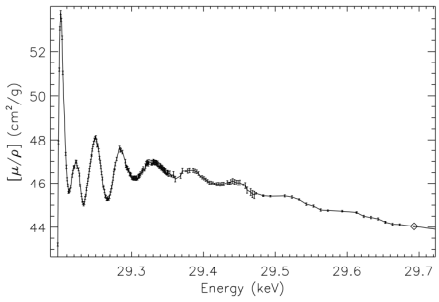
Chris. Chantler, Professor, FAIP; Room 505
X-ray Synchrotron & atomic physics, Quantum Electrodynamics & X-ray Laboratories
Topics for Masters & Higher Degree Students

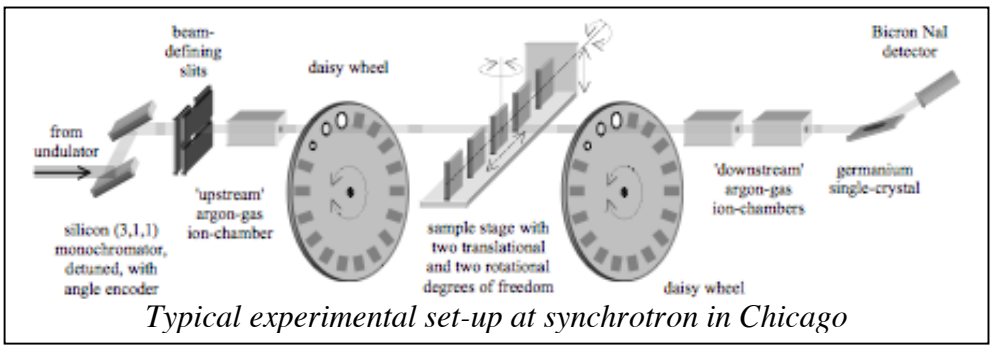


Detail of XAFS for Tin, with error bars giving the absolute accuracy

1. **Can we test QED? Is it true?** We are the only group to test QED in Australia and have just had a breakthrough reported in Physics Today. This was an international team effort and doctoral thesis work but also with contributions from an Honours student.
2. **How can we get structural information from an isolated quantum system – molecule, gas or non-crystalline solid?** We have been the world leaders in extracting structural and quantum information from atomic, molecular and organometallic (i.e. biophysical) systems with advanced experiments and analysis, advancing the techniques used by more than 30% of all synchrotron researchers across the world.
3. **Can I develop or invent a new field of physics?** Yes but probably not in Masters! Recent doctoral students have developed new fields of non-destructive nanoroughness measurement; and electron inelastic scattering (mean free path) experiment and theory; or made major developments in dominant fields of X-ray science or relativistic Quantum Mechanics.

- Facilities: X-ray labs; Synchrotrons around the world & Melbourne; EBIT labs around the world.

Our local laboratories develop new technology in-house, & ask fundamental questions about the universe & matter.



Typical experimental set-up at synchrotron in Chicago

- Two honours students (2005) produced 3 major papers from honours (one high profile Phys. Lett.). Three honours students (2006) got the best experimental thesis in the School (Ramm Prize), and one of the top 3 theory theses.

Both students in 2008 got top marks in theory and experiment. These great results reflect on them, the potential of the field & our group. Martin de Jonge was awarded the Chancellor's Prize (best Doctoral Thesis at Melbourne University), 'Best Synchrotron Thesis in Australia', flew off to an exciting career at the Advanced Photon Source (Chicago) & has now returned to get first light on the Australian Synchrotron on a key beamline. We receive national & international awards for group achievements.

Our **experiments** are two orders of magnitude more accurate than all earlier publications in the field.[1] This has opened up exciting new opportunities & opened our eyes to new phenomena and new ways of testing earlier assumptions. Our experiments have been the *first* to measure scattering[2] & synchrotron bandwidth in photoabsorption experiments, have redefined the international standards for (powder) diffraction[3], and have placed the field of X-ray Absorption Fine Structure (XAFS) on an absolute footing for the first time. Our *relativistic atomic* ***theory*** and tabulation[4] is the most successful currently available in terms of agreement with experiment. Theory must be based on *condensed matter physics* near absorption edges to explain detailed oscillations, which in turn raises new questions. Honours students have developed *new theory* & computational tools for condensed matter science, including the first extended XAFS solution avoiding 'muffin-tin' approximations[5] & the largest (organometallic) XAFS modelled without this assumption,[6] with major implications for biological

---

[1] de Jonge *et al*., *Phys. Rev.* A **71**, 032702 (2005); C Q Tran *et al*., *Phys. Rev. Letts 90 (2003) 257401*

[2] C Q Tran *et al., J. Phys. B37 (2004) 3163-3176;* de Jonge *et al*., *Phys. Rev. A 69 (2004) 022717*

[3] C. T. Chantler et al., *Phys. Rev. A69* (2004) 042101

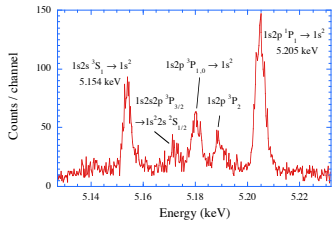
[4] C.T. Chantler, *Theoretical form factor, attenuation and scattering tabulation for Z=1-92 from E=1-10 eV to E=0.4-1.0 MeV*, J.Phys.Chem.Ref.Data 24, 71-643 (1995)**;** C.T. Chantler, J. Phys. Chem. Ref. Data. 29 (2000)

[5] J. D. Bourke et al., *Phys. Lett. A360 (2007);* also Cosgriff *et al., Phys. Lett. A343 (2005) 174*

[6] J. L. Glover et al., 625-627 *CP882, "X-ray Absorption Fine Structure – XAFS13", B. Hedman, P. Pianetta, eds (2007,AIP)*

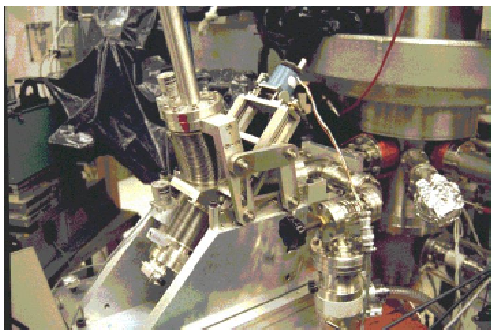
science. Masters students have been developing new fields in non-destructive nano-roughness measurement applicable to nano-circuits and next-generation computation; and developed the new field of absolute fluorescence XERT, which will lead to *ab initio* XAFS determination of nano-structure.

