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Oliver Hoidn

# X-ray Spectroscopies of Warm Dense Matter

Oliver Hoidn

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Reading Committee:

Gerald Seidler, Chair

Marjorie Olmstead

John Rehr

Program Authorized to Offer Degree:  
Physics

University of Washington

## **Abstract**

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Oliver Hoidn

Chair of the Supervisory Committee:  
Professor Gerald Seidler  
Physics

This dissertation provides a perspective on the role of x-ray spectroscopy and diffraction diagnostics in experimental studies of warm dense matter (WDM). The primary focus of the work I discuss is the development of techniques to measure the structure and state variables of laboratory-generated WDM with a view towards both phenomenology and placing constraints on theoretical models. I present techniques adapted to two experimental venues for WDM studies: large-scale laser plasma facilities and x-ray free electron lasers. My focus is on the latter, in the context of which I have studied a dose enhancement technique that exploits nonlocal heat transport in nanostructured targets and considered several aspects of optimizing x-ray diffraction measurements. This work came into play in beam runs at the Linac Coherent Light Source (LCLS) in which my group performed x-ray diffraction studies of several materials heated to eV-scale temperatures. The results from these experiments include confirmation of the persistence of long-range crystalline order upon heating of metal oxides to tens of eV temperarures on the 40 fs timescale. One material, MgO, additionally manifested a surprising anomalous early onset in delocalization of valence charge density, contradicting predictions of all models based on either ground state electronic structure or (high-energy density) plasma physics. This particular result outlines a future path for studies of ordered insulators heated to temperatures on the order of the band gap. Such experiments will offer strong tests of electronic strucure theory, implementing a scientific approach that

sees measurement of real-space charge density via x-ray diffraction (XRD) as a particularly effective means to constrain density functional theory (DFT)-based modeling of the solid state/plasma transitional regime.

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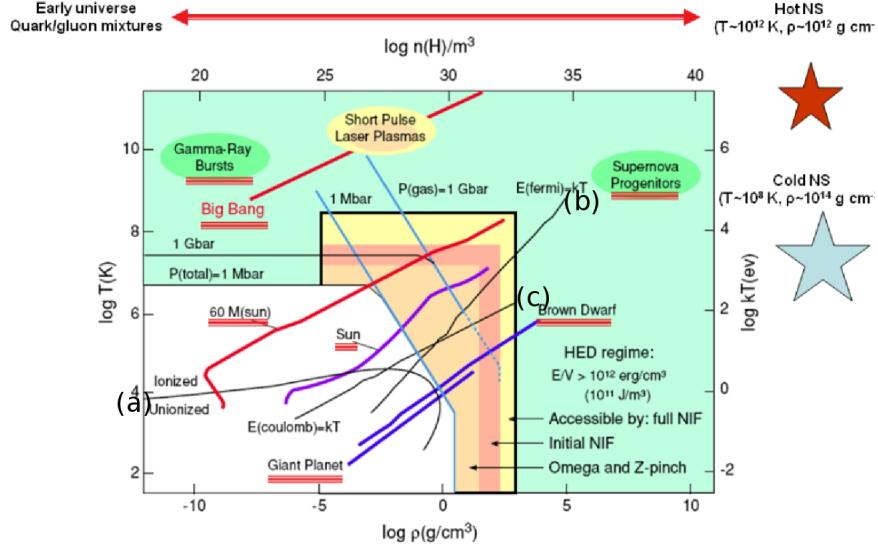
## Chapter 1

### INTRODUCTION

In this thesis I introduce the development of new techniques for the production of materials in the warm dense matter (WDM) regime, and for interrogation of the structure and thermodynamic state of such systems using x-ray diffraction and (to a lesser extent) spectroscopy. The main results include: a scheme for single-shot determination of the static structure factors of WDM systems generated at laser plasma facilities; a technique for enhancing the density of deposited energy in WDM generated at fourth-generation X-ray sources such as the Linac Coherent Light Source (LCLS); and interpretation of experimental data that puts new constraints on the thermalization (both electronic and lattice) of a solid state material upon fs-scale XFEL heating. In addition to this thread of research I discuss some secondary work on the development of software and electronics for energy- and position-sensitive pixel detectors including current applications in the context of soft x-ray laboratory and possible future ones in XFEL, synchrotron, and laser plasma facility-based experiments.

Before proceeding it is useful to define WDM in terms of the microphysical context it occupies. Fig. 1.1 presents a map of thermodynamic parameter space, with the logarithm of density and temperature on the horizontal and vertical axes, respectively. A few bounding curves can be identified. First, ionization occurs at temperatures exceeding approximately 1 eV; this is denoted by curve (a), which forms a boundary between the plasma and condensed matter regimes. Second, curve (b) indicates the boundary at which the Fermi energy is approximately equal to the average thermal energy  $k_B T$ ; i.e. where the electron degeneracy parameter,  $E_f/k_B T$  is of order unity. Third, curve (c) corresponds to a value of 1 for the ratio of the Coulomb energy to the thermal one, also called the plasma coupling parameter  $\Gamma = E_c/kT$ , where  $E_c$  is the Coulomb energy,  $k$  is Boltzmann's constant, and  $T$  is the electron

Figure 1.1: The atlas of high-energy density physics[1]



temperature.

