a fluid, then the classical case is a very useful insight to pursue. Even in the quantum case, because multiple scattering can typically be ignored with neutrons and x-rays, the \( t = 0 \) approximation is particularly valid.

Many texts readily show the relationship between the van Hove correlation functions and the energy exchange in inelastic scattering [7,8]. Pierre and Hansen for example [7] readily show how the Fourier transforms of the van Hove correlation functions are related to inelastic scattering of neutrons. Their energy and momentum are related by the familiar expression

\[
E = \frac{\hbar^2 k^2}{2m}
\]

and for the energy and momentum the dynamical conservation laws require that \( \hbar \omega = E_2 - E_1 \equiv \hbar \omega_{12} \) and \( \hbar k = E_2 - E_1 \equiv \hbar k_{12} \), where \( E_1 \) and \( E_2 \) are the initial and final energies. The probability for such transitions is given by Fermi’s golden rule,

\[
W_{12} = \frac{2\pi}{\hbar} \left[ (2, k_1 | V | l, k_2) \right]^2 \delta(\hbar \omega - \hbar \omega_{12})
\]

where \( V \) represents the perturbation, or the interaction. Pierre and Hansen state this for neutrons, so that \( m \) would be the mass of a neutron and the
transition of states refers to neutrons. Thus, whilst the corresponding correlation functions refer to the nucleus, they are completely and directly analogous with correlation functions from the plasmon field and the same ‘rules’ apply. Both electrons and neutrons are fermions and both have a correlation function and a corresponding form or structure factor associated with their distribution. As the equation $S(-k, \omega) = S(k, \omega)$ describes, assuming the crystal is centrosymmetric, polycrystalline or amorphous, then the invariance can also be analogous to any general fluid, to which the coulombic field is sometimes approximated.

### 6.2.2 The form factor

The relationship between the dielectric function and dynamic form factor $S(q, \omega)$ is four dimensional. One dimension, $\omega$, refers to the energy transfer involved and is actually the Fourier variable that is conjugate to the time correlation $t$. The other three dimensions refer to the scattering angle, $q$, which is the Fourier vector that is conjugate to spatial correlations $r$. The van Hove correlation function (or time-dependent radial distribution function), $G(r,t)$, is the four dimensional Fourier transformation of the dynamic form factor $S(q, \omega)$. For very short times $t$, $G(r,t)$ approximates the radial distribution function $g(r)$. The time argument of $G(r,t)$ is useful in scattering because it describes how the structural correlations are correlated from one moment to the next, when the system is dynamic.

Alternatively, you can view the relationship between $S(q, \omega)$ and $G(r,t)$ as two independent Fourier transformations; one for the time/energy variables and the other for the space/reciprocal space variables. The important thing to note is that all of the structural information is contained in the variables $q$ and $r$, and not in $\omega$ and $t$. Therefore, if density-density spatial correlations are to be measured from EELS, then the spectrum must be measured as a function of both $q$ and $\omega/eV$.

The fact that the form factor here is the Fourier transform of a pair distribution function, is why it is ideal for describing the correlation of the system. However, there are a couple of restrictions with regard to its use for interpreting that linear response function which we call the dielectric function, when applied to electron scattering. The main assumption is that the momentum transfer is unique for each scattering angle. The distribution function, expressed
as is, is based on the first Born Approximation (see appendix 6C), and hence assumes single scattering events. Therefore, it is difficult to account for beam coupling effects and a deconvolution of plural scattering must be performed before expressing the complex components of the function. Since the dielectric formalism is based on the first Born approximation [6] it is also the basis behind why the low loss spectrum is typically described as containing only the imaginary component of a complex function. Whereas since in reality a spectrum containing plural scattering will contain many scattering components both of a coherently correlated and arbitrarily correlated fashion it will be by necessity complex (see Appendix 6A for definition of coherent).

The above description is what is described as the dielectric formulation. It represents scattering as a whole, which is why it is useful because, as shall be shown, it stems directly from the form factor of the material and the form factor is influenced not just by the free electron density, but also by the distribution of the material, i.e. the structure.

So $S(k\omega)$ is the Fourier transform of the radial distribution function $g(r)$ and is typically labelled $\rho(r)$ since the distribution relates to the electron density. It can be seen [3] to be the mean square density fluctuation in the ground state. $S(k\omega)$ is of fundamental importance for the description of longitudinal properties of the electron gas, or, any many-particle system. It yields directly the density fluctuation spectrum and by suitable integrations, both the time-dependant density density correlation function and the pair distribution function as most thoroughly described by Pines [3]. But this description is still essentially based on single scattering events. Thus, even though multiple scattering events mean realistically we are dealing with the distribution function of a distribution function it by no means denies the fact that this representation of the form factor, based on a single scattering event or single distribution function is a very useful description of the exit wave function.
6.2.3 The Patterson

The function which involves the Fourier transform of an electron density distribution is actually the same as what has been referred to as the generalized Patterson function [9]. The generalized Patterson function is, in the words of Cowley [9], “in essence a correlation function giving the spatial correlation of electron densities”.

This is where the electron density function may be described as
\[ \rho(r,t) = \rho_0(r) * g(r,t) \]  \( \text{Eqn 6.4} \)

where \( g(r,t) \) is a distribution function. So the space and time dependant generalized Patterson is then
\[ P(r,t) = \rho_0(r) * \rho_0(-r) * g(r,t) * g(-r,-t) \]  \( \text{Eqn 6.5} \)

This is itself a very descriptive representation of the plasmon spectrum and the Fourier transform of the low loss spectrum could also be considered as a kind of Coulombic Patterson.

How, though, can this distribution be a Patterson? To start with, consider a crystal, which is defined by the function
\[ \phi_f = \phi S \]  \( \text{Eqn 6.6} \)

were \( \phi(u)= \) a set of delta functions, and \( S \) is a shape function,

then \[ \phi_f = \phi(u \*) S(u) \]  \( \text{Eqn 6.7} \)

where the subscript \( f \) denotes that the zero order has been ignored.

Where \( \phi(u,v,w) = \sum \sum \sum V(h,k,l) \phi \left( u - \frac{h}{a}, v - \frac{k}{b}, w - \frac{l}{c} \right) \)  \( \text{Eqn 6.8} \)

including the three dimensions \( u,v,w \), for clarity, and for a crystal with edges \( a_1, a_2, a_3 \), we have
\[ S(u,v,w) = \frac{\sin(\pi u)}{\pi u} \cdot \frac{\sin(\pi v)}{\pi v} \cdot \frac{\sin(\pi w)}{\pi w} \]  \( \text{Eqn 6.9} \)

\[ \phi(r) = \sum_{g=\infty}^g V(g) \exp(2\pi g \cdot r) \]

---

* This derivation was outlined in a set of lectures given by A.F.Moodie in 2000 C.E. at RMIT University.
\[ \sum_{h} \sum_{k} \sum_{l} V(h, k, l) \exp(2\pi i(hx + ky + lz)) \quad \text{Eqn 6.10} \]

This is a description of the potential in a crystal, which can be thought of as a 3 dimensional map in volts of the atomic shapes.

It can be rewritten as \[ \phi(r) = \sum_{g=-\infty}^{\infty} V(g) \left[ \cos \left(2\pi g \cdot r\right) + i \sin \left(2\pi g \cdot r\right) \right] \quad \text{Eqn 6.11} \]

so that if the potential is considered to be real, then

\[ \phi(r) = \sum_{g=0}^{\infty} [A(g) \cos(2\pi g \cdot r) + B(g) \sin(2\pi g \cdot r)] \quad \text{Eqn 6.12} \]

with \( A = \frac{1}{2} [V(g) + V(-g)] \), \( B = -\frac{1}{2} [V(g) - V(-g)] \) and \( V(-g) = V^*(g) \) ...Eqn 6.13

if we suppose that atom \( j \) has the coordinates \( x_i, y_i, z_i \) expressed as fractions of the unit cell and the ‘shape’ in volts, i.e. the distribution of the potential, \( \phi_i(x, y, z) \) The atom on the cell can then be described by

\[ \phi_i(x - x_i, y - y_i, z - z_i) \equiv \phi_i(x, y, z) \ast \delta(x - x_i, y - y_i, z - z_i) \quad \text{Eqn 6.14} \]

which is saying that \( \phi_i(x, y, z) \) is convoluted with a delta function at \( (x_i, y_i, z_i) \)

Now the Fourier transform of this is

\[ \mathcal{F}[\phi_i(x, y, z) \ast \delta(x - x_i, y - y_i, z - z_i)] = \mathcal{F} \phi_i(x, y, z) \mathcal{F} \delta(x - x_i, y - y_i, z - z_i) \quad \text{Eqn 6.15} \]

\( \mathcal{F} \phi_i(x, y, z) \) has been defined as the atomic scattering factor for electrons and

\[ \mathcal{F} \delta(x - x_i, y - y_i, z - z_i) = \exp\{2\pi i(u x_i + v y_i + w z_i)\} \] so that we can say

\[ \mathcal{F}[\phi_i(x, y, z) \ast \delta(x - x_i, y - y_i, z - z_i)] = f(x, y, z) \exp\{2\pi i(u x_i + v y_i + w z_i)\} \quad \text{Eqn 6.16} \]

This equation is for one unit cell so the function is continuous in the variables \( u, v, w \). But the crystal is a unit cell which repeat at the interval \( a, b, c \). This is like saying the crystal is one unit cell convoluted with an infinite array of delta functions at the repeat distance of the unit cell, hence
Chapter 6: Correlations in Plasmon Scattering of Electrons

\[ V(g) = V(u, v, w) \delta(u - h, v - k, w - l) \] is equivalent to

\[ V(g) = f_v(h, k, l) \exp(-2\pi i(hx + ky + lz)) \] ... Eqn 6.17

This can be generalised to \( n \) atoms of type \( i \) as

\[ V(h, k, l) = \sum_{p=1}^{n} f_v(h, k, l) \exp(-2\pi i(hx + ky + lz)) \] ... Eqn 6.18

or to \( m \) types of atoms as

\[ V(h, k, l) = \sum_{i=1}^{m} \sum_{p=1}^{n} f_v(h, k, l) \exp(-2\pi i(hx + ky + lz)) \] ... Eqn 6.19

For a single scattering approximation, the relationship between a wavefunction sufficiently far from the specimen, and one that is emerging from the specimen is the Fourier transform. The Fourier transform of a real function has both amplitude and phase. When the intensity is measured, the phase is lost, but the amplitude will be the square root of the intensity.

We can substitute these into

\[ \rho(r) = \frac{1}{V_C} \sum_{g} F(g) \exp(2\pi i g \cdot r) \] ... Eqn 6.20

i.e.

\[ \rho(h, k, l) = \sum_{h} \sum_{k} \sum_{l} |F(h, k, l)| \exp(2\pi i d(h, k, l)) \exp(2\pi i(hx + ky + lz)) \] ... Eqn 6.21

where again, \( \rho(h, k, l) \) is the electron density distribution, \( V_C \) is the volume of the unit cell, and \( |F(h, k, l)| \) is the square root of the measured intensity of the reflection. This is the structure factor.

If we could measure the exit wavefunction which equals \( \Psi F(h, k, l) \), we could obtain the structure by Fourier transform, that is \( F \Psi F(h, k, l) = \rho(h, k, l) \).