Quantum Electrodynamics is one of the two best-tested theories in physics and science. It is the most trusted example of a Quantum Field Theory in practice. Yet certain problems in its formulation lead people like Roger Penrose to assume that there are fundamental flaws in the theory. Our experiments at the cutting edge[7] may reveal such an inadequacy, by being more sensitive to important terms and interactions than other available tests. Coming experiments can test alternate competing theories. QED is the primary explanation of the interaction of light and charge, and is fundamental to much of the physics which we assume and rely on in the world today. Experimental and theoretical developments in 1998 – 2008 are questioning the current theoretical approaches. Can hints of string theory, extra dimensions, or other formulations be found in atoms?



Recent data testing QED from NIST

Biological systems are linked to our investigations via Crystallography, Powder Diffraction, and XAFS; via development & testing of theory used to interpret these; via developments for mammography; and via lab and synchrotron experiments. Available projects include pure theoretical topics, pure experimental topics, and mixed theory, computation & experimental projects. In our group, a normal experimental or theoretical thesis will naturally learn about the other. Doctorates link theory and experiment together in a coherent whole. http://optics.ph.unimelb.edu.au/~chantler/home.html & optics.ph.unimelb.edu.au/xrayopt/xrayopt.html. Recent developments & papers can be collected from Chris Chantler. Masters will be more successful than earlier honours projects & would expect that results lead to major international publications *within the course*. ***Current topics for Masters and higher degrees:***


Melbourne detector and spectrometer at NIST, USA

1 Atomic & Condensed Physics *Theory*: New computation & theory of atomic radiation, photoionization, scattering with X-rays, IR, Vis, including laboratory astrophysics and the fine structure constant. Applications include precision measurements, crystallography, medical physics, tomography, fundamental X-ray experiments & new types of test of Quantum Electro-Dynamics.

1.1 XAFS, Isolated Particle Approximation models and near-edge structure (scattering, atomic structure & crystals). X-ray Absorption Fine Structure is due to a coherent interaction of an emitted photoelectron wave with its elastically scattered wave, yielding rich structure near absorption edges, which is poorly understood. This is one of the three *most popular experimental X-ray techniques* used [2500 papers pa]. Our aim is to revolutionise the field and create new techniques & understanding for use by all researchers. **[Project*]** Students can analyze and *develop* models, experiment, analytic tools & theory, leading to higher degree projects & new self-consistent theory. Post-doctoral, Masters & honours students have worked on this in 2003-11. Major limitations of current theory *can be addressed within a Masters project*.

1.2 Theory and computation of atomic form factors (scattering of X-rays/diffraction/atomic structure). **[Project*]** Our web-site receives 1200 hits per month. But (our) earlier formulations have limitations. Interesting questions relate to high-energy limits, analytic formulations, S-matrix field theory and correlated perturbation theory. An honours student recently worked on new analytic calculations of relativistic atomic form factors and was awarded school physics prizes for honours. We have several high-profile Phys. Rev. papers on our new developments.

1.3 Dynamical diffraction from curved crystals (diffraction / mosaicity). Development of theory of mosaic diffraction of X-rays is necessary in high-efficiency diffraction experiments in the X-ray regime. We have published the first dynamical theory of X-ray diffraction for non-ideally imperfect curved crystals. This theory can be used to test QED and to understand bonding, both of which are

[7] C.T. Chantler *et al., Phys. Rev. A62 (2000) 042501*; C. T. Chantler *et al., Phys. Rev. A71 (2005) 032702*

major questions in current world research. Mosaic crystals have the lattice plane orientation (or phase relationship) varying with position or depth. This is a promising area for further research.

2 Experiments on X-ray Processes and QED: Investigations using XAFS by our group has yielded accurate measurements probing atomic physics, scattering theory, electron wavefunctions & condensed structure. This has revealed problems about relativistic, QED & other theoretical contributions to observed interactions. [**New Projects***] Masters projects can develop new state-of-the-art detection systems, analyse data to yield new critical tests of QED or complete high-accuracy experiments in labs or at synchrotrons, including the Australian Synchrotron.

2.1 Effect of excitation energy on characteristic radiation: a new ruler in atomic and condensed matter science. A recent invitation from the major international labs in the world has asked us to be involved in determining new standards of energy determination and accuracy. This involves both the preparation of new experiments with Kα sources, and leads to better tests of QED, antihydrogen, better detector technology, and applications to more incisive synchrotron research. Key is a new combined approach to theory and experiment. **[Project*]**

2.2 High-accuracy measurement of photoabsorption. Our synchrotron techniques have surpassed the world's best results by two orders of magnitude in accuracy & have been announced as amongst the top five experiments on two separate beam-lines at one of the world's largest synchrotrons. **[Project*]** We can test critical differences between implementations of relativistic quantum theory. International experiments could be part of a Masters or higher degree. Several doctoral students have worked in this area.

2.3 Absolute measurement of absorption coefficients of gold and zinc using local and international sources [Chris Chantler & Zwi Barnea]. We have the best data in the world to investigate new physics in XAFS (near edge atomic and solid state structure).

2.4 Investigation of X-ray scattering and fluorescence distributions. These investigate the radial electron density in atomic systems. **[Project*]** A Masters project would use existing facilities to investigate the shape of inelastic scattering. Post-doctoral students are working on this.

2.5 Biophysics links with labs & analysis to probe X-ray irradiation, biological structures and catalysis.

2.6 Quantum Electro-Dynamics: X-ray spectrometers for high-precision measurement in X-ray physics and QED. [Project*] Current students have made exciting progress, directly related to new tests of QED. We recently made the highest precision tests of QED for Vanadium atoms (Z=23) using a device called an Electron Beam Ion Trap, with a new measurement, new detector and new spectrometer.[8] We can investigate discrepancies in QED at the level of 2 x 10^{-5} (or 20 parts per million) in medium-Z ions, and are developing state-of-the-art detector and spectrometer equipment to ask whether current discrepancies from theory yield fundamental insights into laws of physics.

2.7 X-ray Extended Face Crystal measurement of absolute intensities for extinction and bonding redistribution of electron density [Zwi Barnea & Chris Chantler]. Diffraction processes require careful measurements on an absolute scale to reveal new physical and structural insights. The X-ray facility can address these issues directly. Associate Professor Barnea originated these techniques. Questions about how structures bind together, of current international interest, can be resolved. A major dilemma over decades has been the inequivalence of symmetric Bragg diffraction peaks which impact upon the popular biological MAD techniques used by state-of-the-art facilities in the US, Japan and Europe.