A second dimensionless parameter according to which plasmas are commonly characterized is the plasma coupling parameter, given by  $\Lambda = 4\pi n \lambda_D$ , where  $n$  is electron density and  $\lambda_D$  is the Debye length (a characteristic screening length that we will introduce shortly).  $\Lambda \gg 1$  corresponds to the case of an ideal plasma, where a large number of electrons is included within one screening length and interactions can therefore be described collectively. Correspondingly, above curves (a), (b) and (c) of Fig. 1.1 is the regime of ideal plasma physics where, as a result of the weak interaction between neighboring ions ( $\Gamma \ll 1$ ), collective interactions predominate over binary collisions ( $\Lambda \ll 1$ ) and quantum statistics can be neglected except for the purpose of calculating blackbody spectra. In this regime continuous, classical modeling treatments are widely-used and fully validated [2]. Below curves (a), (b), and (c) is the low-temperature, intermediate-density realm of condensed matter physics, wherein the potential landscape is built on the interaction between electrons

and ion cores. In this framework finite-temperature effects are incorporated perturbatively. WDM occupies the transitional regime above curve (a) and near the intersection of curves (b) and (c), characterized by partial degeneracy and strong ion-ion coupling. As a result, treatments of plasma physics originating in the classical regime are not applicable to WDM. Solid state physics models similarly fail in the WDM regime due to large, non-perturbative effects of finite temperature on the structure and thermodynamics of WDM [3].

Modeling of the ionization potential depression (IPD) in a plasma is a case in point of the difficulties that manifest themselves with theoretical treatments of WDM. Adequate descriptions of IPD are given the Debye-Hueckel approximation and ion sphere model, which cover opposite regimes of high temperature and low density, and low density and high temperature, respectively. We here briefly introduce both models, with focus on the assumptions and approximations that they adopt.

The Debye-Hueckel model applies to a weakly-coupled plasma in local thermal equilibrium. It identifies the electrostatic potential in the Poisson equation with the mean field generated by a population of Maxwell-Boltzmann-distributed ions or electrolytes. This results in the Poisson-Boltzmann equation which, when solved, gives the electrostatic potential produced by an arbitrary charge distribution. The condition for validity of the Debye-Hueckel model is for the Thomas-Fermi screening length (also called the Debye length) to be much larger than the mean inter-ion separation. This condition is satisfied at comparable and higher temperatures, but lower densities, than those encompassed by the WDM regime. [4]

In the opposite limit, the ion-sphere model describes IPD in a high-density material with  $\Gamma > 1$  (in the low-temperature context IPD is more commonly referred to as pressure ionization). The picture offered by the ion-sphere model is that of a plasma with highly-correlated ion positions and therefore no close encounters between ion pairs. Each ion is treated as a sphere whose potential is unaffected by the presence of neighboring ions. [5] The sphere radius is  $R_0 = (3/4\pi N_i)^{1/3}$ , where  $N_i$  is ion number density, while the orbital radius of the ion sphere's  $n$ th principal energy level is approximately  $r_n = (n^2/Z_n)(0.529\text{\AA})$ . For the  $n$ th bound state to exist it is necessary that  $r_n \leq R_0$ ; thus, IPD manifests itself as a reduction

in the number of bound states as a function of the inter-ion distance  $R_0$ . It should be noted that, although the ion-sphere model is a frequently-used heuristic in high-temperature plasmas with near-ambient densities, it is known to be incorrect in the high-density, strongly-coupled ( $\Gamma \gg 1$ ) regime. Neaton et al. have done ab-initio (DFT) simulation of Li—a free electron-like material under ambient conditions—showing that, contrary to intuitive expectations and the ion-sphere model, it becomes less free-electron like at high densities and additionally loses its common bcc crystal structure. [6] Due to overlap of core electrons, the distortion of electronic wavefunctions in this regime is strongly nonperturbative—again in conflict with the ion-sphere model’s assumptions.

Leaving aside, momentarily, the ion sphere model’s limitations, we might contemplate constructing a model of ionization potential depression that reduces to the ion sphere and Debye-Hueckel models in their respective limits. Doing so is challenging because it allows none of the simplifying approximations invoked by the two limiting cases. One manifestation of the lack of consensus concerning the correct approach is the existence of two mutually-contradictory models for IPD in WDM, those of Stewart and Pyatt [5] and Ecker and Kroll. [7] Though the Stewart-Pyatt model is more widely used and has the virtue of reproducing the ion-sphere and Debye-Hueckel behaviors, its validity has been called into question by recent direct XFEL-measurements of IPD in Al heated to 180 eV. [8, 9] Such conflicts exemplify the persistent difficulty of constructing models with validity across different sub-regimes of WDM.