However, as we can only measure the intensity, then,

\[ \Psi I(h, k, l) = \Psi F(h, k, l) F^*(h, k, l) \] ... Eqn 6.22
So if we Fourier transform equation 6.22 then;

\[ \mathcal{F}_T \mathcal{F} \Psi(h,k,l) = \mathcal{F}_T (\rho(x,y,z) * \rho(-x,-y,-z)) \] …Eqn 6.23

we obtain the Patterson function, which we see to be a function of the electron density distribution of the material.

\[ \frac{1}{V_c} \mathcal{F}[I(h,k,l)] = \frac{1}{V_c} \mathcal{F}[\mathcal{F}^*(h,k,l) \mathcal{F}(h,k,l)] = V_c \rho(x,y,z) * \rho(-x,-y,-z) = P(x,y,z) \] …Eqn 6.24

i.e. \[ P(x,y,z) = V_c \int \int \int \rho(X,Y,Z) \rho(x+X, y+Y, z+Z) dXdYdZ \] …Eqn 6.25

This function can be calculated from experimental data

\[ P(x,y,z) = \frac{1}{2V_c} \sum_{h=-\infty}^{\infty} \sum_{k=-\infty}^{\infty} \sum_{l} \left( |F(h,k,l)|^2 \exp\{-2\pi i (hx + ky + lz)\} \right) \] …Eqn 6.26

\[ F(\vec{h}, \vec{k}, \vec{l}) = F^*(h,k,l) \], i.e. \[ F(\vec{h}, \vec{k}, \vec{l}) = |F(h,k,l)| \] …Eqn 6.27

so \[ P(x,y,z) = \frac{1}{2V_c} \sum_{h=-\infty}^{\infty} \sum_{k=-\infty}^{\infty} \sum_{l} \left( |F(h,k,l)|^2 \exp\{-2\pi i (hx + ky + lz)\} \right) \] …Eqn 6.28

\[ P(x,y,z) = \frac{1}{V_c} \sum_{h} \sum_{k} \sum_{l} I(h,k,l) \cos\{2\pi (hx + ky + lz)\} \] …Eqn 6.29

and the intensity can be measured. We note that \[ P(x,y,z) \] always has a centre of symmetry since \[ \cos\{2\pi (hx + ky + lz)\} \] is an even function of \[ x,y,z \].

\[ \rho(h,k,l) = \rho_{\text{unit}}(h,k,l) * \delta_S \] …Eqn 6.30

\[ F(h,k,l) = [F_{\rho_{\text{unit}}}] \delta_{\text{RS}} \] …Eqn 6.31

So an EELS spectrum contains the measured intensity distribution for the potential. If we Fourier transform it, according to equation 6.24 we get the Paterson for the material. Now whilst the intensity, as equation 6.29 describes, is real, the distribution of the Fourier transform will always be symmetric (see figure 6.4 for example). Equation 6.31 shows the structure factor is the Fourier transform of the electron density distribution. So it does not
matter in this context how many times the wavefunction has been scattered as the wavefunction is a complete representation of the density distribution, and from there, it can be proceeded to be analysed as such, i.e. the Patterson.

Figure 6.3. *a*) is a simple type of plasmon spectrum and *b*) the FFT of *a*). The FFT is taken with the zero loss peak removed and the horizontal scale is a logarithm of the intensity (arb. units, the use of a time domain is also discussed in section 6.3.3.1) (see Section 6.2 for further details)

Why bother to consider the distribution as a Patterson? A possible application would be to map the electron density distribution out for a material. The distribution is effectively giving
the structure factors for each orientation, and as such a low loss or density map could be obtained.

To do this though, each distribution for each beam would have to be successively measured. In the spectra above, a large aperture was typically used. If the EELS spectra are collected with a large entrance aperture, so that the $q$ has been completed integrated out of the differential cross-section, then the Fourier transform will only provide information about time correlation. For an interpretation of the $q$ dependent data, the effects of multiple scattering must either be avoided or removed in some manner. Standard Fourier log de-convolution no longer works in such cases as the assumption of statistical independence between successive inelastic scattering events breaks down. Researchers have generalised the Fourier-log approach for such cases [10] but the analysis is complicated.

As long as the momentum and space representation is used, then we will not have a time domain but rather a spatial domain in the Fourier transform. However, the spatial information is still of a convoluted distribution. Placing an aperture around each diffracted beam does not exclude this problem as the ‘physics’ occurs in the sample. The beams remain coupled, aperture or no aperture, however, the advantage of the Patterson description is that a distribution taken for each beam has a different structure factor and thus will give spatial information. The energy is still coupled, but the structure factor gives information of the nature of the coupling which is a consequence of the structure distribution. The difference between collecting one beam, or $n$ beams will be seen in the intensity, not the distribution.

6.2.3.1 What’s happening? (Details of the Patterson)

When performing a Fourier transform, if the original specimen has a large background of plural scattering, then the corresponding FT will consist of numerous peaks. If on the other hand there is little background, but distinguishable plasmon peaks, then the Fourier transform will have a smooth distribution.

The axis of the Fourier transform of the low loss spectrum is in the time domain, not the energy domain, thus any correlation must be concerned with correlations in the time domain; they are reciprocal to the spatial domain. A peak of correlation in the time domain relates
therefore to the spatial correlation of the material, and it is the analysis from the point of view of a Patterson that reveals this.

We should be able in the energy and momentum domains to see a negative spectrum, however, this is not the case. In the domain of the Fourier transform, understanding negative time is conceptually difficult, however from the perspective of the Patterson, it is just the $\mathbf{g}$ vector we are referring to. However, the phase of the wave is lost, thus, all we see is the positive component in the spectrum, because we are after all only seeing the causal effect. To see the negative time would be anti causal, which is fundamentally why we can’t see the phase and why we need to measure the phase relative to a further point of time if we are to have any hope of measuring it.

The low loss spectrum is in the energy domain (Table 6.1) and the relationship to the momentum domain can be seen through the relationship $E = \frac{p^2}{2m} + V$, where $p$ is the momentum and $V$ the potential energy. For each representation, the Fourier transform elucidates the corresponding space and time domains. The space and time representation is a fundamental property of wave mechanics, and so the consideration of the space representation has the advantage of being the representation in which the Patterson is applicable.

<table>
<thead>
<tr>
<th>Representation</th>
<th>Corresponding uncertainty relation</th>
<th>Domain of low loss</th>
<th>Domain of Fourier transform of low loss</th>
<th>Analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy-time</td>
<td>$\Delta E \Delta t \approx \hbar$</td>
<td>Energy</td>
<td>Time</td>
<td>Form factor</td>
</tr>
<tr>
<td>Momentum-space</td>
<td>$\Delta p \Delta x \approx \hbar$</td>
<td>Momentum</td>
<td>Position</td>
<td>Patterson</td>
</tr>
</tbody>
</table>

There is one further problem with what this section has been describing which is the fact that the distribution is also dependent on the coupling between beams, not just energy transfers. If, in the event we could set up a single beam diffraction, which had no dynamical coupling, it would be the position momentum equivalent to a single energy transfer, in which case we loose the difficulty associated with the multiple coupling (please don’t confuse multiple coupling with multiple scattering. Looking a ladder diagram, (figure 5.1 for example), multiple scattering is the vertical loops, coupling is the horizontal ones). However, it is an
unlikely event since the nature of diffraction demands that there be many beams (even the two-beam set up is an approximation) and in order for such a coupling to be discounted the specimen would have to be sufficiently thin, as to discount sufficient multiple scatterings for these processes to retain their relevance (see figure 6.5 and 6.6).

It has been stressed that the form factor is equal to the Fourier transform of charge distribution, and the scattering amplitude due to a distributed charge is equal to the scattering amplitude due to point multiplied by the form factor. But the Patterson is neither, because of...
the subtle difference pointed out in figures 6.4 and 6.5. This is in essence the advantage of a Patterson description. Because of this coupling that is intrinsic in multiple scattering, the convolution of intensities cannot be avoided, unlike in light, x-ray and neutron scattering. As has been stressed, this is why the form factor is not appropriate for multiple scattering. We don’t have a density distribution in the low loss spectrum, rather a convolution of density density distributions for each and every point in time.

\[ \mathbf{K} = \mathbf{k} - \mathbf{k}' \]

Figure 6.6 A geometric representation of the scattering process in electron diffraction. \( \mathbf{k}' \) is the scattered vector. The \( \mathbf{g} \) vector is the vector between the zero order diffracted beam and the 1\(^{st}\) order diffracted beam. The anpassung represents the excitation error which is the difference between the \( \mathbf{K} \) vector and the \( \mathbf{g} \) vector where such an error is prevalent. This difference is due to the Ewald sphere intersection not exactly satisfying the Bragg angle; the excitation error is due to a non-perfect coupling factor between the zero and first order beams. Where there is no excitation error, \( \mathbf{K} = \mathbf{g} \).
6.3 Quantum field theory description

The Ehrenreich-Cohen method [13] neatly describes the Hamiltonian of the interaction of electrons among themselves as

\[
H = \int \psi^*(x) \left( -\frac{\hbar^2}{2m}\Delta \right) \psi(x) d^3x + \frac{1}{2} \int \psi^*(x) \psi^*(x') \frac{e^2}{|x-x'|} \psi(x) \psi(x') d^3x d^3x' \quad \text{Eqn. 6.32}
\]

where if the creation and annihilation operators are expanded with respect to plane waves normalized in the volume \( V \):

\[
\psi^*(x) = \sum_k a_k^* e^{i k x} \frac{1}{\sqrt{V}} \quad \text{Eqn. 6.33}
\]

\[
\psi(x) = \sum_k a_k e^{i k x} \frac{1}{\sqrt{V}} \quad \text{Eqn. 6.34}
\]

\[
H = \sum_k E_k a_k^* a_k + \frac{1}{2} \sum_{k_1, k_2} W(k_1, k_2; k_3, k_4) a_{k_1}^* a_{k_2}^* a_{k_3} a_{k_4} \quad \text{Eqn. 6.35,}
\]

where here \( W \) is given by

\[
W(k_1, k_2; k_3, k_4) = \frac{1}{V^2} \int \int e^{-i k_1 x \cdot x'} \frac{e^2}{|x-x'|} e^{i k_2 x \cdot x'} d^3x d^3x' \quad \text{Eqn. 6.36}
\]

So the incident particle wave function is scattered upon losing energy to the exchange functional \( W \) of the free or partial free electron continuum of the system, and subsequently undergoes a 90° phase change, and switches to the negative function, as it does under any general scattering process.

\[
\phi(r) = (2\pi\hbar)^{3/2} \int e^{ip \cdot r/h} \phi(p) dp \quad \text{Eqn. 6.37}
\]

\[
\phi(p) = (2\pi\hbar)^{-3/2} \int e^{-i p \cdot r/h} \phi(r) dr \quad \text{Eqn. 6.38}
\]

are 3 dimensional Fourier transforms of each other, and show that coordinate conversion through the negative in the exponential comes about from the ‘folding’ of functionals that occurs in the scattering process. Since every virtual energy exchange induces a loss of momentum of the quanta or incident particle,

Haken very elegantly describes

\[
1 = \nu \sum_k \frac{\bar{n}_{k+q} - \bar{n}_k}{-\hbar \Omega_q - i\hbar \alpha + E_{k+q} - E_k} \quad \text{Eqn. 6.39}
\]
The eigenvalues for this equation represent those values of the frequency $\Omega$ and damping factor $\alpha$ for which a plasmon excitation could possibly occur. The dominant excitations are those close to $E_{k+q} - E_k$, however we see that there are actually numerous possible excitations available close to $E_{k+q} - E_k$ in the system. In reality these are excitations that are small enough so that in most spectra, they would not be observed, however it is possible that in the future, systems may well have the resolution to observe them. The degree to which these excitations are correlated in the sense that their intensity is superimposed sufficiently to be observed, would depend on the degree of correlation in their distribution.