All topics lead to higher degrees, & research papers within a Masters project; most can lead to

- precision tests of QED (in systems such as He-like Vanadium & H-like Nickel) or
- new understanding of atomic & condensed matter physics & fundamental X-ray spectroscopy (How accurate is atomic physics for a real atom?)

---

[8] J.D. Gillaspy, Y. Aglitskiy, E.W. Bell, C.M. Brown, C.T. Chantler, et al., *Overview of the EBIT Program at NIST*, Physica Scripta, **T59**, 392-395, 1995; C.T. Chantler, et al., *Absolute measurement of the resonance lines in heliumlike vanadium on an electon-beam ion trap*, Phys. Rev. A 29 (2000).

Each experimental topic is a fundamental research area. This work is both in-house and in collaboration with NIST (Washington DC), the University of Oxford & Synchrotrons (Japan, Chicago). Other research on X-ray experimental measurement[9] has links with industry. Projects linked with medicine & mammography have yielded publications & patents. Our group has links with biological & biochemical groups & investigations in Australia & around the world.

MSc 2012 – extension and development of new cluster theory - XAFS FDM technique [inelastic mean free paths] [Jay]. Application to new field of inelastic mean free paths; band theory; XANES; EXAFS

MSc 2012 – development of new theory of atomic spectra and continuum regions [John]. Applications to laboratory astrophysics; the fine structure constant; international tables; theory of resonant transitions in relativistic QM; QED

MSc 2012 – biological & organometallic systems [JJC; Feiters (Europe); Stephen Best (Chemistry)]

MSc 2012 – application of molecular codes within the cluster framework [Feng, Swinburne]

MSc 2012 – installation and operation of sources – new tools for science [AP]

- including largest LIEF grant and first major ARC grant for synchrotron development [Australian Synchrotron] – the first XERT experiment in Australia!

MSc 2012 – analysis of XAFS data for Cu_2O anomalies & organometallics [Jack/Nick/Adelaide]

MSc 2012 – analysis of XERT data for fluorescence and solutions [Jack/Nick/Chemistry]

MSc 2012 – powder diffraction analysis & experiments [JK, ZB, CTC, NR]

MSc 2012 – EFC experiments, MAD and anomalous dispersion, & modeling [ZB, Nick]

Possible Components

[MSc] Feiters: sequel… complex organometallic clusters by (non-muffin-tin) FDM…

[MSc] Cu_2O anomaly [Barbara / Jack / Jay / Denis Testamale]

[MSc – Lucas, Jack, Nick] Error analysis and encoding – i.e. making FEFF work

[MSc Theory] FDM Theory and implementation for a least-squares fitting technique to experimental data; AXAFS & unresolved transitional arrays

[MSc Theory] Sequel to Andrew / John. K alpha doublet scaling for hole satellite spectra for copper and Mn… as a function of incident electron or photon energy. Atomic photionisation cross-sections pre- & post- edge

[MSc Exp] Detector Gas Resolution Study; Crystal Redesign & control; Horizontal Spectrometer; digitization design / study

[MSc Exp] Lab. Scattering; Absolute Absorption Coefficient; analysis; Drosophila

[MSc Exp] Lab. EFC / Detector testing

[MSc – Jack] Chris Howard … XANES pre-edge, on-edge features for perovskites

[Nick, JK] New Si / LaB_6 powder diffraction standard result based upon ZnSe?

---

[9] C.T.Chantler, *Photographic response to X-ray irradiation I: Estimation of the photographic error statistic, and development of analytic density-intensity relations*, Applied Optics **32** 2371-2397, 1993.

Breaking News – Physics Today [October 2012]:

Highly charged ions challenge QED

Energy transitions in the three-body systems are intriguingly different from what theory calculates.

Quantum electrodynamics (QED), the relativistic field theory describing interactions of light and charge, is justly celebrated for the astonishing accuracy with which it predicts, for example, the anomalous magnetic moment of the lone electron. But the reach of QED extends to substantially more complex systems. One class of objects amenable to experimental study and QED calculation includes helium-like ions with atomic number Z of about 25 and two orbiting electrons. In those three-body entities, the significant nuclear charge enhances the QED interactions.

A recent experiment by an international team led by Christopher Chantler (University of Melbourne, Australia) has made the most precise measurement to date for the energy of a specific atomic transition, called the *w* transition, in helium-like titanium $^{22}Ti^{20+}$ at the NIST EBIT and has obtained a value that disagrees with QED by three standard deviations. But the bigger surprise came when the group reviewed the published literature for *w* transitions in helium-like ions with Z between 16 and 36.

Taken as a whole, the experimental data differed from theory by five standard deviations, and, as the figure shows, a least-squares fit through the data indicates that the discrepancies scale as Z^3. (The green swath displays the 68% confidence interval for the fit.) Chantler and company note that the mismatches between experiment and theory potentially involve a variety of QED effects with various Z dependencies. Future experiments in the unexplored Z = 27–31 range, they say, could further systematize the discrepancies and guide theoretical work. (C. T. Chantler et al., *Phys. Rev. Lett.***109**, 153001, 2012.)—Steven K. Blau

Measurements of Electron Inelastic Mean Free Paths in Materials

J. D. Bourke and C. T. Chantler*

School of Physics, University of Melbourne, Parkville, Vic, 3010 Australia

(Received 10 February 2010; published 20 May 2010)

We present a method for determining inelastic mean free paths (IMFPs) in materials using high-accuracy measurements of x-ray absorption fine structure (XAFS). For electron energies below 100 eV, theoretical predictions have large variability and alternate measurement techniques exhibit significant uncertainties. In this regime, the short IMFP makes photoelectrons ideal for structural determination of surfaces and nanostructures, and measurements are valuable for studies of diverse fields such as low-energy electron diffraction and ballistic electron emission microscopy. Our approach, here applied to solid copper, is unique and exhibits enhanced sensitivity at electron energies below 100 eV. Furthermore, it is readily applicable to any material for which sufficiently high accuracy XAFS data can be obtained.

DOI: 10.1103/PhysRevLett.104.206601 PACS numbers: 72.15.Lh, 61.05.cj, 73.50.Gr, 78.70.Dm

The electron inelastic mean free path (IMFP) is the average distance travelled between successive inelastic collisions for an electron moving with a particular energy in a given medium [1]. It is of fundamental importance for a quantitative understanding of electron transport, for electron energy loss spectroscopy and for high-resolution transmission electron microscopy—exciting fields capable of imaging materials at an atomic level [2] and sensitive to changes in interatomic bonding [3]. The mean free path is also crucial for investigations of linear dichroism using photoelectron diffraction [4]; structural investigations using auger electron spectroscopy [5] and x-ray photoelectron spectroscopy [6]; organic semiconductor development for spintronics [7]; and even studying Coulomb explosions triggered by femtosecond x-ray pulses in free-electron lasers [8,9].