Recent technological progress offers the prospect of an exit from this apparent impasse. Via femtosecond-scale pump-probe experiments, X-ray free electron lasers have the ability to produce well-controlled states of known density and temperature on a timescale where lattice motion may be neglected. Compared to all other formerly-accessible experimental regimes, these highly-constrained systems are much more tractable through *ab initio* theoretical approaches. Vinko et al.’s successful finite-temperature density functional theory (DFT) modeling of the IPD in a variety of experimental systems is an encouraging early fruit of this development. [10]

## 1.1 Motivations for study of WDM

In addition to the basic physics questions intrinsic to the WDM regime, there are a number of points of contact between WDM and particular problems in other fields. This interaction has been bolstered in recent years by rapid development of laser plasma facilities and x-ray free electron lasers (XFELs) with unprecedented experimental capability for producing WDM and probing its physical properties. This has brought many previously-intractable physical regimes into the scope of both empirical investigation and numerical simulation.

### 1.1.1 Astrophysical modeling

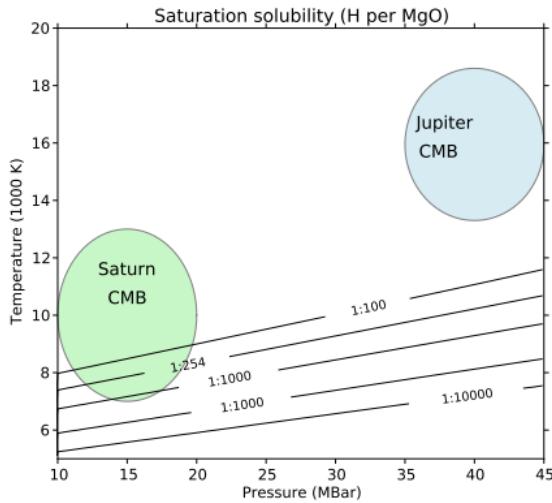
A large contribution to this growth in interest is the relevance of WDM theory as a microphysical basis on for models of various systems in planetary and stellar astrophysics. Here we introduce two examples in which this relationship is salient.

The interiors of both rocky and gas giant planets contain dense, and in some cases Fermi-degenerate, plasmas at 1 eV-scale temperatures. Examples include the iron under conditions of the earth's core (pressure = 3 Mbar; T = 6000 K), whose viscosity and equation of state (EOS) has consequences on convective heat transfer and the formation of earth's magnetic field. [11] Similarly, modeling of the evolution and structure of gas giant planets depends on the EOS of H under the regime of gas giant interiors. The existence of metallic H caused by pressure ionization at Mbar-scale pressures has been predicted [12], but the mechanism for its onset is poorly understood at the level of theoretical models for the EOS: although a first-order dielectric-to-metal phase transition has been postulated, current approaches do not attempt to model pressure ionization, instead limiting themselves to interpolation between the better-understood atomic and fully ionized limits. [13]

The solubility physics of binary WDM mixtures combining H with species found in rocky planetary bodies has direct consequences on mass transport across the core-mantle boundary in gas giant planets. It also has crucial importance in the modeling of gas giant formation, where the solubility of H with rocky elements bears on the plausibility of the planetesimal

accretion hypothesis for gas giant genesis, which requires condensation of H and He around a rocky core. [14]

Figure 1.2: Saturation solubility of MgO in H as a function of pressure and temperature from *ab initio* calculation by Wilson et al. The temperature conditions of the core-mantle boundaries of Saturn and Jupiter are indicated. [14]

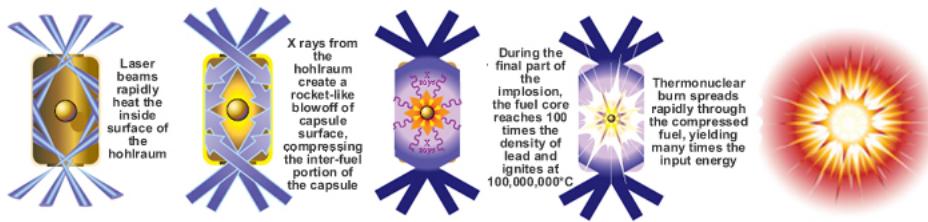


Another case in which the material properties of warm dense matter determine the behavior of an astrophysical object is that of white dwarfs, whose envelopes consist of a hot, partially Fermi-degenerate plasma. Modeling the cooling of white dwarfs is a topic of interest, especially in the context of the importance of type 1a supernovae as ‘standard candles’ for measuring distances to distant galaxies. [15] Doing so, however, requires knowledge of stellar envelope opacities, equations of state (EOS), and transport properties, many of which properties are currently unknown to within factors of order unity. The absence of understanding of the simplest available system—the hydrogenic one-component plasma—underscores the difficulty of this thread of research.

### 1.1.2 Inertial Confinement Fusion

The effort to reach controlled fusion through implosion of deuterium-tritium fuel capsules—an approach termed inertial confinement fusion—has progressed significantly in the last decade due to completion of laboratory facilities capable of producing high-energy density (HED) plasmas with densities and temperatures approaching levels needed for ignition. Fig. 1.3 shows a schematic of an ignition technique called indirect drive. In this configuration the ICF target, which consists of a hollow spherical capsule of ablator material filled with deuterium-tritium fuel, is confined in a hollow capsule of a high-Z material (the Hohlraum). A multi-TW, ns-duration duration laser passes through apertures in the Hohlraum and heats the Hohlraum to blackbody temperatures on the order of several hundred eV. [16] The resulting thermal spectrum of soft X rays isotropically heats and ablates the fuel capsule's surface, causing its interior to implode by conservation of momentum. Typical parameters of the plasma created at maximum compression include areal densities (capsule density  $\times$  radius) of 0.3 g/cm<sup>2</sup> and temperatures of the order 10 keV. [1, 17]