It is also interesting to note that the value of excitation would appear to be closer to 1 in the event that $q$, the scattering vector, equals zero. This then refers to the scattering angle of the incident particle, and it is well described in the classical plasmon dispersion theory that the dispersion of plasmon scattering has a significant angular dependence. This theory would then suggest that plasmon excitation is more probable for scattering angles close to $q=0$, so for periodic systems this would be representative of been orientated ‘down the zone’. The Ehrenreich-Cohen method has happened to use the momentum and position representation, which is consistent with the Patterson description.

The particle exchange involves a virtual energy exchange, because the particle interacts with a coloumbic field, not individual particles. Just considering the uncertainty principle alone makes the idea of a near relativistic particle, interacting with another fundamental particle of equal spin, that is defined in an orbital state, seem to be an improbable event. Particularly since we cannot determine where the electron is likely to be at a particular time. However, these statements are can only be made if one chooses to ignore duality interpretation that the electron is everywhere and obeys the energy and time dependant uncertainty principle of $\Delta E \Delta t = \hbar/2$, i.e. obeys a wave-field description.

The fact remains that if you put a periodic sample in a microscope, take a spectrum, with no objective aperture, change the angle of orientation, take another, you will find small differences predominately in the intensity ratios of the various features in your spectrum. If the same is done with an amorphous sample you will not find such differences since dispersion will have an angular dependence. However, if you have a large collection angle in your spectrum collecting device, then all the tilting in the world will not reveal any change in
the low loss spectrum, because you are collecting all, or at least most of the exiting wave. An amorphous sample is the same. There is of course the so called cutoff angle, \( q_c \). This is due to the fact that once the incident particle has interacted with the sample, it still has to exit, and progress to the spectrometer. This is greatly affected by the degree to which its wave is diffracted and scattered. Remember, whilst the wavepacket does not hold when all \( \zeta \) differ appreciably from \( \zeta_0 \), the model does not exclude any n-beam coupling effects (see chapter 5).

The description that this study has used suggests that the intensity distribution in any n-beam coupling effect changes for different angles of orientation. This is the key behind the phenomenon of dispersion in plasmon excitations. The wave-packet that ensues for higher order plasmon scattered electrons is subject to dispersion because the excitation errors between coupled beams increases for higher order scattering, as well as for higher numbers of coupled beams. Another way to say this would be that the arbitrarily correlated scattering increases when the excitation error increases. Thus, the weighting between coherently correlated excitations and arbitrarily correlated excitations changes and dispersion is effectively a measure of this.

The discussion here has effectively kept switching between a particle interaction description and a wave interaction description, and is in essence an analogue to the wave-particle duality theorem. Just as there is a duality in the energy propagation, so too is there in its interaction.

So collecting a spectrum with a large collection aperture makes sense if the feature one is looking at does not have a directional dependence. Dispersion does have a directional dependence because of the change in weighting of correlation. Bonding and phonon oscillation also have a directional dependence. However, plasmon oscillation is much less dependant because it is much less localised. It is the weighting that is dependent, not the probability of excitation. Band overlap, as is mentioned on numerous occasions, has a directional dependence. However, the degree of overlap affects the degree of correlation, not the probability with which the plasmon scattering will take place.

### 6.4 Plasmon scattering as a form of independent excitation

A description of such a process would be that the electron looses energy to the plasmon via the perturbation of the plasmon field creating a oscillatory disturbance in the density of
plasmon states. These states, consisting of valence and conduction electrons, are the states of the collective columbic field of the specimen. In creating such a disturbance, the amount of energy lost to this excitation is quantized because it is subject to a transition probability (Fermi’s golden rule) which decreases for higher order, i.e. larger transitions, respectively. So a second order plasmon loss transition is less probable than a first order transition, and these transition probabilities are the same every time an incident electron undergoes another scattering event. Since the first order transition is more probable, it is the most likely seen on a spectrum in the instance of the specimen being thin. Thin specimens are often preferred because of the problems associated with plural scattering. In thick specimens, however, as has been mentioned, multiple plasmon peaks are themselves a form of plural scattering.

It was described in ref. [10] how the width of the plasmon peaks broadened with a larger FWHM for higher order losses. Of course the Pearson-type/Poisson distribution indicates that statistically this should occur [10]. But this description is then generally associated with the description of higher order loss being physically due to more independent scattering events. With this picture, if a second order plasmon transition peak is seen on a low loss spectrum, this then could be due to a probe electron exciting a conduction electron to a second order state. Alternatively, this could be due to a probe electron exciting two first order plasmon excitations. In both cases the probe electron will have lost an energy of $E_\rho = 2h\omega_\rho$, although they will not have the same phase, since in the first case the electron scattered once, and in the second it scattered twice, so there will be a phase change for each scattering event.

Where the higher order losses are due to larger energy transfers, say one scattering event, then the increase in FWHM of the excitation peaks on the low loss spectra could be attributed to the uncertainty principle alone. If we consider the argument of a localized wave packet, it will tend to be composed of a large number of different frequencies. The more nearly monochromatic the packet is, the broader its transform becomes. So if the frequency spread is nearly zero, the packet, that is the Fourier transform of the distribution is so broad that its lifetime is extremely large. Denoting the uncertainty in the frequency spread by $\Delta \omega$ and the uncertainty in lifetime, we can write $\Delta \omega \approx \frac{2\pi}{\Delta t}$. On the other hand if the degree of monochromaticity is described in terms of the spread in $k$ (where $k = \omega/c$) the smaller the value of $\Delta k$ the greater the extent of the packet in coordinate space. We see $\Delta k \approx \frac{2\pi}{\Delta x}$ and so end up with familiar expressions like $\Delta E \Delta t \approx h$. So for higher order plasmon loss events, the
packet is generally very broad, because the lifetime of these less probable transitions is very short, which again is just being consistent with Fermi’s golden rule. It leads to a greater dispersion, and it is this dispersion that is generally described in terms of large angle scattering due to greater momentum exchange and thus a Poisson broadening of the distribution of higher order losses.

The wavefunction described as it is in a Patterson, is expressed as a function of position. This is why the structure can be determined. The wavefunction in this representation is effectively a linear combination of delta functions, such that \( \psi(x) = \int \psi(X) \delta(x - X) d^3X \) where the coefficients of the formula are complex numbers.

However, if the quantum state is represented as a linear combination of momentum states, \( \exp(iP \cdot x/\hbar) \), we get

\[
\psi(x) = \left(2\pi\right)^{-3/2} \int \psi(P) \exp(iP \cdot x/\hbar) d^3P \quad \text{...Eqn. 6.40}
\]

That is, the momentum representation is the Fourier transform of the position representation. Wavefunctions, and corresponding wavepackets can be described equally well in either the momentum or position representation. The functions, or more accurately, distributions described here are the moduli squared of these functions. Hence they have an intensity on the vertical scale. Whilst the Fourier transform has a symmetric distribution, the EELS spectra do not since they are measuring this intensity, and the intensity is measured in the energy time domain.

The Fourier transform is analogous with an integration over a continuum of states. Where this Fourier transform is represented by such an integral as

\[
\frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dx' \varphi(x') e^{-ikx'}
\]

one can see that in the absence of any localization in \( k \), the uncertainty can be reduced in the spatial distribution of the function. Perhaps more useful, is for long lifetimes, we also get a greater frequency localisation, and thus energy determination of the plasmon excitation. The fact that plasmons have such a long lifetime [14] is intrinsically beneficial in terms of energy localisation. The fact that the spectrum of plasmon loss maps the density distribution also means, that as the function is the deconvolved loss spectrum, it also effectively provides a self or auto or time correlation over and very large lifetime. Thus this very simply represents a time-dependant distribution function.
The picture discussed here is interesting in the context of remarks made by Fanidis et al. [15] who describes equation 6.41:

\[
I(g) = \sum_{E,\epsilon} \rho(E) \left| FT\left( \phi_{E+\epsilon}^E (r) \right) \right|^2 \quad \text{...Eqn. 6.41}
\]

as showing that the intensity distribution obtained from a crystal in thermal equilibrium is obtained by adding the intensity distribution obtained from the different stationary states (isolated system) with the corresponding elements of the density matrix of the system as weighting factors. Fanidis endeavours to point out that the lack of a wave function in the mixed-state situation makes the direct calculation of the probability density function impossible. However, if we take the Fourier transform of the inelastic component of the low loss spectrum, we effectively skirt the issue, that numerically is very difficult. The probability density distribution function of the intensity is a map of the variation of intensity in the inelastic component, which is directly due to the density distribution of the energy states. It is conceded though, that this distribution does not take into account all energy states of the system, only those in the plasmon region of the system. Nonetheless, recalling comments made on the difficulty associated with non-commuting eigenstates in the correlation function (section 6.3.1.1), we see that the generalised Patterson can be seen as a distribution of non-commutating mixed state eigenstates.

### 6.5 Plasmon Scattering and its Dependence on \( q \)

Whilst the low loss spectrum is an electron energy distribution, the distribution is not in \( k \), thus, where \( k = 0 \) the distribution is representative of \( S(\omega) \) not \( S(k\omega) \). This means when we wish to measure the density distribution as a function of energy fluctuation, we acquire the intensity as a function of time, whereas if we sum the intensity of the plasmon loss over a range of \( \theta \), then the intensity is a function of angle, and would give a result directly analogous to that of the kind of spectrum one acquires in a neutron scattering experiment.

This is not to say that it would give the exact same information as is acquired in a neutron scattering experiment. Fundamentally, this is because we are probing a different region of the specimen. Whilst plasmon scattering scatters from the excited valence and conduction region
of the coloumbic field, neutron scattering scatters from the core of an atom, and receives information about the spin state and short range oscillation of the phonons.

Where the distribution of correlation is taken over $\theta$, one must still be mindful of the arguable dependence of the plasmon dispersion on $q$ (the scattering angle). There have been many discussions on this matter (see references [16-18] for example) and this issue is particularly noticeable with crystalline specimen. As mentioned in section 6.5, the spread or dispersion effect is a result of a change in beam coupling, or change in the distribution of Bloch wave excitations. The possibility of low $k$ anomaly is not a direct issue of this investigation. However, having a large collection angle will ensure a large sampling in $k$ space and render $q$ dependant effects insignificant. This is not ideal if good spatial resolution is required, or if doing a $q$ dependant experiment. However, it is in the experience of this study, that a large collection aperture ensures the orientation of the specimen is of little consequence as figure 6.7, for example, shows.

![Image](image.png)

**Figure 6.7** The difference between the two selected area diffraction patterns of hexagonal barium cuprate are obvious in terms of orientation. However, the corresponding form and features of the low loss spectra taken in these two orientations show very little difference.
The lack of importance in orientation is also applicable to amorphous samples. Changing the angle of incidence in an amorphous sample of course is meaningless. However, the dispersion effect still has a dependence on the scattering vector $q$. This is because the degree of coherent coupling between branches varies with $q$, and this is no different for an amorphous sample which has a set of satisfied scattering angles dependent on the radial distribution function of the material. It is interesting to note that a previous investigation [19] noted a certain set of angles where the plasmon seemed to be stronger. This too can be explained through the degree of coupling between beams, which is going to be greater for certain angles; Recall the imaging in chapter 5 was setup in a two-beam condition for example, which had a maximum coupling effect, and greatest coherent correlation in the plasmon scattering.