However, IMFPs are difficult to determine experimentally, especially at energies below 100 eV–200 eV [10]. As discussed later, different models have predicted large differences in IMFP values in this region, and there has not been a reliable method for assessing the low-energy limits of calculations and predictions which are used for many cognate fields.

Theoretical approaches and computations have large challenges. While theory is well developed for the determination of IMFPs for a free-electron material [11], most solids exhibit complex energy loss functions which require a new approach. It is common to compute IMFPs using experimentally determined optical dielectric functions, or analytic predictive formulae based on these [12]. Empirical curves may also be used when more detailed tabulations are unavailable [13]. These approaches can give applicability at high electron energies, but tend to show discrepancies below 200 eV.

Our work focusses on x-ray absorption fine structure (XAFS) as a solution to this problem. Thousands of papers on XAFS demonstrate its value in probing material structure down to atomic displacements at the femtometer scale [14]. XAFS theory [15] has shown recent success in the region where it is highly sensitive to the IMFP [16]. We match this theory to experimental XAFS determined by the x-ray extendedrange technique [17]. This technique provides us with the unprecedented accuracy required to extract the IMFP. In particular, this data is extremely valuable for low-energy electron diffraction (LEED) [18], ballistic electron emission microscopy (BEEM) [19], and experimental configurations where IMFPs for electron energies below 100–200 eV play a role. For much higher electron energies (eg., 200 keV STEM), primary processes will be quite different but secondary scattered photoelectrons may be treated with this new information.

XAFS refers to the complex series of oscillations seen in the photoelectric absorption curve of a material, immediately following an absorption edge. These oscillations convey important structural information about the absorbing material, most notably the relative positions of atoms in the crystal lattice. They are produced by interference between the outgoing photoelectron wave functions from the absorbing atoms, and the returning wave functions backscattered from atoms in the surrounding region. Since this interference is strongly dependent on the photoelectron energy, the short lifetimes of the photoelectrons cause an energy uncertainty and thus a smearing of the XAFS curve.

The finite IMFP reduces the wave amplitude which diminishes interference (coherence) between the outgoing and incoming waves. Because of the Fourier relationship between the reflected wave function and the resulting XAFS spectrum, this exponential damping leads to a broadening of the XAFS peaks with corresponding energy uncertainty. This effect is particularly clear below 100 eV where the amplitude of the XAFS oscillations is high. To quantify the coherence of the interference, we require knowledge of the photoelectron lifetime or, equivalently, the IMFP.

X-ray mass attenuation coefficients and imaginary components of the atomic form factor of zinc over the energy range of 7.2–15.2 keV

Nicholas A. Rae, Christopher T. Chantler, and Zwi Barnea
School of Physics, University of Melbourne, Victoria 3010, Australia

Martin D. de Jonge
Australian Synchrotron, Victoria 3168, Australia

Chanh Q. Tran
La Trobe University, Victoria 3086, Australia

James R. Hester
Australian Nuclear Science and Technology Organisation, New South Wales 2234, Australia
(Received 16 July 2009; published 22 February 2010)

The x-ray mass attenuation coefficients of zinc are measured in a high-accuracy experiment between 7.2 and 15.2 keV with an absolute accuracy of 0.044% and 0.197%. This is the most accurate determination of any attenuation coefficient on a bending-magnet beamline and reduces the absolute uncertainty by a factor of 3 compared to earlier work by advances in integrated column density determination and the full-foil mapping technique described herein. We define a relative accuracy of 0.006%, which is not the same as either the precision or the absolute accuracy. Relative accuracy is the appropriate parameter for standard implementation of analysis of near-edge spectra. Values of the imaginary components f'' of the x-ray form factor of zinc are derived. Observed differences between the measured mass attenuation coefficients and various theoretical calculations reach a maximum of about 5% at the absorption edge and up to 2% further than 1 keV away from the edge. The measurements invite improvements in the theoretical calculations of mass attenuation coefficients of zinc.

DOI: 10.1103/PhysRevA.81.022904 PACS number(s): 32.80.Aa, 32.80.Fb, 32.30.Rj, 61.05.cj

I. INTRODUCTION

The x-ray atomic form factor is the fundamental parameter describing the interaction of x rays with matter. Accurate values of the mass attenuation coefficient and hence of the dielectric function are vital for many areas such as particle energy loss functions [1], electron energy loss spectroscopy [2], crystallography [3,4], tomography [5], and polarizability and reflectometry [6]. A wide range of atomic [7], molecular [8], and solid-state [9,10] features can be calculated given accurate values of x-ray atomic form factors of the constituent elements.

Theoretical estimates of atomic form factors have been tabulated since early in the development of x-ray science for all elements across a wide range of energies. The National Institute of Standards and Technology (NIST) currently supports two such tabulations; XCOM [11,12] and FFAST [13–15]. Significant differences exist in the values of the form factors from these tabulations across a wide range of energies and elements [13,16], the largest being at and immediately above absorption edges [17]. These discrepancies lead to a significant problem when calculating mass attenuation coefficients in these regions.

Figure 1 shows the percentage difference between various experimentally or theoretically determined mass attenuation coefficients of zinc and the corresponding theoretical values calculated using FFAST. Despite experimental errors between 1% and 2% quoted by the various authors, the values are inconsistent, have a spread of about 10%, and generally do not agree with theoretical values. Above the absorption edge at 9.623 keV, there are few reported measurements of mass attenuation coefficients of zinc. Given these inconsistencies, uncertainty, and spread, existing experimental results cannot be used to distinguish different theoretical approaches (Fig. 1).

The absorption edge region is of particular importance for widely used synchrotron techniques such as x-ray absorption fine structure (XAFS) [22] and x-ray absorption near-edge structure (XANES) [9]. The need for accurate measurements of the mass attenuation coefficient in this region has been noted by other groups [23] and in particular the measurement of K-shell [24] and L-shell [25] jump factors and jump ratios has been of concern. Investigation of photoeffect cross sections for subshells depends upon accurate experimental data and should preferably cover a range of energies to avoid key systematics [26]. In the edge region, accurate values of the mass attenuation coefficient are needed to derive structural and chemical information, such as for example elemental and phase concentrations derived from the edge height [27].