Figure 1.3: Schematic of indirect-drive inertial confinement fusion shot. [18]



Although its end state falls well within the regime of a classical plasma, the fuel capsule transitions through the WDM state during compression. The opacity and EOS of warm dense matter therefore has a strong influence on the development and propagation of shocks during ablation of the fuel capsule, which in turn affects the optimization of various experimental parameters, including fuel capsule geometry and temporal profile of the laser driver. Accurate modeling of the fuel capsule's transport properties under the WDM regime

is equally important for understanding the development during compression of hydrodynamic instabilities, which are known to be a major obstacle to the efficient coupling of laser energy into fuel compression. [19]

## **1.2 Experimental Generation of WDM**

WDM conditions may be generated using X-ray free electron lasers (XFELs) and several varieties of lasers, found both in large-scale facilities and laboratory-scale systems. Here we provide an overview of existing technologies.

### *1.2.1 Long-pulse lasers*

Lasers with pulse durations on the order of nanoseconds and energies of 1 kJ or more are among the most versatile tools for producing high energy density states, including warm dense matter. In the most common use cases of long pulse lasers the target is a bulk material, and coupling of laser energy into it occurs in two stages. First, the laser rapidly generates a coronal plasma at the material's surface. Once the electron density of this plasma exceeds the laser wavelength's critical density the laser becomes electromagnetically shielded from the material's interior and can no longer transfer energy to it. In the context of direct drive (where the material is a target to which laser energy is directly coupled), subsequent energy transfer occurs by thermal conduction of energy from the surface plasma to higher-density regions as well as by compression of the target resulting from ablation of its surface. In the case of indirect drive, the laser's energy is used to heat a surface (typically the interior of a Hohlraum) that provides a thermal bath which, in turn, couples to the target via its blackbody radiation.

The ns duration of long-pulse lasers matches the timescale on which mechanical and hydrodynamic processes occur on typical target scales. Long-pulse lasers are thus suited to generating ramp and shock compression, notably including for the application of ICF. The largest-scale laser plasma facilities—Omega EP at the Laboratory for Laser Energetics in Rochester, NY and the National Ignition Facility—are long-pulse laser systems targeted

toward the ICF program.

### 1.2.2 Short-pulse lasers

Short pulse lasers are a second class of systems used to generate HED conditions. They are typically defined by pulse durations on the order of a picosecond or less, down to as little as  $\sim 1$  fs. Short-pulse laser systems arose after the development of chirped pulse amplification in the 1980s and have proliferated ever since, especially with the recent advent of compact (university laboratory-scale) versions with tens of Joules of pulse energy, sufficient to generate scientifically interesting HED conditions. [20, 21] The largest-scale short pulse lasers have pulse powers up to 100 TW, with durations on the order of 10 to 100 fs.

Due to the smaller total energies of short-pulse lasers and the relatively slow cooling timescale of materials heated above ambient conditions *regardless* of the pump duration, short-pulse lasers are used to generate HED conditions under direct-drive configurations alone. Energy is coupled into a target indirectly (as is the case with long-pulse systems) via ‘hot’ MeV-scale electrons generated in the laser’s interaction with plasma at the target surface. In the (typical) case where bulk heating is required, the target thickness is small compared to the hot electrons’ stopping range, causing them to reflux through the target once it acquires net positive charge. This process lasts on the order of one ps and thus sets the time resolution of experiments in which the short-pulse laser is used to both heat and probe the target. [22]

### 1.2.3 X-Ray Free Electron Lasers

The advent of X-ray free electron lasers (XFELs) is a major advance in capability for WDM research. Existing incarnations of these sources, notably the Linac Coherent Light Source (LCLS), provide  $10^{14}$  photons in tunable monochromatic pulses with durations of 10 fs or greater. While the energies per pulse are smaller than those attainable with a short-pulse laser, they are largely sufficient to produce HED states with temperatures in excess of 100 eV. [23] Because XFELs can heat volumetrically, they are free of the primary deficiency of

lasers with respect to the task of generating dense plasmas: namely, the latter can only heat bulk materials indirectly and over durations of 1 ps or longer, which exceeds the timescale for changes in WDM, preventing the study of short-lived transient states.

The ability to generate (and probe) WDM on truly inertial timescales, wherein atomic nuclei are effectively frozen, has been duly exploited in early pioneering studies at the LCLS. It forms the basis, for example, for a new thread of materials science research on nonthermal lattice and spin dynamics. [24, 25] Likely even more significantly, it is the enabling feature for macromolecular crystallography under the ‘diffract before destroy’ paradigm. The possibilities surrounding rapid generation of WDM is a topic to which I return in chapters 3 and 6. [23]

### **1.3 X-ray diagnostics of WDM**

Experimental studies of WDM suffer from a substantial complication: the opacity of WDM to photons is large at energies up to the soft x ray regime. As mentioned in section 1.2.2, in the context of laser heating this is merely a frustration; for the purposes of measuring the conditions of a bulk WDM system, however, the need for direct detection of radiation originating from the target’s interior makes optical probes wholly ineffective. Determination of the structure and thermodynamic state variables of a dense plasma therefore requires sufficiently penetrating radiation; for this reason, the large majority of WDM diagnostics are x ray photon-in photon-out measurements. [26]

In the remainder of this section I provide an overview of the various available techniques.