Indeed it has been concluded in the past that it is the high momentum region that should be considered when studying plasmon dispersion, and that the low $q$ region is affected by band structure effects [20]. This is another way of saying that only a certain set of angles need be considered when studying the phenomenon of dispersion in plasmon loss. This view has been contested and debated though. Sturm’s prediction [16], verified by Sprösser-Prou [20], is that there is a negligible influence of band-structure effects on the long wavelength dispersion. Then a study by Möller and Otto [17] reported results that suggested that interband transitions were of greater influence than the plasmon dispersion at low scattering vectors.

Thus, what angles and factors that influence plasmon dispersion have not been entirely clear up to this point. It has certainly not been contradicted in this investigation that dispersion has an angular dependence. This means that the dispersion and intensity ratio of the low loss to zero loss peaks will vary with varying $q$. However, it is the form of the spectrum and the particular features in it that do not change.

It should be considered though that in this investigation, the probe, i.e. the incident electron beam, was quite broad, to the extent that is was larger than the spatial dimensions of any unit cell studied. In the case of EELS with STEM, i.e. EELS with higher spatial resolution, on the other hand, the band structure should be expected to have a far greater effect on the core loss features of the EELS spectrum. Where the probe has a probe with a cross over that is specific enough to transmit down a single column of atoms, the band structure effects should begin to be able to be seen in the spectrum. They should have an effect in the sense that changing the probe orientation will excite a group of electronic states that have a different degree of
overlap and thus cross section for one orientation, than they do another. This is not a viewpoint of contest in this investigation. Rather it should be remembered that the plasmon loss is a non-localised coulombic distribution. Thus, whilst the effects on the core loss of EELS will be quite identifiable, the bonding orientation for example, will have a very little effect on the energy of the plasmon excitation, and the form of the low loss spectrum. However, it is not suggested that an effect is completely absent, since valence and conduction band density will be affected. Instead, it suggests that orientational dependence will be small enough to be ignored, at least in the scope of this investigation.

Thus the suggestion that the high momentum region should be considered when studying plasmon dispersion makes sense, by virtue of the fact that the low q scattered electrons have a similar path and therefore are not going to change as much as high q scattered electrons for a given orientation change. But the effect is important for the core loss studies, not the low loss studies. Band structure effects to date have been ignored for the changes apparent in any given orientational change will be negligible, provided that the spatial resolution (i.e. dimension of the probe) is less that a unit cell dimension of the crystal. Even with a probe of say dimensions equal to a unit cell, the specimen would also have to be thin enough to discount probe broadening. Thus, band structure effects should be accounted for in the low loss, only in the condition that there is sufficient spatial resolution in the probe.

6.6 Origin of plasmon peak spreading (dispersion) and the Landau background.

The density distribution function is a time-dependant representation of the system, as it is the Fourier transform of the low loss spectrum, which is a distribution over the energy perturbation of the system. Since the density distribution function is a distribution over all states (Ergodic principle) one can typically see a distribution that appears to be independent of any so called ‘memory’ between scattering events. This is because any such memory correlation would be washed out in the integration (or sum which is effectively from 1 to \(\infty\)). A further point to support this view is the fact that the dielectric function can be pulled out of the form factor, given that it is based on a single scattering correlation [6].

It has been surmised in the past that there is a memory effect between independent scattering events due to the long lifetimes of the states of excitation [10,14]. This effect seems to be
based on a questionable property. However, particle description places this demand when describing the propagation effects of the incident particle. It can be seen that if the wave description is taken into account, such memory is appropriately described as the energy coupling of such transitions along the wave, much like the ladder diagram of figure 5.1 demonstrated.

The lower order plasmon peaks bear a closer resemblance to a Gaussian distribution. However, the higher the order of the plasmon peak the more its distribution will resemble a Poisson distribution, as the more arbitrarily correlated states are involved. Again, since Poisson statistics assumes statistically independent events, one might assume that this contradicts the premise that these events are correlated. However, the distribution is one of a probability factor, and not determined by the events themselves. Indeed the contention of the wave description, and the model of Goodman et al. [27] both indicate that they are correlated through a coupling of energy transfers. The simple fact that you can form an image from these higher order events, suggests coherence and thus a correlation between energy distribution. It is the probability of the energy transition in the excitation that is independent, not the scattering event per se since the wave function is coupled. This is why each scattering event has an equally weighted probability associated with it. This is why a Poisson distribution can be seen when multiple plasmon peaks are evident, even though the wave function is coupled.

It was found during the filtering of plasmons, in Chapter 5 for example, that for the two-beam case, as we move away from the Bragg angle, a large background, peaking around the maximum of the envelope, can be seen. This is because as we move away from the Bragg angle, the contribution of arbitrary states to the spectrum increases. Down the Bragg angle for the two-beam condition, the spectrum is coming from those electrons involved predominately in the two-beam interaction and thus far less background is seen. This point has not so much to do with dispersion, but rather the fact the fewer beams in the excitation process correspond to fewer excitation errors, and a greater correlation in the plural scattering. This in turn corresponds to a greater coherence in the electrons involved in the plasmon interaction. This large background ‘hump’ (figure 6.8 for example) fits a so called Landau distribution [21].
Figure 6.8. Low loss spectrum of YBaCuO(123) ceramic. The sample is thick thus shows a good example of the ‘hump’ or Landau distribution under the multiple plasmon excitations.

The landau distribution represents that spread of energy loss that is a function of mean energy loss, its relative value with respect to mean binding energy of the electrons within the material, and its value with respect to the maximum possible energy transfer which the probe particle can make to an electron in a single interaction. Statistically, it is just the fluctuation of energy loss around the mean. So whilst this distribution will naturally change with differing mean electron density, and sample thickness, such as figure 6.9 demonstrates, the degree to which the beams are coupled will also affect the statistical spread in the energy loss, and hence affect the Landau distribution. The smaller the degree of energy coupling, i.e. the more arbitrary the correlation in scattering, the more the distribution will look like a random fluctuation, i.e. the larger the ‘hump’ and smaller the discernable plasmon peaks will be. Figure 6.10 shows how the increasing contribution of arbitrarily correlated scattering increases the Landau distribution, because all the images are from the same specimen area with the same thickness. Thus the increasing Landau distribution is not due to increasing thickness, but rather increasing decoherence. Figure 6.11 is a ladder loop representation of this process [21,22].
Figure 6.9 Two low loss spectra of silicon present a classic example of the increased Landau distribution with increased thickness (a) rmfp = 0.75  b) rmfp = 1.71). The increase is not due to thickness per se, rather due to the increased amount of scattering, which increases the ratio of arbitrarily-correlated to coherently-correlated scattering. b) also shows the increase in FWHM of the plasmon peaks which fits the Poisson distribution relationship as discussed in this section and section 6.4.

The mean free path for higher order losses increases as the electron undergoes a greater number of scattering events. This increase leads to a reduction in the intensity of the exiting electron, through a well known Poisson statistical relationship, and enabling them to travel greater thicknesses. But in addition to energy transfer occurring by means of inelastic scattering, there is also interaction and energy transfer between the forward scattered central and diffracted beams.

Now whilst this coupling relates to whether we see a low loss of multiple plasmon peaks, or one with a large ‘hump’, it is also the foundation of dispersion in plasmon scattering. That is to say, the reason the plasmon dispersion changes for different orientations, is due to the interactions of the dynamically diffracted beams being coupled to each other. The degree of coupling is dependant on the distribution of intensity in each beam. As has been described in section 7.2 and 7.4, this is also intimately concerned with why plasmon filtered images favour low q coupled beams. The excitation states involved will have a higher degree of correlation compared to the difference in high q beams. Thus, a two-beam orientation is desirable in such experiments. Alternatively, a large collection angle incorporating the central beams will also
limit the q dependence of dispersion in the low loss spectrum. However, including too many beams increases the contribution of incoherence in the plasmon excitation and increases the ‘hump’, hence reduces the ‘form’ of the low loss that is desirable in plasmon filtered imaging experiments, if that is what is being sought after.

Figure 6.10 a), b), c), and d) are dark filed images of a silicon wedge, and their respective line scans, as described in figure 5.7 and 5.8. a) is unfiltered, b) zero loss filtered and c and d the 1st and 2nd plasmon loss filtered scans respectively. These images are a good example showing as higher order plasmon loss peaks are filtered, the degradation of the signal-to-noise ratio is apparent. i.e. the Landau distribution increases with respect to the coherent peaks because the ratio arbitrarily correlated to coherently correlated scattering is increasing (see section 5.3 for full details).
Thus we have said that the dependence of dispersion on \( q \) is a result of the change in intensity distribution in the diffracted beams, given that these beams are coupled. The coupling of the beams that was testified to by the model chapter 5 is also verified by the statistical spread. This is because the statistical distribution corresponds to the classical model of event coupling, which involves a memory function. Over a large time the statistical spread is more akin to a collection of independent processes, than coupled ones.

### 6.7 Validity of plasmon scattering in large angles

Images taken in the past with selected energy loss in the conventional transmission microscope have shown an amazingly close similarity to zero loss, elastic images. It has been implied that these processes were rather delocalised on the interatomic distance scale with low momentum transfers and corresponding scattering angles that are small in relation to the Bragg angle [23].

Such an implication is due to the idea of plasmon scattering being a delocalised phenomenon. Therefore, since only low momentum transfer occur, plasmon scattered electrons would not be observed in high scattering angles. The experiments in this investigation proved otherwise.

Figure 6.11 *Ladder loop diagram showing a large degree of arbitrary correlation (which invokes a de-coherence) in 6 diffracted beams, and contributes to the ‘hump’.*

![Ladder loop diagram showing a large degree of arbitrary correlation](image)
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As is suggested in ref. [14], plasmon scattering is rather a combination of both. Whilst those electrons that constitute the plasmon states are indeed delocalised, or more accurately, have a non-local [24] potential, this does not place a necessity for those probe electrons to have a predominately localised coupling domain. Hence there is nothing preventing the momentum transfer process, i.e. the virtual photon exchange, from being localised. Nonetheless studies have claimed to show otherwise [25].

It is the idea of delocalisation that leads to the common belief that all plasmon scattering should be confined to small angles. Particularly, when considering formulations such as those of Yoshioka [26] where one sees the plasmon interaction, found in the interaction energy term, is separated right at the start of the derivation. This may provide the impetus to forevermore consider this inelastic component of plasmon scattering as a separable interaction of minor contribution. However, to assume that these interactions are fundamentally independent, whilst mathematically convenient, would be an unwise interpretation from a physical perspective. Indeed in a multiply scattered beam, there is no reason why the incident electron wave would interact with each electronic region of the material in some kind of progressive manner. Rather the plasmon loss interactions couple into the elastic dynamically scattered beams, as the model presented in Goodman et al. [27] contends.

The wavefield is considered as a single wavefunction, not the sum of parts. It does not scatter sequentially and elastic and inelastic scattering is not separable.

Figure 6.12 shows the zeroth order diffracted disc, or central disc of a [111] CBED zone axis pattern. The disc has been imaged on the CCD of a GIF PEELS spectrometer. Figure 6.12a) is unfiltered. As soon as an energy selecting slit in placed around the zero loss peak of the low loss spectrum, we see the HOLZ lines become evident. One could say that the diffuse of the unfiltered beam is due to the inelastic electrons incoherently contributing to the lack of image formation. However, in looking at figures 6.13 c) and d) we see that the electrons contributing to a plasmon excitation are themselves able to form an image of the disc along with the HOLZ detail, and the same is true for figure 6.14. Indeed, figure 6.14 shows the HOLZ in the 1st order Laue zone which is an undisputable large angle scattering process. It is true that the diffuse of the unfiltered discs are formed by inelastic scattering which is most likely due to incoherent coupling of plasmon and phonon scattered waves. However, it is a classic example of how those electrons that loose energy in a correlated fashion are able to maintain coherence. What’s more, even in the 2nd order plasmon filtered disc, one can still make out
the HOLZ lines. The brightness artificially altered in figure 6.12e to make the HOLZ lines more visible, due to the lower intensity of these electrons. These images are all further evidence of the capacity for large angle scattering of plasmon scattered electrons.