The discrepancies between theory and experiment, between theory and theory, and between experiment and experiment led the International Union of Crystallography (IUCr) to conduct a study of problems associated with the measurement of x-ray mass attenuation coefficients [28,29]. The study found that systematic errors had not been quantified, leading to discrepancies greater than the individual measured uncertainty. Such measurements could not be used to distinguish among different theoretical approaches. The study found that a key tool for determining sources of error was to perform measurements on different thicknesses of absorbing material.

J. Phys. B: At. Mol. Opt. Phys. **43** (2010) 085001 (15pp) doi:10.1088/0953-4075/43/8/085001

Measurement of the x-ray mass-attenuation coefficients of gold, derived quantities between 14 keV and 21 keV and determination of the bond lengths of gold

J L Glover[1], C T Chantler[1], Z Barnea[1], N A Rae[1] and C Q Tran[2]

[1] School of Physics, University of Melbourne, Victoria 3010, Australia
[2] Department of Physics, La Trobe University, Victoria 3086, Australia

E-mail: chantler@unimelb.edu.au

Received 30 December 2009, in final form 11 February 2010
Published 23 March 2010
Online at stacks.iop.org/JPhysB/43/085001

Abstract
The x-ray mass-attenuation coefficients of gold are measured at 91 energies between 14 keV and 21 keV using synchrotron radiation. The measurements are accurate to between 0.08% and 0.1%. The photoelectric mass-absorption coefficients and the imaginary component of the form factors of gold are also determined. The results include the L_I edge and are the most accurate and extensive gold dataset available in this energy range. An analysis of the L_I edge XAFS showed excellent agreement between the measured and simulated XAFS and yielded highly accurate values of the bond lengths of gold. When our results are compared with earlier measurements and with predictions of major theoretical tabulations, significant discrepancies are noted. The comparison raises questions about the nature of discrepancies between experimental and theoretical values of mass-attenuation coefficients.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

X-ray form factors and attenuation coefficients describe the interaction of x-rays with matter and are widely applied throughout science. For example, medical x-ray images and CT scans are generated by measuring the spatial variation of the x-ray attenuation by the body [1, 2]. The associated values of the imaginary part of the atomic form factor are used in crystallography for the elucidation of protein structures by the multiple anomalous dispersion (MAD) technique [3, 4]. Attenuation coefficients are also essential for the study of bonding and the local atomic structure of materials and molecules using the x-ray absorption fine structure and near-edge structure analysis [5, 6]. More generally, with the increasing use of x-rays at medical facilities and synchrotrons, it is essential to have accurate reference values of mass-attenuation coefficients and form factors. Despite their wide use, large discrepancies exist in the experimental [7, 8] and theoretical literature [9] and for most elements the value of the mass-attenuation coefficient is only known to an accuracy of a few per cent.

X-ray mass-attenuation coefficients can be calculated using relativistic quantum mechanics. Although several assumptions are necessary to make them tractable, such calculations have been made and compiled into theoretical tabulations. The two theoretical tabulations recommended by the National Institute of Standards and Technology (NIST) are XCOM [10] and FFAST [9, 11]. These tabulations can be critically tested by comparison with high-accuracy experiments, and in recent years there have been several notable comparisons—mostly for medium-Z elements and often at K-edge energies. Significant discrepancies were observed between the tabulations and experiment, especially at and above the K-edge where differences reached 5% [12–15]. In contrast, there are very few high-quality experimental measurements available for high-Z elements or at L edges and in these regions the accuracy of theory is yet to be critically tested.

Journal of
Applied Crystallography
ISSN 0021-8898

Received 20 July 2009
Accepted 3 November 2009

X-ray absorption fine structure for single crystals

Christopher T. Chantler,[a]* Chanh Q. Tran[b] and Zwi Barnea[a]

[a]School of Physics, University of Melbourne, Australia, and [b]Department of Physics, La Trobe University, Australia. Correspondence e-mail: chantler@unimelb.edu.au

X-ray absorption fine structure measurements are a prime tool at synchrotrons around the world, accounting for over 30% of all synchrotron research. They are incisive tools for elucidating local structure, ionization state and coordination geometry. However, in general, it has not been possible to apply them to perfect or near-perfect crystals, and their dominant application is to micro-samples, powders, metals and solutions. The reasons for this are given, and an experimental technique to yield high-precision data for good crystals is developed. This widens the applicability of the technique dramatically, and permits standards and calibration samples to be used and transferred for new types of measurement. It is shown that this is particularly appropriate for discrete measurements of absorption, X-ray absorption fine structure and X-ray absorption near-edge spectroscopy, and in cases of strong oscillations.

1. Introduction

A standard X-ray absorption fine structure (XAFS) measurement will measure the transmission of a sample as a function of energy above a particular absorption edge. The sudden jump in absorption coefficient at the edge indicates that enough energy is imparted by the incoming photon to release the bound photoelectron, in the inverse photo-effect. In the region extending some eV to keV above the edge, strong oscillations are often seen. These oscillations reflect the interference effect due to the photoelectron wave scattering from the surrounding electron density and interfering with the original outgoing wave. A schematic diagram illustrating the process is given in Fig. 1. This fine structure can then be inverted (or Fourier transformed) to display the radial electron density at some distance from the atom containing the absorption edge that emitted the photoelectron (Sayers *et al.*, 1971).

Hence, the structure observed is used to characterize the solid-state electron wavefunction (Rehr & Albers, 2000), and thereby can be fitted to a number of theoretical models (Newville, 2001; Joly, 2001; Bourke *et al.*, 2007) to obtain oxidation states of species (Ryser *et al.*, 2005; Takahashi *et al.*, 2002), nearest-neighbour distances (Hwang *et al.*, 2000), coordination numbers (Matteo *et al.*, 2005; Ravel *et al.*, 2006) and thermal parameters (Fornasini *et al.*, 2004) and to confirm structural evaluations (Gawelda *et al.*, 2006). For complex species such as organometallics (Glover *et al.*, 2007) or biologically active systems (Loll *et al.*, 2005; Haumann *et al.*, 2005) this technique can very usefully characterize the active centres of bioactive or chemically active molecules.

The XAFS technique has found its dominant application to micro-samples in the environmental and earth sciences (Hedman & Pianetta, 2007*a*), biological and medical solutions (Hedman & Pianetta, 2007*b*), thin films (Wei *et al.*, 2000), powders (Artiolia *et al.*, 2006), solid solutions (Greaves & Sen, 2007), melts (Okamoto *et al.*, 2002), and metals and alloys (Felderhoff *et al.*, 2004). However, in general, it has not been possible to apply XAFS to perfect or near-perfect crystals (Glover & Chantler, 2007; Riggs-Gelasco *et al.*, 1995; Crozier, 1997). We discuss one precondition for obtaining good XAFS spectra – that coherent scattering of the incident X-ray is negligible compared to the photo-absorption amplitude – and explain the consequences of this condition. In particular, this condition has limited the application of the technique to the above types of samples and has limited the potential for defining transfer and calibration standards. We discuss how this significant limitation can be addressed to enable useful and high-precision experiments on high-quality crystals and crystallites of intermediate perfection.