#### *1.3.1 Scattering*

Elastic scattering and nonresonant inelastic X-ray scattering (NIXS) are among the most-frequently probed signals for inferring the structure, temperature and ionization state of WDM. In dense plasmas generated by long-pulse lasers, where LTE is commonly assumed, NIXS also serves as a probe of temperature.

For a given sample, the sum of scattering interactions is characterized by the double-differential scattering cross section (DDCS)  $d^2\sigma/d\Omega d\omega$ , which describes the probability of a photon to scatter into a solid angle increment  $d\Omega$  within an energy loss interval  $d\omega$ . Within the independent-electron and first Born approximations the DDCS is given by

$$\frac{d^2\sigma}{d\Omega d\omega} = r_0^2 \left(\frac{\omega_2}{\omega_1}\right) |\vec{\epsilon}_1 \cdot \vec{\epsilon}_2^*|^2 S(\vec{q}, \omega), \quad (1.1)$$

where

$$S(\vec{q}, \omega) \equiv \sum_F \sum_j \langle F | \exp(i\vec{q} \cdot \vec{r}_j) | I \rangle|^2 \delta(E_F - E_I - \hbar\omega). \quad (1.2)$$

The first term in equation 1.1 is the Thomson cross section, which describes the interaction between a probe photon and a single electron;  $S(\vec{q}, \omega)$  is referred to as the dynamic structure factor, and encapsulates all system-specific properties.  $I$  and  $F$  are initial and final states of the sample with energies  $E_I$  and  $E_F$ , respectively, and the second summation in 1.2 is over electrons in the scatterer.

Following Chihara [27], the typical treatment of a dense plasma separates the dynamic structure factor into several components:

$$S(\vec{q}, \omega) = |f_I(q) + f_e(q)|^2 S_{ii}(q, \omega) + S_{ff}(q, \omega) + S_{bf}(q, \omega), \quad (1.3)$$

$S_{ii}$  is the atomic/ionic structure factor,  $f_I$  and  $f_e$  are the form factors for the ion and a surrounding cloud of screening charge. [27]  $S_{ff}$  contains scattering from free, delocalized electrons, and  $S_{bf}$  represents Raman-type bound-free transitions resulting from scattering from tightly-bound core level electrons. Note that spherical symmetry has been assumed: all terms of the structure factor depend only on the magnitude of  $\vec{q}$ .

The first term corresponds to elastic ( $\omega = 0$ ) scattering, and is connected to the dense plasma's pair distribution function by a Fourier transform. Though not a component of the NIXS signal, it must often be considered in simulations and analyses of NIXS data, wherein

the Bethe sum rule and other conserved quantities consist of integrals over the entire energy-loss domain of the dynamic structure factor. [28] Elastic scattering is a highly-useful probe of structure; we consider it separately in section 1.3.1.

The free-free contribution to  $S(q, \omega)$  can be expressed in terms of the free-electron dielectric function  $\epsilon(q, \omega)$  via the fluctuation-dissipation theorem.[29]

$$S(q, \omega) = \frac{\epsilon_0 \hbar q^2}{\pi e^2 n_e} \frac{1}{1 - e^{\hbar \omega / k_B T_e}} \text{Im}\left(\frac{1}{\epsilon(q, \omega)}\right), \quad (1.4)$$

The random phase approximation (RPA) is typically used as an approximation for  $\epsilon(q, \omega)$ , but more recent treatments incorporate a perturbative treatment of electron-ion interactions using the Born-Mermin Approximation. [30, 31] The scattering contribution of  $S_{ff}$  consists of a pair of plasmon peaks with opposite, equal-magnitude energy offsets from the elastic scattering peak. Electron density is inferred from the magnitude of the Plasmon peak shifts while temperature is obtained from the ratio of intensities of the two peaks, following the principle of detailed balance. [32, 33]

Although the connection of temperature and density to the free-free component of the dielectric function is well-founded, there are two obstacles to effective interpretation of collective scattering data from WDM systems; one is theoretical and the other experimental. First, the validity of established treatments of the dielectric function has been called into question, with recent plasmon spectrum calculations based on MD-DFT simulations showing a significant change in the plasmon profile compared to that predicted by the Born-Mermin Approximation. [34, 35] Second, the plasmon peak suffers from poor signal to background and has a small separation from the elastic scattering peak under typical WDM electron densities, making it difficult to resolve. As a result only a handful of experiments to date have pursued this technique.