Figure 6.12 central disc of a [111] zone-axis silicon diffraction pattern. a) and b) are the unfiltered and zero loss filtered images respectively. c) and d) the 1st and 2nd order plasmon filtered images respectively. e) is the 2nd order plasmon filtered image with the brightness artificially enhanced to show the HOLZ lines in the center of the disc.
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Figure 6.13 Low loss filtered images of a silicon diffraction pattern. The (422) CBED discs in a [111] zone axis pattern, including the HOLZ feature can be readily seen. a) is the unfiltered image, b) the zero loss filtered image, c) and d) are the 1st and 2nd order plasmon filtered images, respectively. c) and d) provide evidence that plasmon scattering is indeed applicable for high angle scattering.
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Figure 6.14 Filtered images the 1st order Laue zone circle in the same [111] zone-axis silicon diffraction pattern as in figure 6.13. a) is the unfiltered image, b) the zero loss filtered image, c), d) and e) are the 1st, 2nd and 3rd order plasmon filtered images, respectively. The plasmon filtered images including the HOLZ feature are constructed from only plasmon loss electrons and provide evidence that plasmon scattering is indeed applicable for high angle scattering.
One careful investigation however, discounted the above interpretation [25]. According to a Bloch wave derivation, there was no formal evidence of plasmon scattering in large angles. Experimental proof was shown by placing an objective aperture over higher order (larger angle) diffraction discs in aluminium. They put an objective aperture around a disc, then energy filtered it, where as in this investigation, the pattern as a whole was first energy filtered, then the disc (diffraction spot) selected and imaged.

The retaining question between the fore mentioned investigation [25] and the current one therefore, is to understand what the difference is between a higher order diffracted disc (conceived as being a beam that has undergone a large angle of diffraction), and large scattering angle detail such as HOLZ, including many beams, that is derived from a specifically selected set of inelastic energies. The answer is very little since the physics occurs in the sample, before any apertures, slits or spectrometers begin to molest the beam. The coupling factor of the beams occurs during the diffraction. The only thing affected by placing an aperture over one beam will be a reduction in the intensity, not a reduction in the dynamical effect of the other beams as they are not considered to be independent of each other.

In the context of the interpretation in this investigation, ‘their’ [25] loss of contrast is to be explained as being due to larger excitation errors for higher order beams, which destroys the correlation in the plasmon excitation (less coherent coupling between beams). The dominant form of coherent contrast in their images can only be expected to be from elastically scattered beams. Indeed, elastic scattering remains the dominant form of contrast in this investigation. However, whilst the contrast and intensity is not as great as is found in elastic scattering, it is nonetheless readily evident for plasmon scattering in large angles.

Another point that is worth noting is that the results here derive from a zone-axis orientation. This would seem to suggest that an explicit two-beam orientation is not essential as the coupling model of ref. [30] and chapter 5 contends. However, this derives from the symmetry of the structure. It is known [28-32] that certain symmetries can be reduced to two-beam form. Thus, whilst the orientation of the specimen in the present investigation has an approximate seven-beam diffraction pattern (figure 6.15 and 6.17), its symmetry allows this to reduce to two-beam coupling. It is interesting to note that the symmetries that are reducible to
two-beam symmetry are also frequently associated with materials that exhibit a simple form of plasmon spectrum.

Figure 6.15 CBED pattern of silicon down the [111] zone-axis showing the central beam and the (200) beams. The (400) beams can just be seen around the edge.

When the whole system is in two-beam orientation the problem can be solved analytically. Furthermore, if a zone-axis pattern is reducible to a two-beam form then the corresponding two-beam solution for the whole system will be effective. It is seen that amongst other things, the approximations involving the interference of all the wave fields are good and that plasmon scattering can take place at high angles for instance in the upper layer lines of the pattern.

Figure 6.16 Ladder loop diagram showing a large degree of correlated correlation which encourages coherence in 6 diffracted beams. This is a scenario that is likely where the excitation errors are small, which is similar to picturing the energy levels of each vertical loop as been close to equal.
Figure 6.17 The seven beam symmetry is reducible to a group of two-beam or set of double scattering loops.

It is emphasized that such scattering cannot properly be envisaged as scattering from the lattice and subsequently from plasmons, since the solution refers to the wave-field as a whole. This does not say that such derivations, and their corresponding physical picture are incorrect per se. Rather, it points out that such a way of thinking can only be associated with those particular derivations that do consider the elastic and inelastic scattering as being separable.

**The wavefield is considered as single wavefunction, not the sum of parts. It does not scatter sequentially and elastic and inelastic scattering is not separable.**

So we can see two advantages of a plasmon filtered pattern from an effective two beam orientation. One, it verifies the model described by Goodman *et al.* [27], and two, not only does it suggest the importance of the form of the low loss spectrum but correlates that with the symmetry of the specimen. A specimen that produces a plasmon or low loss spectrum of the necessary ‘form’ will typically have a reducible symmetry.

An important concept from this model is that of wave-particle duality. Since the solution refers to the wave-field as a whole, it is instructive to consider the consequence in real terms. If a wave function was made up from a single electron, it would contain all the information that one associates with elastic and inelastic scattering. It is unfortunate that this could not be measured, however, since the wavefunction is localised as soon as the spectrometer collects it. This is why the spectrum is a distribution of localised events.
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6.8 Conclusions

There is a significant structural invariance to the correlations discussed in this chapter. The plasmon excitations, and the associated band gaps are not directly related to whether they are being formed from the body of an amorphous, polycrystalline or crystalline specimen. Rather the degree of orbital overlap is the dominant influencing factor on the form.

Evidence has also been shown for plasmon scattered electrons to scatter into large angles. It would appear that plasmon scattered and elastically scattered electrons demonstrate remarkable similarity in the features they exhibit. However, the intensity is reduced and the implications for dynamical models would be a reduced intensity in the final image. There is also evidence of n-beam coupling conforming to a symmetry reduction into a two-beam form.

The reason the plasmon dispersion changes for different orientations is due to the interaction of the dynamically diffracted beams being coupled to each other. Therefore, the weighting between coherently correlated and arbitrarily correlated inelastic scattering (plasmon scattering) varies.
6.9 Appendix

Appendix 6A: Experimental procedure:

All EELS low loss spectra were acquired and processed in an identical fashion. They were acquired in image mode with a large (90 µm) objective aperture, ensuring a total summation over all $q$ scattering vectors and placing the reciprocal image at the spectrometer face. It should be noted that whether it is preferable to collect an EELS spectrum in image or diffraction mode will depend on the experiment being performed. It is generally recommended that STEM mode is used because of the greater spatial resolution. However, if, for reasons above, for example, one chooses TEM mode, then one can either have the microscope intermediate lenses in image or diffraction mode. Either mode is acceptable, although the advantage of diffraction mode is you can be sure of what $g$ vectors are being included in the acquisition. However, for the purpose of filtered imaging, when using a post column PEELS system, you have to ‘squeeze’ the image into the ‘tiny hole’ of the GIF, and the image mode will need to be used. Omega filters would be a much more desirable setup for filtered imaging as distortion introduced in bending the beam through an electromagnetic prism is removed. This is well known, however PEELS systems are more desirable for spectrum acquisition. So it’s a case of ‘horses for courses’ and in any event, the present investigation has shown that such filtered imaging is readily achievable in a PEELS post column setup.

The zero loss peak of each spectrum has been removed before the Fast Fourier Transform was performed. This process was carried out in the digital micrograph software package [2]. Figure 6.2 shows the complex components of the spectrum.
Figure 6A.1 The real and imaginary components of the Fast Fourier Transform of a low loss spectrum (vertical scale is arb. intensity).

The modulus of the complex components are then taken and multiplied by a factor of $(2\pi)^{-1}$. The respective spectra shown are on a log scale and the horizontal scale is with respect to energy channels from the 1024 array. Each channel corresponds to the Fourier transform of a scale that is in the energy domain, thus is in the time domain (This energy time domain conversion is discussed in section 6.3.3.1).

In addition, it is interesting to note that the resulting spectra are practically a pseudo sinc function, which has been multiplied by a Heaviside step function due to the array cut off of the spectrum at channel 1024. To minimise the Heaviside contribution to the spectrum, a low ‘tail’ or ‘background’ is desirable during acquisition, which can be achieved by avoiding lengthy periods of acquisition.

Since the sinc function (figure 3D.15b in Appendix 3D for example) is similar to the transform that is descriptive of Fraunhoffer diffraction for a square aperture, it may be said that this function is just another scattering distribution function. A real example of this was shown in chapter 3, Appendix D.

Appendix 6B: Coherence

A question retaining to the aspect of coherence in the low loss remains: what is meant by coherence? In simple optics, coherence is the superposition of wave amplitudes. However, it
could also be thought of in the sense of equal phase. If \( n \) scattering waves are coherent, then typically, they are thought of as having an equal phase. However, when considering the degree of coherence in a wave-particle that has undergone a quantum mechanical interaction with some given field, the coherence becomes a term better defined by the degree of correlation apparent.

A definition of coherence presented by Glauber [33] gives the necessary condition that the normalised correlation functions all have unit absolute magnitude

\[
\left| g^{n}(x_{1} \cdots x_{n}) \right| = 1, n = 1, 2, 3, \ldots \quad \text{Eqn. 6B.1}
\]

So that if there exists a function \( \varepsilon(x) \) say, independent of \( n \), such that the correlation functions for all \( n \) may be expressed as the products

\[
G^{(n)}(x_{1} \cdots x_{n}, x_{n+1} \cdots x_{2n}) = \varepsilon^{*}(x_{1}) \cdots \varepsilon^{*}(x_{n}) \varepsilon(x_{n+1}) \cdots \varepsilon(x_{2n}) \quad \text{Eqn. 6B.2}
\]

This then leads to the definition by Glauber [33]...‘any classical field of non-random behaviour has correlation functions which fall into this form, and such fields are at times called coherent in communication theory’.

Furthermore it is interesting to note that if the field to be in an eigenstate of the operators \( E^{(+)} \) and \( E^{(-)} \) say, then the correlation functions for such states would factorise to the desired form. The operators \( E^{(+)}(r,t) \) and \( E^{(-)}(r',t') \) do not commute, however, so no state can be an eigenstate of both. Not only are these operators non-Hermitian, but failure of each to commute with its adjoint shows that \( E^{(+)} \) and \( E^{(-)} \) are non-normal as well. Operators of this nature cannot be diagonalised, but nonetheless have eigenstates.

**Appendix 6C: First and higher order Born approximation**

The following is an exert from a basic text book on quantum mechanics by Anderson [34]. He provides a very useful demonstration of the derivation of the higher order Born approximation, which unfortunately, few books bother to do. Another book that does give a useful description for example is that of Fetter and Walecka ref. [35]. Using Greens
propagators, the multiple scattering is accommodated; however the scattering is still assumed to be independent. Independent in the sense that each scattering event occurs in a separate time frame, is causal, and occurs such that when a scattering event takes place, it has no connection or virtual particle exchange with any other scattering event. This is because, in separate time frames, such a process would be anti-casual.