2. The problem: discontinuities and singularities in experimental data sets

The typical XAFS spectrum as illustrated in Fig. 2 for metallic tin has sharp features on the absorption edge, progressing to

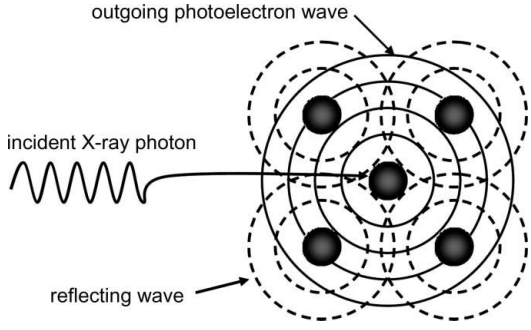


Figure 1
Illustration of the interference of the outgoing and returning photoelectron waves for a simple geometry, leading to X-ray absorption fine structure.

Eur. Phys. J. Special Topics **169**, 147–153 (2009)

DOI: 10.1140/epjst/e2009-00985-8

THE EUROPEAN PHYSICAL JOURNAL SPECIAL TOPICS

Review

Development and applications of accurate measurement of X-ray absorption

The X-ray extended range technique for high accuracy absolute XAFS by transmission and fluorescence

C.T. Chantler[a]

School of Physics, University of Melbourne, Parkville, Vic. 3010 Australia

Abstract. Over recent synchrotron experiments and publications we have developed methods for measuring the absorption coefficient in the XAFS (X-ray Absorption Fine Structure) region and far from an edge in neutral atoms, simple compounds and organometallics which can reach accuracies of below 0.02%. This is 50–500 times more accurate than earlier methods, and 50–250 times more accurate than claimed uncertainties in theoretical computations for these systems. The data and methodology is useful for a wide range of applications, including dominant synchrotron and laboratory techniques relating to fine structure, near-edge analysis and standard crystallography. The experiments are sensitive to many theoretical and computational issues, including correlation and convergence of individual electronic and atomic orbitals and wavefunctions.

1 Development and history of XERT and applications

Traditionally, measurements of absorption of X-rays by ideal condensed matter systems have provided critical data for experimental tabulations [1,2], tests of theoretical computations and databases [3–10], and material for experimental-theoretical empirical syntheses [11,12]. These are then used in plasma diagnosis, X-ray and radiographic filters, anode tube design, medical imaging, weapons research and fundamental investigations to name a few.

Computational issues suggested that relativistic theory from the 1970's was limited and needed to be addressed with more developed computational schemes [13,14]. The new results of the 1990's and 2000's are certainly superior. However, different formulations still remain discrepant from one another by several or even 10–20% especially in near-edge or soft X-ray energy regimes for many elements. This is one key issue which has sparked not only our series of experimental investigations, but also those of many other research groups.

Careful studies from 1987 and 1990 began to define some issues and problems in the careful measurement of attenuation coefficients in general and in the accurate determination of photoabsorption coefficients in particular [15,16]. Development of modelling and computation has enabled the resolution of several earlier discrepancies between experiment and theory [17,18], yielding the FFAST database (http://physics.nist.gov/ffast). However, in many cases the experimental data has been inconsistent between or within datasets, with apparent precisions of order 1%–20%, which therefore has prevented detailed investigation of the experimental or theoretical discrepancies. It was claimed that accuracies below 1%, even for metals or single crystalline elements, were not possible (due to the difficulties of addressing experimental systematics). We developed some of the principles earlier established by the International

[a] e-mail: chantler@unimelb.edu.au

J. Phys. B: At. Mol. Opt. Phys. **43** (2010) 074021 (9pp) doi:10.1088/0953-4075/43/7/074021

First measurement of Lyman alpha x-ray lines in hydrogen-like vanadium: results and implications for precision wavelength metrology and tests of QED

J D Gillaspy[1], C T Chantler[2], D Paterson[2,3], L T Hudson[1], F G Serpa[1,4] and E Takács[1,5]

[1] National Institute of Standards and Technology, Gaithersburg, MD 20899-8422, USA
[2] University of Melbourne, Parkville, Victoria 3052, Australia

Received 9 September 2009, in final form 30 September 2009
Published 19 March 2010
Online at stacks.iop.org/JPhysB/43/074021

Abstract
The first measurement of hydrogen-like vanadium x-ray Lyman alpha transitions has been made. The measurement was made on an absolute scale, fully independent of atomic structure calculations. Sufficient signal was obtained to reduce the statistical uncertainty to a small fraction of the total uncertainty budget. Potential sources of systematic error due to Doppler shifts were eliminated by performing the measurement on trapped ions. The energies for Ly α_1 ($1s\text{-}2p_{3/2}$) and Ly α_2 ($1s\text{-}2p_{1/2}$) are found to be 5443.95(25) eV and 5431.10(25) eV, respectively. These results are within approximately 1.5 σ (experimental) of the theoretical values 5443.63 eV and 5430.70 eV. The results are discussed in terms of their relation to the Lamb shift and the development of an x-ray wavelength standard based on a compact source of trapped highly charged ions.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

In addition to their traditional use for high-temperature plasma diagnostics and as a testbed for fundamental theory, hydrogen-like ions have been proposed as the basis of a calculable x-ray wavelength standard [1, 2] or even as a hyperfine clock frequency standard in the THz to infrared spectral range [3]. Such standards could be disseminated via an electron beam ion trap (EBIT) [4], which provides a relatively compact and affordable source of hydrogen-like ions of arbitrary Z. The development of EBITs that fit on a tabletop and operate at room temperatures has been recently reviewed [5]. Before a calculable x-ray standard can be established, however, it is necessary to verify that the spectral lines emitted from the trapped hydrogen-like ions are not significantly perturbed by effects such as satellite line contamination or other potential sources of systematic error.