We finally turn our attention to the last term of 1.2,  $S_{bf}$ , whose contribution to the inelastic DDCS is often referred to as x-ray Thomson scattering (XRTS). Obtaining state variable information from a system's bound-free scattering contribution is dependent on the underlying model of electronic structure used; as a result, various treatments exist,

including the Impulse Approximation (IA) of Eisenberger and Platzman, wherein the bound-free contribution to XRTS is equivalent to Doppler-broadened Compton scattering; the plane wave form factor approximation (PWFFA) of Schumacher, which attempts to extend the IA by incorporating electron binding energies; and calculation of matrix elements using a real space Green's function (RSGF) formalism applied to atomic clusters, as implemented in the atomic spectroscopy code FEFF. [36, 37]

In current practice, measurement of the bound-free component of XRTS from WDM is performed in the large- $q$  regime, where the Compton feature is broad and can be measured using high-efficiency (but low-resolution) HOPG-based spectrometers. [33] As such, single-particle bound-free scattering is more readily measured than collective excitation features. Since an early demonstration of the technique by Glenzer et al. it has been frequently implemented at both laser plasma and XFEL facilities.[38] Despite some fruitful outcomes, the large statistical uncertainties in XRTS spectra—particularly at laser plasma facilities, where single-shot measurements are photon-starved—make the inference of state variables difficult, and dependent on one’s choice of electronic structure model. [3] Mattern et al. have demonstrated this concretely by comparing theoretical fits to XRTS data of shock-compressed Be, and argue that the lack of rigorous validation of electronic structure models for WDM models strongly undermines their validity for first-principles measurement of state variables. [37]

### 1.3.2 Coherent Scattering

Coherent scattering is the zero-energy loss component of the double differential cross section. The inference of structural information from coherent scattering varies by material; two primary cases present themselves.

First, for amorphous materials, such as hot dense plasmas generated by ramp- or shock-compression and lacking long-range order, the scattering amplitude is isotropic and is characterized by the one-dimensional static structure factor, which is connected by a Fourier transform to the material’s pair correlation function. Inference of the full pair correlation

function is in practice frustrated by the difficulty of inverting a limited momentum transfer range-sampling of the structure factor, but even in the most information-limited scenarios a density can nevertheless be recovered from the structure factor's first correlation peak. Although coherent scattering measurements from dense plasmas have been demonstrated in the context of long-pulse laser compression experiments, implementation difficulties unique to that environment prevent its adoption as a routine technique. We address these difficulties, and proposed solutions, in chapter 3. [39]

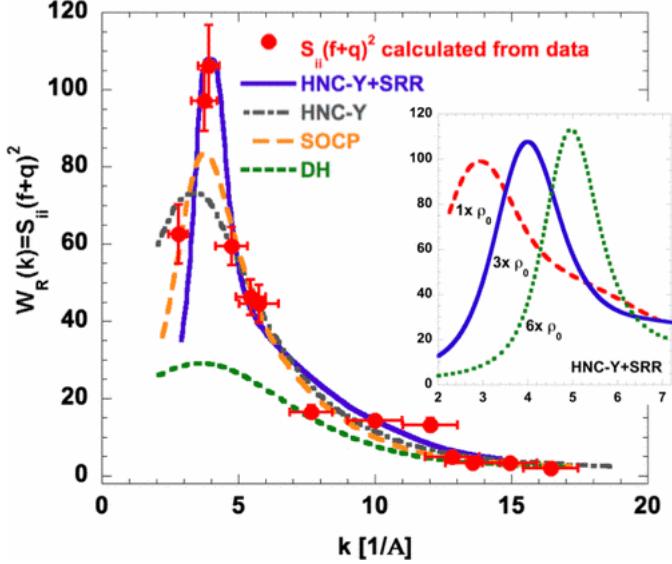
Second, in materials with long-range crystalline order, as typically found in XFEL-based experiments (whose timescales are shorter than the thermalization rate of electronic and ionic degrees of freedom), the coherent scattering amplitude is given by

$$F(\vec{q}) = \sum e^{i\vec{q}\cdot\vec{R}_n} \sum f_j(\vec{q}) e^{i\vec{q}\cdot\vec{r}_j}, \quad (1.5)$$

where the first summation is over all lattice vectors  $\vec{R}_n$  and the second, referred to as the *unit cell structure factor*, is over positions  $\vec{r}_j$  of atoms within the unit cell. By the convolution theorem, the crystal's scattering amplitude in reciprocal space is equal to the product of the lattice and unit cell structure factor. The coherent scattering signal is therefore a discrete sampling of the unit cell structure factor at individual Bragg peaks with momentum transfers corresponding to vectors of the reciprocal lattice.

In the context of XRD from a material undergoing thermalization under fs XFEL heating, the crystal scattering amplitude's decomposition into lattice and unit cell components has a direct correspondence to interpretation of structural change. The onset of long-range lattice disorder is readily identifiable as a quenching in Bragg peaks roughly proportional to  $e^{-q^2}$ . Evolution of the unit cell structure factor, on the other hand, is dependent on the details of atomic level populations and the material's finite-temperature electronic structure, and can be used as a test of competing theoretical models of both.