Whilst the summation of each interaction is representative of the whole wave function, it does not directly couple each excitation state in the multiple scattering process. Rather, the effect on the progressive wave function is taken into account. The only way to couple each excited state is through a virtual exchange. This can be done through a Feynman path integral method, and is represented by the loop diagrams as discussed in the introduction of section 2.5. It can also be accommodated through standard Dirac notation, in the realm of quantum electrodynamics, and is one of the distinguishing feature of QED that makes it different from standard quantum mechanics.

Where the scattering process is regarded as a time-dependant transition from an initial to a final plane weave state, Fermi’s golden rule can be applied.

\[ R = \frac{2\pi}{\hbar} \left( \langle f \mid V \mid i \rangle \right)^2 \rho(E_f) \] \hspace{1cm} ...Eqn. 6C.1

and with the density of final states for free particles, written as

\[ \rho(E_f) = \frac{mL^3}{2\pi^2\hbar^2} \left( \frac{2mE_f}{\hbar^2} \right)^2 = \left( \frac{mL^2k_f}{2\pi^2\hbar^2} \right)^2 \] \hspace{1cm} ...Eqn. 6C.2

The differential scattering cross section for a solid angle subtended can be written as

\[ \frac{d\sigma}{d\Omega} = \frac{R}{4d\Omega} = \left( \frac{mL^3}{2\pi^2\hbar^2} \right)^2 \left( \frac{k_f}{k_0} \right)^2 \left( \langle f \mid V \mid i \rangle \right)^2 \] \hspace{1cm} ...Eqn. 6C.3

so for elastic scattering of plane waves \( k_f = k_0 \) and equation 6C.3 becomes

\[ \frac{d\sigma}{d\Omega} = \left( \frac{mL^3}{2\pi^2\hbar^2} \right)^2 \left[ \int L^3 e^{i\frac{k_f}{r} \cdot r} V(r) e^{i\frac{k_0}{r} \cdot r} d\tau \right]^2 \] \hspace{1cm} ...Eqn. 6C.4

And

\[ f(\theta) = \frac{m}{2\pi\hbar^2} \int L^3 e^{i\frac{k_0}{r} \cdot r} V(r) e^{i\frac{k_f}{r} \cdot r} d\tau \] \hspace{1cm} ...Eqn. 6C.5

This is the first Born approximation and assumes only single scattering events since the term is only first order.

Using Green’s function method, where a function acts as a propagator for the wave function
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If a solution for the equation

\[ (\nabla^2 + k^2)\psi(r) = -4\pi \rho(r) \] ...Eqn. 6C.6

Uses a superposition of point sources

\[ \rho(r) = \int \delta(r-r')\rho(r')dr' \] ...Eqn. 6C.7

Then we can write equation 6.C6 with a Green’s function, \( G(r, r') \), which acts as a propagator for the wave function, hence

\[ (\nabla^2 + k^2)G(r, r') = -4\pi \delta(r-r') \] ...Eqn. 6C.8 and we can write a solution for equation 6C.6 as

\[ \psi(r) = \int G(r, r')\rho(r')dr' \] ...Eqn. 6C.9

This then allows Schrödinger’s equation, in the form,

\[ (\nabla^2 + k^2)\psi(r) = \frac{2m}{\hbar} V(r)\psi(r) \] ...Eqn. 6C.10

To be written as

\[ \psi(r) = -\frac{2m}{\hbar^2} \int G(r, r')\psi(r')\psi(r')dr' \] ...Eqn. 6C.11

The scattering amplitude can be written as

\[ f(\theta) = -\frac{m}{2\pi\hbar^2} \int e^{-ikr} V(r')\psi(r')dr' \] ...Eqn. 6C.12

Where \( G(r, r') \) is the solution of

\[ (\nabla^2 + k^2)G(r, r') = -\delta(r-r') \] ...Eqn. 6C.13

So to determine this, Poisson’s equation in electrostatics is used so that

\[ G(r, r') = \frac{e^{ik|r-r'|}}{4\pi|k-k'|} \] ...Eqn. 6C.14

And using these equations, the equation for a scattered wave, in the form

\[ \psi = Ae^{ikz} + f(\theta)e^{ikr} \] can be written as

\[ \psi = e^{ikz} - \frac{m}{2\pi\hbar^2} \int \frac{e^{ik|r-r'|}}{4\pi|r-r'|} V(r')\psi(r')dr' \] and where

\[ |r-r'| \rightarrow r \]

\[ \psi = e^{ikz} - \frac{m}{2\pi\hbar^2} \int \frac{e^{ikr'}}{4\pi} V(r')\psi(r')dr' \] ...Eqn. 6C.15

Where the scattering angle is the angle between the incident beam and \( r \), i.e. scattering vector subtended by the scattering solid angle. However, unlike equation 6.C5 we have a total wave function for multiple scattering.

The solution for \( \psi(r') \) may be written as
\[ \psi(r') = e^{ikr'} - \frac{m}{2\pi\hbar^2} \int G(r',r'')\psi(r'')\psi(r')dr'' \quad \text{...Eqn. 6C.16} \]

Which upon substitution into equation 6C.15 we find

\[ \psi(r') = e^{ikr'} - \frac{m}{2\pi\hbar^2} \int G(r',r'')\psi(r')e^{ikr'}dr' + \left( \frac{m}{2\pi\hbar^2} \right)^2 \int \int G(r',r'')W(r',r'')G(r'',r')\psi(r'')dr'' \quad \text{...Eqn. 6C.17} \]

and so on.

Each successive iteration replaces the wave function in the integrand by the solution in the next lowest approximation. Thus, the first integral contains the wave function in the zero order approximation, which is the incident plane wave. The second integral may then be evaluated by replacing \( \psi(r'') \) by the wave function obtained from the Born approximation. This then is called the second Born approximation. In general the \( n^{\text{th}} \) Born approximation consists of replacing the wave function in the \( n^{\text{th}} \) integrand of the iterative expansion by the solution obtained in the \( (n-1)^{\text{th}} \) approximation.

### 6.10 References


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CHAPTER 7

The low loss form and the significance of electron distribution

This chapter is concerned with a key point concerning plasmon spectra. That is, the relationship between materials that present a plasmon spectrum of the ‘ideal’ form and those that don’t.
7.1 Introduction

Two derivations [1,2] considered in Appendix 7A and 7B, illuminate well the connection between pendellösung and the coulombic energy distribution in a material. There is a definite relation between pendellösung and the dispersion surface. Indeed, Howie [3] in 1963 suggested that the action of scattering from one two-beam dispersion surface to another, i.e. from say energy level $E_n$ to $E_m$, by the excitation of a plasmon, implies that inelastically scattered electrons would also produce thickness fringes. He endeavoured to present such thickness fringes for n plasmon events, assuming that they were obtained by means of ‘some device’ capable of selecting electrons of a given energy loss [3]. Of course there is no suggestion of a coherently scattered wave packet progression, as he did not present such an argument on the basis of a formulation that combined the elastic and inelastic mechanisms. This is really just another way of saying that there is a definite relation between the coulombic distribution, and the degree of energy coupling that can occur between two or more beams. Pendellösung is the effect of coherent correlation, in accordance with Glauber’s definition. How does this relate to the form of the low loss spectrum when we have described the ‘ideal’ form as being the result of this coherent correlation. Thus those materials the have this ‘ideal’ form should have an equivalent coloumbic distribution, since they have an equivalent form of coherent correlation.

However, whilst many materials can be orientated into a two-beam setup and subsequently demonstrate this coherent energy coupling called pendellosung. The orientation and the pendellosung have no bearing on whether the material will have a low loss spectrum of the ‘ideal’ form.

What property in the material determines whether it will have a low loss spectrum of the ideal form? This chapter investigates some ideal materials, looks at their low loss spectra and the material’s density of states (DOS) to further explain current understanding of this subject.
7.2 Computational details

In this chapter, the DOS plots are all simulated using the CAmbridge Serial Total Energy Package or CASTEP [4]. CASTEP is similar to the VASP package described in chapter 4 being a plane-wave pseudopotential code. At the time CASTEP had a better Graphical User Interface (GUI) and was simpler to employ for the purpose of DOS calculations. CASTEP was only employed for the generic DOS plots presented in this chapter, principally used to display the DOS around the Fermi level. The DOS were obtained from data which contains the density of states determined as the difference in the integrated density of states between two ‘pins’ or nodes on a grid. Ultrasoft pseudopotentials based on one developed for norm-conserving potentials developed by King-Smith [5] were used. Only the LDA functional was employed for the DOS calculation and the energy cutoffs were 320 eV, 160 eV, 270 eV and 180eV for copper, aluminium, boron phosphate and silicon, respectively. All structures were obtained from the CASTEP database (as found in Wycoff [6]) and were not geometrically optimised before calculating the DOS. The purpose of acquiring the DOS was not so much to do with gaining an accurate value and indeed, as has been commented on in previous chapters, DFT is not very good at determining band gaps, but rather, it is simply to gain a qualitative picture of the DOS in and around the Fermi level.

7.3 The form

The simple form of the plasmon response of a material does not in itself indicate whether it is going to be a conductor or not. Indeed the quintessential conductor, copper, does not exhibit this kind of spectrum, and has a low degree of correlation (figure 7.1) whereas aluminium, which is also a very good conductor, does (see figure 7.2). Indeed, the aluminium in figure 7.2 is actually a polycrystalline sample, so it breaks the symmetry requirement of section 6.9, although as it is polycrystalline its coulombic distribution is going to be more homogenous, with respect to its coulombic distribution, than many crystalline materials.

Copper, a transition element, has significant d electron contribution above and below the Fermi level (figure 7.1). The effect of this appears to destroy any clear correlation in the plasmon excitations. It still has a significant plasmon contribution, after all, if it didn’t, it would not be such a good conductor. But this result would seem to suggest that the
conductivity of a material is independent of any plasmon correlations. If we look at aluminium and gold, both polycrystalline samples in this case, and silicon and TiAl (as extensively studied in chapters 5 and 6), both single crystal specimens, they would seem to suggest that any plasmon coherence is not directly related to whether the material is a single crystal, polycrystalline or amorphous. However, since plasmons have a longitudinal correlation length many times greater than a single unit cell, this is to be expected.

Figure 7.1 Low loss spectrum of cold rolled copper sample (2.04mfp).

Figure 7.2 Low loss spectrum of polycrystalline aluminum foil (Sample courtesy of Dr. T.Petersen 1.75mfp).

Figure 7.3 Low loss spectrum of electropolished gold foil (0.71mfp).
Table 7.1 shows a comparison of the *form* to other related properties, as determined experimentally from the low loss spectra acquired in this study. This comparison shows that the consistent property affecting the *form* of the material’s low loss spectrum is the presence of d or higher orbitals. The addition of d electron states appears to contribute greatly to the degradation of the plasmon coherence. Looking at the DOS of these materials (figures 7.4-7.7) it can be seen that these higher states typically extend out and beyond the Fermi level, and mix with the lower s and p states. Thus, a conclusion to be drawn from this is that the number of energy coupling branches is dramatically increased, leading to the weighting of arbitrary correlation to coherent correlation to become too great. Symmetry is related to the form in so far as those materials that do have these higher electron states subsequently have a lower symmetry.

**Table 7.1**

Comparison of the plasmon *form* with other relating properties of metals and ceramics.