Although the physics of quantum electrodynamics (QED) underlying the calculations of hydrogen-like V emission is believed to be highly reliable, it is important to test this assumption as well as to check for 'evaluation errors' (mistakes in implementing the known physics). An example of the latter can be found in a recent QED calculation which contributed to the determination of the fine structure constant. When two evaluation errors were discovered in the calculation of 891 Feynman diagrams, a shift in the eighth-order term was 53 times larger than the reported uncertainty, resulting in a 6.5 σ shift in the inferred value of the fine structure constant [6]. Fortunately, no such evaluation errors have been found in the most widely used tabulations of QED results for the

[3] Present address: Australian Synchrotron, 800 Blackburn Road, Clayton, Vic 3168, Australia.
[4] Present address: Booz Allen Hamilton, 3811 North Fairfax Drive Suite 600, Arlington, VA 22203-1707.
[5] Present address: University of Debrecen, Experimental Physics Department, Bem tér 18/A, Debrecen, Hungary, H-4026.

Hydrogenic Lamb shift in Ge^{31+} and the fine-structure Lamb shift

C. T. Chantler*
School of Physics, University of Melbourne, Victoria 3010, Australia

J. M. Laming
Space Science Division, Code 7674L, Naval Research Laboratory, Washington, DC 20375, USA

J. D. Silver
Clarendon Laboratory, University of Oxford, Parks Road, Oxford OX1 3PU, United Kingdom

D. D. Dietrich
Lawrence Livermore National Laboratory, Livermore, California 94550, USA

P. H. Mokler
Max-Planck-Institut fur Kernphysik, D-69117 Heidelberg, Germany
and Gesellshaft für Schwerionenforschung (GSI), D-6100 Darmstadt, Germany

E. C. Finch
Department of Pure and Applied Physics, Trinity College, Dublin, Ireland

S. D. Rosner
University of Western Ontario, London, Ontario, Canada N6H 3K7
(Received 30 March 2009; published 14 August 2009)

Using x-ray diffraction and beam-foil spectroscopy, we have determined precise wavelengths for Lyman α_1 and Lyman α_2 in hydrogenic germanium of $1.166\,993\,8 \pm 33 \pm 169$ and $1.172\,433\,6 \pm 39 \pm 170$ Å. Hydrogenic germanium Ge^{31+} $1s$-$2p_{3/2}$ and $1s$-$2p_{1/2}$ Lamb shifts are measured to be $66\,080 \pm 237 \pm 1121$ and $67\,169 \pm 281 \pm 1237$ cm^{-1}, respectively. This 14 ppm measurement of the wavelengths thus provides a 1.8% measurement of the $2p$-$1s$ Lamb shift and is an improvement by a factor of 3 over previous work. Fitting the full two-dimensional dispersion relation, including Balmer and Lyman series, limits random and systematic correlation of parameters. Dominant systematics are due to diffraction parameters including crystal thickness and alignment, differential Doppler shifts due to the variable location of spectral emission downstream of the beam-foil target, and dielectronic, $2s$-$1s$, and $4f$-$2p$ satellites. Models developed are applicable to all relativistic plasma modeling in beam-foil spectroscopy at accelerators. The technique also reports the germanium $2p_{3/2}$-$2p_{1/2}$ fine structure as $397\,617 \pm 251 \pm 512$ cm^{-1}, representing a 0.14% measurement of the fine structure and a 71% measurement of the QED contribution to the hydrogenic germanium fine structure, an improvement of a factor of 6 over previous work. We also report a precise measurement of heliumlike resonances and fine structure.

DOI: 10.1103/PhysRevA.80.022508 PACS number(s): 31.30.jf, 12.20.Fv, 34.80.Dp, 32.30.Rj

I. INTRODUCTION AND OVERVIEW

The use of beam-foil spectroscopy for the production of highly charged ions is well known [1–3]. In particular, the production of one- and two-electron species by this method permits a precise test of QED [4–8]. Theoretical evaluation of the hydrogenic and heliumlike energy levels enables derivation of the Lamb shifts.

Impressive precision of low-Z measurements has led to investigations of nuclear form factors and polarization, which involve interesting physics in their own right [8,9]. Meanwhile, medium-Z techniques have been developed over the last two decades, with a view to probing QED in the regime of high effective coupling strength [10–12]. Motivation arises from the increasing significance of higher-order QED terms, together with the $(Z\alpha)^4$ dependence of the lowest order QED contributions, depending on the formalism used for the theoretical expansions [13,14]. The dependence upon $Z\alpha$ indicates another strong motivation for these investigations, namely, that as $Z\alpha$ approaches unity for high-Z elements, the convergence of higher-order terms may fail, and additional interactions may in principle be observed.

However, rate processes and relative intensities inside and outside the foil have not received the same attention. With sufficient precision, these may be used to deduce dominant interactions within the foil. This corresponds to a dominant uncertainty in beam-foil measurements because of differential source and cascade locations and hence differential Doppler shifts, as we discuss. The effect on absolute and relative x-ray emission intensities as a function of target thickness is compared to model predictions. The observation of one- and two-electron spectra as a function of foil thickness allows

*chantler@unimelb.edu.au

Theoretical Determination of Characteristic X-Ray Lines and the Copper $K\alpha$ Spectrum

C. T. Chantler* and A. C. L. Hayward
School of Physics, University of Melbourne, Melbourne, Australia

I. P. Grant
Mathematical Institute, Oxford University, Oxford, United Kingdom
(Received 9 May 2009; published 16 September 2009)

Core excitations above the K edge result in $K\alpha$ characteristic x-ray emission. Understanding these spectra is crucial for high accuracies in investigations into QED, near-edge x-ray structure and advanced crystallography. We address unresolved quantitative discrepancies between experiment and theory for copper. These discrepancies arise from an incomplete treatment of electronic interactions. By finding solutions to relativistic multiconfigurational Dirac-Fock equations accounting for correlation and exchange corrections, we obtain an accurate reproduction of the peak energies, excellent agreement of theory with experiment for the line shapes, good convergence between gauges, and account for the $K\alpha$ doublet ratio of 0.522 ± 0.003:1.

DOI: 10.1103/PhysRevLett.103.123002 PACS numbers: 32.30.Rj, 31.30.jf, 32.80.Hd

Spectroscopic lines resulting from atomic transitions gave the first insights into atomic structure and quantum mechanics [1]. Today, the most well tested theory in nature [2–4], quantum electrodynamics (QED), is probed using the same techniques. The $K\alpha$ spectrum, a designation from the early days of quantum mechanics, denotes the transition $2p \rightarrow 1s$. For heavier atoms, the fine splitting between the $2p$ states results in distinct peaks for the $2p_{1/2} \rightarrow 1s$ ($K\alpha_2$) and $2p_{3/2} \rightarrow 1s$ ($K\alpha_1$) transitions.