Figure 1.4: Experimental elastic scattering intensity of shock-compressed Al at OMEGA-60, compared to several hypernetted chain (HNC), Debye-Hueckel (DH), and screened one-component plasma (SOCP) models. [39]

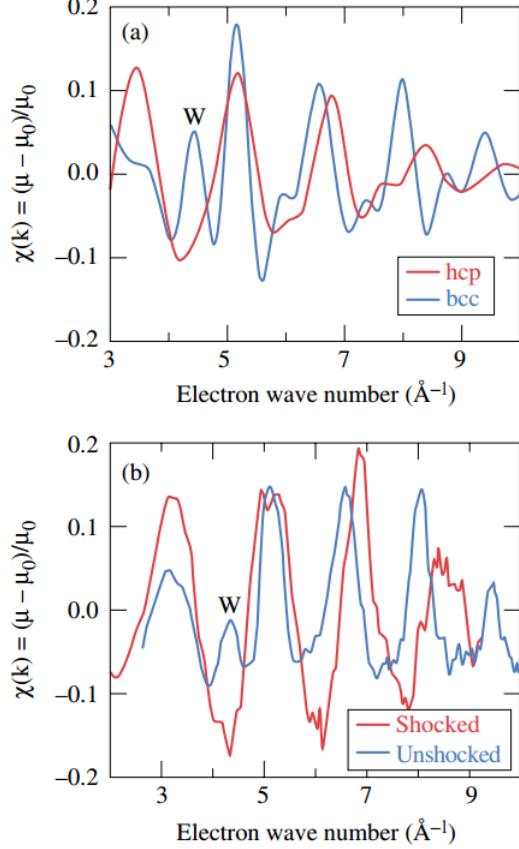


### 1.3.3 X-ray absorption

X-ray absorption spectroscopy (XAS) may be used to measure the structure and unoccupied electronic density of states of WDM systems. The information available by X-ray absorption near-edge spectroscopy (XANES) and X-ray absorption fine structure (XAFS) is the same as in other scientific contexts, but the experimental implementation differs in a few respects. In all instances, the short duration of WDM states requires instantaneous collection of absorption spectra using a source with broad-band spectrum. At laser plasma facilities this is arranged using a spherical capsule of CH polymer imploded using a long-pulse laser that emits a thermal spectrum with a  $\sim 1$  MeV temperature (check this).[40] This so-called broadband backlighter has been used to collect XAFS for the study of compression-induced phase transitions, such as that from bcc to hcp Fe driven by ns shock-compression.[41]

XANES measurements on dense plasma have also been performed at laser plasma facilities. This requires narrower-band illumination compared with XAFS, which has been

Figure 1.5: (a) FEFF calculation of XAFS for hcp and bcc phases of Fe, compared to (b) experimental data taken on ambient and shock-compressed Fe at the OMEGA laser. [41]

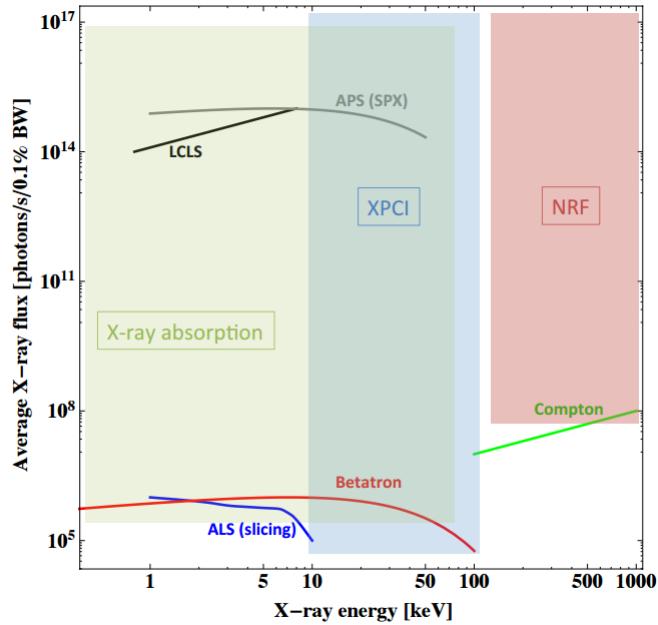


achieved using short pulse laser-driven multicomponent X-ray fluorescence backscatterers. Levy et al., for example, have used this technique to demonstrate XANES-based thermometry based on measurement of the K-edge slope in Al isochorically heated to 3 eV. [42]

Laser wakefield accelerator X-ray sources generate fs-duration broadband X-ray emission, affording time resolution that surpasses what is possible with laser-driven backscatterers. This makes wakefield accelerators especially well-suited to X-ray absorption spectroscopy of WDM generated at XFEL facilities.[43] The combination of wakefield accelerators with XFELs promises the unprecedented possibility of XFEL pump-probe experiments with simultaneous fs-duration interrogation of the target using broad- and narrow-band hard X-rays.

This combination also enables XAS measurements of low-Z materials, which is much more challenging at laser plasma facilities as a result of the mismatch between the short penetration lengths of x-rays near the K-edges of low-Z species and the relatively large target thicknesses (tens of microns) needed for effective laser ablation.