<table>
<thead>
<tr>
<th>Material</th>
<th>Conductor</th>
<th>Partially filled energy band</th>
<th>Relative degree of single crystal symmetry †</th>
<th><em>Form of low loss spectrum</em></th>
<th>Orbitals</th>
<th>Dependence of <em>form</em> on orientation*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>Semi</td>
<td>Yes</td>
<td>High</td>
<td>Ideal</td>
<td>s,p</td>
<td>No</td>
</tr>
<tr>
<td>TiAl</td>
<td>Yes</td>
<td>No</td>
<td>High</td>
<td>Ideal</td>
<td>s,p</td>
<td>No</td>
</tr>
<tr>
<td>Cu</td>
<td>Yes</td>
<td>No</td>
<td>High</td>
<td>Poor</td>
<td>s,p,d</td>
<td>No</td>
</tr>
<tr>
<td>Al</td>
<td>Yes</td>
<td>No</td>
<td>Polycrystalline</td>
<td>Ideal</td>
<td>s,p</td>
<td>No</td>
</tr>
<tr>
<td>Au</td>
<td>Yes</td>
<td>No</td>
<td>High</td>
<td>Poor</td>
<td>s,p,d,f</td>
<td>No</td>
</tr>
<tr>
<td>SiO₂</td>
<td>No</td>
<td>Yes</td>
<td>High</td>
<td>Good</td>
<td>s,p</td>
<td>No</td>
</tr>
<tr>
<td>Ba₃Ti₅Ru₉O₁₉</td>
<td>Semi</td>
<td>Yes</td>
<td>Low</td>
<td>Poor</td>
<td>s,p,d</td>
<td>No</td>
</tr>
<tr>
<td>CuO</td>
<td>No</td>
<td>Yes</td>
<td>Low</td>
<td>Poor</td>
<td>s,p,d</td>
<td>No</td>
</tr>
<tr>
<td>BaTiO₃</td>
<td>Semi</td>
<td>Yes</td>
<td>Low</td>
<td>Poor</td>
<td>s,p,d</td>
<td>No</td>
</tr>
<tr>
<td>BP*</td>
<td>Semi</td>
<td>Yes</td>
<td>High</td>
<td>Ideal</td>
<td>s,p</td>
<td>No</td>
</tr>
<tr>
<td>C (graphite)</td>
<td>Yes</td>
<td>Yes</td>
<td>Low</td>
<td>Poor</td>
<td>s,p</td>
<td>Yes</td>
</tr>
<tr>
<td>YBa₂Cu₃O(123)</td>
<td>Yes</td>
<td>Yes</td>
<td>Low</td>
<td>Good</td>
<td>s,p,d</td>
<td>Yes</td>
</tr>
<tr>
<td>PbRuO₃</td>
<td>Yes</td>
<td>Yes</td>
<td>Low</td>
<td>Poor</td>
<td>s,p,d</td>
<td>No</td>
</tr>
</tbody>
</table>

* refers to the *form*, not dispersion

** refers to low loss as published in EELS Atlas by [7]

† relative to each other only
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Figure 7.4 Simulated DOS of copper showing s, p and d orbital contributions.

Figure 7.5 Simulated DOS of pure aluminium showing s and p orbital contribution.

Figure 7.6 Simulated DOS of boron phosphate showing s and p contribution.
Two of the samples in Table 7.1 present an exception to the trend, graphite and YBaCuO(123). The YBaCuO(123) has d electron states, yet has a good low loss spectrum form. Graphite has no d or higher electron states yet has a poor low loss form. However, what they do have in common with each other is a directional dependence in their conductivity and low loss spectrum form. Graphite, for example, only conducts in one direction, between the planes of carbon and YBaCuO(123) has CuO planes of superconductivity. Interestingly though, CuO by itself has a poor low loss spectrum form, but then YBaCuO(123), being the high temperature superconductor that it is, would have to be considered unique in many respects. It would be interesting to look at other high temperature superconductors to see if they also have this orientational dependence on the form.

The significance of figure 7.8 is the degradation of the form of the low loss spectrum that silica has in comparison to silicon. Even though we have just implied that d states are the most significant factor that contributes to the form degradation, this is not the cause of degradation in silica. The addition of oxygen to silicon does not add any d electron states. However, the band gap in silica is very large, and as it is an insulator, it has fewer ‘free’ states to couple and thus we see this degradation that results from the addition of the oxygen to the silicon which removes many of the free states. The states are said to be more ‘tightly bound’ as a result of the oxygen lowering the binding energy in the crystal.
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At this stage we can consider three criteria for indicating the presence of multiple plasmon loss transitions;

1. A specimen must be thick or dense enough.
2. The coulombic distribution must be reasonably continuous over a range greater than the interatomic distance i.e. the longitudinal correlation length of the plasmon.
3. There must be a sufficiently small d or higher state contribution, with sufficient ‘free’ electron contribution, i.e. sufficient non-local distribution.

The fact that free electron and conduction electrons both share the same kind of response and correlation effects from a perturbing field suggests that a correlated response is possible where an independence is present between the excited plasmon field states and the valence electrons. These valence states are heavily influenced by core electrons, core-hole effects, overlapping orbitals and whether the states are subsequently ‘tightly bound’.

Using this interpretation then, a plasmon is any correlation amongst the excited states that exhibits an independence from the core field. So, whilst copper has an abundance of free electrons, these electrons are greatly affected by the d orbitals. However, because most insulators have a conduction band too far above the Fermi level, they also don’t exhibit such correlations. An example in between these two cases can be seen in figure 7.4 where the contribution above the Fermi level is minimal in relation to the afore mentioned materials. Therefore, the density of mixed states is not as great, and identifiable multiple plasmon excitation peaks are present. However, the contribution from arbitrary, as opposed to coherent states, is sufficient to broaden out the plasmon peaks and increase the ‘hump’ under them.
Lastly, there is also the evidence that, due to this independence, and the fact that these correlations occur over many interatomic distances, such correlations do not depend on whether the excitation is over a single crystal or polycrystalline or amorphous sample. This is not a new concept; indeed Harrison [8], and Gold [9] were amongst the first to discuss it in the 60’s. However, experimental verification is sparse, and current theory describes the behaviour of plasmon excitation quite well. The plasmon excitations, and the associated band gaps are not directly related to whether they are being formed from the body of an amorphous, polycrystalline or crystalline specimen. This is also why representations and calculations based on the free, or ‘nearly’ free electron models do so well at estimating the band structure and plasmon fields of polyvalent metals, even if they are insulators. These representations will provide a good estimation as long as the amount of coherence of the plasmon field is sufficient enough for core effects to have little influence the plasmon field, or free electron behaviour.

7.4 Conclusions

The definition of the plasmon can be considered as being any correlation amongst the excited states that exhibits an independence to the core field. The criterion for multiple excitations include: i) A specimen must be thick or dense enough, ii) the homogeneity of the coulombic distribution must be reasonably continuous over a range greater than the interatomic distance i.e. the longitudinal correlation length of the plasmon, and iii) there must be sufficiently little contribution from d or higher energy states.

The reason the plasmon dispersion changes for different orientations is due to the interaction of the dynamically diffracted beams being coupled to each other. Therefore, the weighting between coherently correlated and arbitrarily correlated inelastic scattering (plasmon scattering) varies.
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7.5 Appendix

Appendix 7A: The dispersion surface

It is instructive to the point out that the foundation of the dispersion surface is closely related to what is known as a band structure:

As outlined in ref’s. [1,2] we may consider that a steady state wave function describing the behaviour of an electron moving in a potential \( V(r) \) of the crystal as a whole obeys Schrödinger’s equation

\[
\nabla^2 \psi(r) + \left( \frac{8\pi^2 m e^2}{\hbar^2} \right) \left[ E + V(r) \right] \psi(r) = 0 \quad \text{Eqn 7A.1}
\]

From this, with direct substitution, when the potential is zero, analogous to the electron moving through a vacuum, the solution is given by

\[
\psi(r) = \exp\left(2\pi\chi \cdot r\right) \quad \text{Eqn 7A.2}
\]

provided that the magnitude \( \chi \) of the wave vector \( \chi \) is chosen so that

\[
\hbar^2 \chi^2 / 2m = eE \quad \text{Eqn 7A.3}
\]

So then in order for a solution to be applicable to an electron moving through a crystal, a suitable potential is required. A general form of this is

\[
V(r) = \frac{\hbar^2}{2me} \sum_g U_g \exp\left(2\pi\chi \cdot r\right) = \sum_g V_g \exp\left(2\pi\chi \cdot r\right) \quad \text{Eqn 7A.4}
\]

The summation extends over all reciprocal lattice vectors \( g \) and the coefficients for the actual crystal potentials \( U_g \) are constants. The \( V(r) \) is assumed to be invariant under a crystal lattice translation, and assuming that it must be real gives us

\[
U_g = U_{-g}^* \quad \text{Eqn 7A.5}
\]

So this then lets us pursue a Block wave solution of sufficient generality with wave vector \( k \),

\[
\psi(r) = b(k, r) = \sum_g C_g(k) \exp\left(2\pi(k + g) \cdot r\right) \quad \text{Eqn 7A.6}
\]
If we substitute this into equation 7A.1, we obtain a complicated sum of exponentials, but can equate the coefficient by multiplying each exponential term separately to zero. This then gives a set of equations satisfied by the wave amplitudes

\[
\left\{K^2 - (k + g)^2\right\}C_g(k) + \sum U_h C_{g-h}(k) = 0 \quad \text{... Eqn 7A.7}
\]

Where

\[
K^2 = \frac{2meE}{\hbar^2} + U_0 = \chi^2 + U_0 \quad \text{... Eqn 7A.8}
\]

The prime on the summation in equation 7A.7 indicates the values of \( h=0 \) are not included. \( K \) is the magnitude of the electron wave vector in the crystal after correction for the wavelength change due to the mean crystal potential \( U_0 \).

If there are \( N \) terms appearing in the equation 7A.6, then we have \( N \) plane waves in our Bloch wave, and there will be \( N \) equations each of \( N \) terms. Using then the two-beam approximation, the equations reduce to two:

\[
\left(K^2 - k^2\right)C_0(k) + \sum U_{-g} C_g(k) = 0 \quad \text{... Eqn 7A.9}
\]

\[
U_g C_0(k) + \left(k^2 - (k + g)^2\right)C_g(k) = 0 \quad \text{... Eqn 7A.10}
\]

So if the determinant formed by the coefficients vanishes

\[
\begin{vmatrix}
K^2 - k^2 & U_{-g} \\
U_g & K^2 - (k + g)^2
\end{vmatrix} = \left(k^2 - K^2\right)\left((k + g)^2 - K^2\right) - U_g U_{-g} C_g(k) = 0 \quad \text{... Eqn 7A.11}
\]

And since \( K, k \) and \( |k + g| \) are very large in comparison with the differences between them, the equation reduces to

\[
(k - K)(|k + g| - K^2) = \frac{U_g U_{-g}}{4K^2} = \frac{U_g^2}{4K^2} \quad \text{... Eqn 7A.12}
\]
Equations such as 7A.3 and 7A.12 which related the wave vector to the energy are called dispersion equations and generally restrict the wave vector to lie on some kind of surface called the dispersion surface.

Band structures are usually exhibited as plots of energy versus wavevector in the first Brillouin zone. However, these equations are also called dispersion equations and the surface of the plot can be referred to as a dispersion surface.

Dispersion surfaces for low energies are familiar as Fermi surfaces, however, for high energies, the bands are referred to as branches with which we associate the wave vectors $k$ and $k + g$ extending to a reciprocal lattice. It depends on whether the representation is that of an electronic orbital, or a reciprocal lattice point. However, essentially, the equations and the plot are the same.