These diagram lines (Fig. 1) are the standard candles of x-ray spectroscopy. Wavelength-dispersive experiments, the cornerstone of high accuracies for most of the x-ray regime, are almost exclusively defined by angles, which must be calibrated to these peaks [5]. Alignment of experimental data with physical parameters requires positions and intensities of multiple peaks. Experiments usually have numerous systematics to account for, such as nonlinear scaling, diffraction and slit broadening, and the constraint of key parameters yields more critical and definitive results [6,7].

Elementary statistical arguments suggest that the $K\alpha_2$:$K\alpha_1$ integrated intensity ratio should be 0.5:1; in reality this ratio increases slowly with atomic number Z [8–11]. The simplest correct explanation is that the rate of deexcitation of the $1s$ hole by capture of a $2p_{1/2}$ electron is greater than that for capture of a $2p_{3/2}$ electron. Hence by virtue of the faster decay rate, the linewidth of $K\alpha_2$ is greater than that of $K\alpha_1$ [12,13]. The increase of the intensity ratio with Z is supported by nonrelativistic Hartree-Fock calculations [14] especially when shell coupling is taken into account.

Relativistic effects become more pronounced as Z increases in the transition metal region of the periodic table [15] and fully relativistic theory should be used. Indicators include the growth of intermediate coupling as Z increases and the need to introduce energy offsets and dispersion scales [15–17] when trying to reconcile theory and experiment. Most earlier work modeled this by fitting spin-orbit parameters to experimental splittings of diagram lines [15,17]. Other studies indicated the need for relaxation and rearrangement of the atom prior to emission [15,18]. The outermost $4s$ has usually been ignored [17,19–22].

The complex structure of $K\alpha$ lines, which are not a simple sharp doublet, has been the source of much speculation: explanations invoke both atomic and solid state mechanisms [14,17]. Generally, the observed spectrum has been fitted to a sum of line profiles whose individual positions and strengths are determined solely by the fitting process without recourse to *ab initio* models. Explanations range from Kondo-like interaction of conduction electrons with core-hole states [23], final-state interactions between the core hole and the d shell [24], electrostatic interactions of the $3d$ and $2p$ shells [25] to $3l$ shake-up processes [13,19]. The first and last of these explanations have yielded good fits to particular subsets of data.

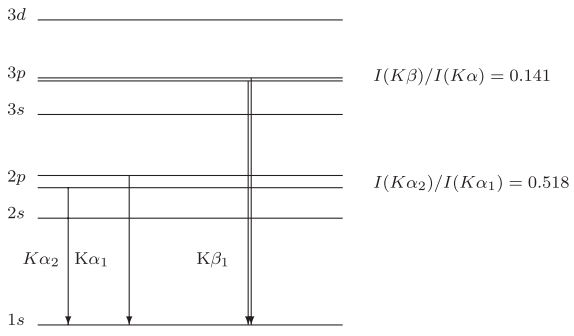


FIG. 1. Dominant radiative transitions between subshells. A statistical population would predict 0.5:1 for $K\alpha_2/K\alpha_1$, and 1:6 for $K\beta/K\alpha$. Quoted experimental ratios from [8].

Physics Letters A 373 (2009) 1177–1180

Contents lists available at ScienceDirect

Physics Letters A

www.elsevier.com/locate/pla

Nano-roughness in gold revealed from X-ray signature

J.L. Glover [a], C.T. Chantler [a,*], Martin D. de Jonge [b]

[a] School of Physics, University of Melbourne, Australia
[b] Australian Synchrotron, Clayton, Victoria, 3168, Australia

ARTICLE INFO

Article history:
Received 21 January 2009
Accepted 22 January 2009
Available online 31 January 2009
Communicated by V.M. Agranovich

PACS:
78.70.Dm
32.80.Aa
47.54.Jk
68.35.bd
68.35.Ct

Keywords:
Roughness
Materials characterisation
Synchrotron radiation

ABSTRACT

We present a new method for investigating roughness for surface structure and internal inhomogeneity down to the nano-scale for thin, nano-structured and opaque materials. The method uses careful measurements of the X-ray mass-attenuation coefficient and is applied to measure the magnitude of the roughness of gold foils. The technique is unique, providing insight into both surface and internal roughness. We show that moments of the distribution function of surface and internal structure can be investigated using this method, and discuss observable signatures. The approach is non-destructive and very sensitive as a local in situ measurement and as a diagnostic for accurate characterisation.

1. Introduction

We report a new technique for investigating roughness from the mm to nm scale. This non-destructive technique determines the roughness of a sample by careful measurement of the X-ray mass-attenuation coefficient. The technique provides insight into both surface and internal roughness. It can be applied to a wide class of samples and can be useful in nano-fabrication, surface-science, high-precision optics and in many other areas requiring non-destructive characterisation of internal or surface roughness.

The roughness of a sample can be divided into two components: surface roughness and internal inhomogeneity. Surface roughness is a measure of the small-scale variability in surface height across a sample and is widely studied using numerous existing techniques including stylus [1] and optical profilometry [2], atomic force microscopy (AFM) and scanning tunnelling microscopy (STM) [1,3], transmission electron microscopy (TEM) and scanning electron microscopy (SEM) [4,5] and X-ray reflection [6].

Internal inhomogeneity (which will be referred to as internal roughness) is manifest in the density non-uniformities and voids within the bulk of the sample. X-rays are extremely penetrative and can interrogate the bulk of a sample, allowing the measurement of roughness not only at the surface but also within the bulk. Hence our technique can provide unique insight into internal roughness and open exciting new research opportunities, including studies of nano-structures in cement [7], energy conversion devices [8], and the effects of nano-scale roughness which lead to effects on stresses [9].

Our technique can be summarised as follows. Measurements of the X-ray mass-attenuation coefficient are made over a range of energies on the sample of unknown roughness that is being investigated. Measurements are also made on a set of thicker reference samples of low roughness. The attenuation of the unknown sample is compared to that of the reference samples and the difference is calculated. The magnitude of the roughness can then be determined based on the size and form of this difference.

2. Measuring mass-attenuation coefficients

The X-ray mass-attenuation coefficient $[\frac{\mu}{\rho}]$ quantifies the extent to which a material absorbs and scatters X-rays. In order to measure the mass-attenuation coefficient accurately, we use the X-ray extended range technique (XERT) [10–12], which can correct for a wide range of systematic errors including scattering [13], fluorescence [14], harmonics [15], bandwidth [16], and the attenuation of the ion-chambers and air-path. The XERT has produced the most accurate measurements of the mass-attenuation coefficient in the

* Corresponding author.
E-mail address: chantler@ph.unimelb.edu.au (C.T. Chantler).

0375-9601/$ – see front matter
doi:10.1016/j.physleta.2009.01.043