We then see the connection between the dispersion surface (or energy band distribution) and the reciprocal lattice. This in turn is related to the symmetry of the pattern and hence crystal. Therefore the relation between symmetry and wave coupling can be seen. This is why symmetry is a good indication of whether the low loss is going to be of the ideal form. The band structure and the symmetry are intimately related. They are one and the same thing for all intense purposes, because the electron distribution and the atomic distribution are one and the same thing. This is why the scattering effects derived from these are the same. Bearing in mind that the symmetry is an effect of the coulombic distribution, and the reciprocal lattice is the effect of the symmetry, so symmetry is not the cause, only an indication.

**Appendix 7B: Bloch wave formulation**

The formulation for the dispersion surface adopted Bloch wave formulation [3]. The concept of the Bloch state was developed by Felix Bloch in 1928, to describe the conduction of electrons in crystalline solids. This is where the wave function for a transmitted forward scattered wave can take the form of a block wave.

$$\psi(r) = \phi_g(z) \exp(2\pi i K \cdot r) + \phi'(z) \exp((2\pi i K + g) \cdot r) \quad \text{Eqn 7C.1}$$
So that for a perfect crystal, the two roots of the resulting quadratic gives:

\[
\psi(r) = b^1(K^1, r) = C_0^1 \exp(2\pi i k^1 \cdot r) + C_g^1 \exp((2\pi i k^1 + g) \cdot r) \quad \ldots \text{Eqn 7C.2}
\]

\[
\psi(r) = b^2(K^2, r) = C_0^2 \exp(2\pi i k^2 \cdot r) + C_g^2 \exp((2\pi i k^2 + g) \cdot r) \quad \ldots \text{Eqn 7C.3}
\]

Which can be combined into one wave expression with the coefficients determined

\[
\psi(r) = \psi^1 \left\{ \cos \left( \beta / 2 \right) \exp \left( 2\pi i k^1 \cdot r \right) - \sin \left( \beta / 2 \right) \exp \left( (2\pi i k^1 + g) \cdot r \right) \right\} + \psi^2 \left\{ \sin \left( \beta / 2 \right) \exp \left( 2\pi i k^2 \cdot r \right) + \cos \left( \beta / 2 \right) \exp \left( (2\pi i k^2 + g) \cdot r \right) \right\} \quad \ldots \text{Eqn 7C.4}
\]

This equation embodies an important qualitative conclusion that results from dynamical theory. That is, rather than thinking of the electron as described by, say, two, plane waves with varying amplitudes, sometimes it is more convenient to think of it as a linear combination of the two functions \( b^1 \) and \( b^2 \). These functions each consisting of a definite combination of plane waves are the fundamental solutions of dynamical diffraction theory, known as Bloch wave functions. Put succinctly, a Bloch wave is an amplitude modulated electron plane wave.

The usefulness of the Bloch wave description is that it is considered to propagate through the perfect crystal with constant amplitude and definite wave vector. Ideally, if we could determine the amplitude of the two block waves (two-beam approximation) we could have complete knowledge of the total wave function at all points in the crystal and determine the intensities at the exit surface.

\( \psi^{(1)} \) and \( \psi^{(2)} \) are determined by a boundary condition at the top of the crystal, \( z = 0 \), where the amplitude of the transmitted wave \( \phi_0 \) is unity, and the amplitude of the diffracted wave is \( \phi_g \) zero. This implies the conditions

\[
\phi_0(0) = \psi^{(1)} \cos \left( \beta / 2 \right) - \psi^{(2)} \sin \left( \beta / 2 \right) = 1 \quad \ldots \text{Eqn 7C.5}
\]

\[
\phi_g(0) = -\psi^{(1)} \sin \left( \beta / 2 \right) + \psi^{(2)} \cos \left( \beta / 2 \right) = 0 \quad \ldots \text{Eqn 7C.6}
\]

when

\[
\psi^{(1)} = \cos \left( \beta / 2 \right), \psi^{(2)} = \sin \left( \beta / 2 \right) = 1 \quad \ldots \text{Eqn 7C.7}
\]
This implies that the relative amounts of the two Bloch waves excited depends, therefore, on the orientation of the crystal. Expressions for the transmitted and diffracted wave amplitudes at depth \( z \) in the crystal can then be obtained from equations 7C.1 and 7C.4 to yield expressions for \( (k^{(1)} - \mathbf{K}) \cdot \mathbf{r} \) and \( (k^{(2)} - \mathbf{K}) \cdot \mathbf{r} \).

\[
\phi_s(z) = \psi^{(0)} \cos(\pi \Delta k z) - i \cos \beta \sin(\pi \Delta k z) \quad \text{Eqn 7C.8}
\]

\[
\phi_g(z) = i \sin \beta \sin(\pi \Delta k z) \quad \text{Eqn 7C.9}
\]

Where \( \Delta k = \sqrt{1 - w^2/\xi_g} \) so that at the exit surface, the intensities are given by

\[
1 - |\phi_0(t)|^2 = |\phi_g(t)|^2 = \sin^2 \beta \sin^2 \left( \pi \sqrt{1 + w^2} \frac{t}{\xi_g} \right) \quad \text{Eqn 7C.10}
\]

\[
= \frac{1}{1 + w^2} \sin^2 \left( \pi \sqrt{1 + w^2} \frac{t}{\xi_g} \right) = \left( \frac{\pi}{\xi_g} \right)^2 \sin^2 \left( \frac{\alpha s}{\pi} \right) \quad \text{Eqn 7C.11}
\]

The Bloch wave formulation presents an equivalent result to the phase grating approximation in terms of energy coupling, i.e. they both describe pendellösung. Importantly, though, is the relationship between the dispersion surface and this energy coupling. The equation;

\[
(k - \mathbf{K})(k + \mathbf{g} - \mathbf{K}^2) = \left[ \frac{U_g U_{-g}}{4K^2} \right]^2 = \left[ \frac{U_g}{4K^2} \right]^2 \quad \text{Eqn 7C.12}
\]

which describes the dispersion surface, can just as well be derived from the two roots of the Bloch wave formulation, presented above, since the formulation is one and the same.

\[
\psi(r) = b^1 (K^1 \cdot r) = C_g^1 \exp((2\pi \mathbf{g}^1 \cdot \mathbf{r}) = C_g^1 \exp((2\pi \mathbf{g}^1 + \mathbf{g}) \cdot \mathbf{r}) \quad \text{Eqn 7C.13}
\]

\[
\psi(r) = b^2 (K^2 \cdot r) = C_g^2 \exp((2\pi \mathbf{g}^2 \cdot \mathbf{r}) = C_g^2 \exp((2\pi \mathbf{g}^2 + \mathbf{g}) \cdot \mathbf{r}) \quad \text{Eqn 7C.14}
\]

A Bloch wave formulation of the connection between plasmon scattering and the dispersion surface can be seen in ref. [10].
7.6 References

CHAPTER 8

Summary of Conclusions
And future work

‘Imagination is more important than knowledge’

A. Einstein.

8.1 Summary of conclusions

The form of the low loss spectrum was found to have a greater dependence on the presence of d, or higher, electron states, than the structural phase. The significance that these higher electron states have is the degradation they cause in the degree of coherent correlation in the low loss spectrum.

It was also found, in the case of barium ruthenium titanate, that a possibility exists for the low loss to identify a dopant configuration. The band gap is the most important feature with regards to identifying this and its size is subject to magnetic properties of the material as well as orbital correlation within the material. According to the energetics of the system, a more stable structure exists when the two ruthenium atoms are placed within the same octahedral group in the unit cell, as opposed to having one in each octahedral group. In the ruthenium doped structures that contain a Ru(2)-Ti(2) interaction, a magnetic moment is induced on the ruthenium atoms. This was found to induce changes in the DOS which is potentially identifiable in the low loss spectra. However, the current limits of resolvability in most EELS spectrometers have prevented such a difference from being experimentally confirmed in this investigation.
The definition of the plasmon can be considered as being any correlation amongst the excited states that exhibits an independence from the core field. The criteria for multiple excitations include: the specimen being thick enough, the coulombic distribution must be reasonably continuous over a range greater than the interatomic distance i.e. the longitudinal correlation length of the plasmon, and there must be a sufficiently small number of higher electron energy states present in the material, however, there must still be a sufficient amount of ‘free’ electron content.

It was also concluded that for materials, and in orientations in which the two-beam approximation can be expected to have some validity, that the ladder approximation described in this investigation will have comparable validity, provided that the low-energy-loss spectrum is of a ‘simple’ type, such as that of Si or TiAl.

The reason the plasmon dispersion changes for different orientations is due to the interaction of the dynamically diffracted beams being coupled to each other. Therefore the weighting between coherently correlated and arbitrarily correlated inelastic scattering (plasmon scattering) varies for different scattering angles.

The ladder approximation can be extended to describe many-beam interactions but, beyond the effective three-beam approximation, it becomes complicated, and in particular loses the simple ‘wave-packet’ form.

Imaging from successive plasmon loss peaks was found to enhance the contrast of defects at increasing depths in the crystal. This enabled the capacity for a Hirsch-Howie-Whelan analysis to be carried through at thicknesses otherwise inaccessible at the operating voltage.

Evidence was also shown for plasmon scattered electrons to scatter into large angles. It would appear that plasmon scattered and elastically scattered electrons demonstrate remarkable similarity in the features they exhibit. However, the intensity is reduced and the implications for dynamical models would be a reduced intensity in the final image. There is also evidence of n-beam coupling conforming to a symmetry reduction into a two-beam form.
In concluding this investigation, it is interesting to note that an important concept from the model discussed in chapter 6, and throughout, continues to be that of wave-particle duality. Since the solution refers to the wave-field as a whole, it is instructive to consider the consequence in real terms. If a wave function was made up from a single electron, it would contain all the information that one associates with elastic and inelastic scattering. Unfortunately, it is not envisaged that we can actually measure this, since as soon as the spectrometer collects the wavefunction, it localises it. This is why the spectrum is a distribution of localised events, and will continue to be envisaged as such.

‘...chronic dissonance is merely the normal state of affairs between engineers [scientists] and politicians.’

E. N. Luttwak.

8.2 Future work

If there is a greater band gap present when the 1/3 ruthenium doped material has a pairing of spin, then theoretically this can provide a mechanism for experimentally determining how the dopant is arranged in a given material. Modern high resolution EELS should have the capacity to determine this. However, in this particular study, the band gap difference was found to be significantly less than 1 eV. An attempt was made to observe such a difference in a high resolution EELS system, however, the question with regards to the band gap difference for the different ruthenium stoichiometries could not be resolved. One problem encountered was the presence of an asymmetric large tail on the zero loss peak, combined with occupied electron states above the Fermi level. This is something that possibly ‘newer’ apparatus (circa. 2006) with monochromators, in conjunction with aberration correctors, might be able to resolve.

It was also pointed out in chapter 5 that if the EELS spectrometer could separate the two spins, much like a Stern-Gerlach experiment, it could potentially distinguish between the two dopant configurations. A spin dependant EELS would enable a ‘local’ micro or nano range means of identification. As was mentioned, this apparatus is yet to be realised, and another possible
source of future advancement, particularly given that Spin Polarised EELS is a rich area of investigation at present.

The quantum field theory description of plasmon excitations highlighted the fact that whilst the dominant excitations are those close to \( E_{k+q} - E_k \), there are actually numerous possible excitations available in the system. In reality these are excitations that are small enough such that in most spectra they would not be observed. However, it is possible that in the future, systems may well have the resolution to observe them. We would then be observing energy loss to individual excitation states.

Finish