Figure 1.6: Parameter spaces of several x-ray techniques (X-ray phase contrast imaging (XPCI), x-ray absorption, and nuclear resonance fluorescence (NRF)), overlaid with curves indicating the regions of parameter space accessible by various x-ray source technologies and individual facilities.[43]

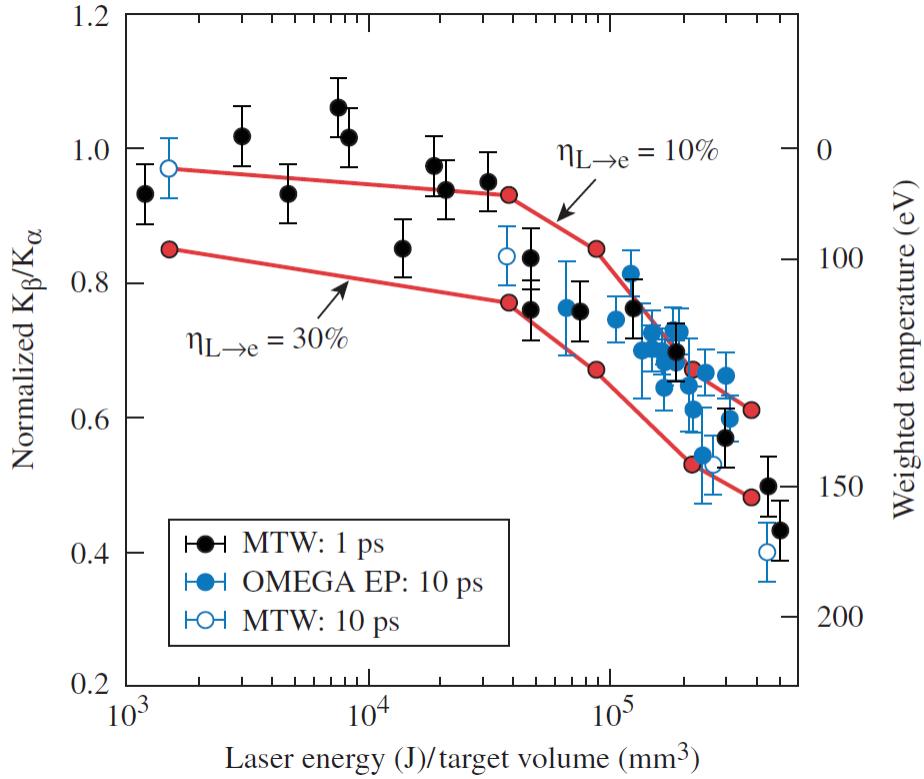


### 1.3.4 X-ray Emission and X-ray Fluorescence

X-ray fluorescence spectroscopy (XRF) is an extensively used probe in experiments studying the interaction of high-intensity lasers with solid targets. In short-pulse laser experiments involving mid-Z elements heated to temperatures comparable to or larger than M-shell binding energies the ratio of  $K_\beta$  to  $K_\alpha$  emission is used as a measurement of temperature. Modeling the coupling efficiency between high-power laser and electrons in a solid-density target is

of considerable significance to the effort to understand optical radiation-matter interactions at high laser intensities ( $> 10^{19} \text{ W/cm}^2$ ); in this context, inference of target heating using  $K_\beta/K_\alpha$  branching ratios provides a useful consistency check in the application of models to experimental data.[22, 44]

Figure 1.7: Experimental  $K_\alpha/K_\beta$  ratios of emission from Cu foil heated by short-pulse lasers, with inferred electron temperature on the right vertical axis. Model calculations are heating for hot electron coupling efficiencies  $\eta_e$  equal to 10% and 30% [22]



X-ray emission spectroscopy (XES), the finer-grained cousin of XRF, provides more detailed information on the occupied density of states in a material and can be sensitive to valence-level excitations in the ‘tepid’ transitional regime between ambient and warm dense matter states. [45] It has seen use primarily at XFEL facilities, where higher shot rates and probe intensities make the collection of datasets with satisfactory statistical quality eas-

ier.[46] The advent of XFELs as the first high-intensity, monochromatic, and tunable WDM probes has also enabled resonant inelastic X-ray scattering (RIXS) measurements, which has made possible the direct measurement of ionization potential depression on a fs timescale, as demonstrated by Vinko et al.[8, 23]

#### **1.4 *Dissertation Outline***

The overarching theme in this thesis is the relationship, and frequent feedback, between scientific discovery and the development of new experimental technique. To begin, in chapters 2 and 3 I introduce the application of the electron transport Monte Carlo code PENELOPE to modeling nonlocal transport of energy in x ray-illuminated nanostructured targets. This modeling validates a concept for nanostructured XFEL target design that I discuss in chapter 3. In Chapter 4 I introduce a scheme for single-shot measurement of the static structure factors of disordered dense plasmas produced at large-scale laser facilities such as Omega and NIF. In chapters 5 and 6 I discuss experimental results of a recent experiment at the LCLS in which we established bounds on the timescales for thermalization of the lattice in XFEL-heated metal oxides and measured the consequences of XFEL heating on electronic charge density, with subsequent comparisons to different model predictions. In chapters 7 and 8 I describe an instrument-development effort toward an inexpensive, but uniquely capable, CMOS-based X-ray camera for use in laboratory, synchrotron, and XFEL-based radiography and spectroscopy. Finally, in Chapter 9 I document UW-XAP, a software tool for streamlined realtime data collection and analysis at the LCLS.

## Chapter 2

### PHYSICS OF PENELOPE

This chapter serves as background material for Chapter 3, in which we present the use of the Monte Carlo Code PENELOPE for the simulation of electron transport in nanostructured XFEL targets. [47]

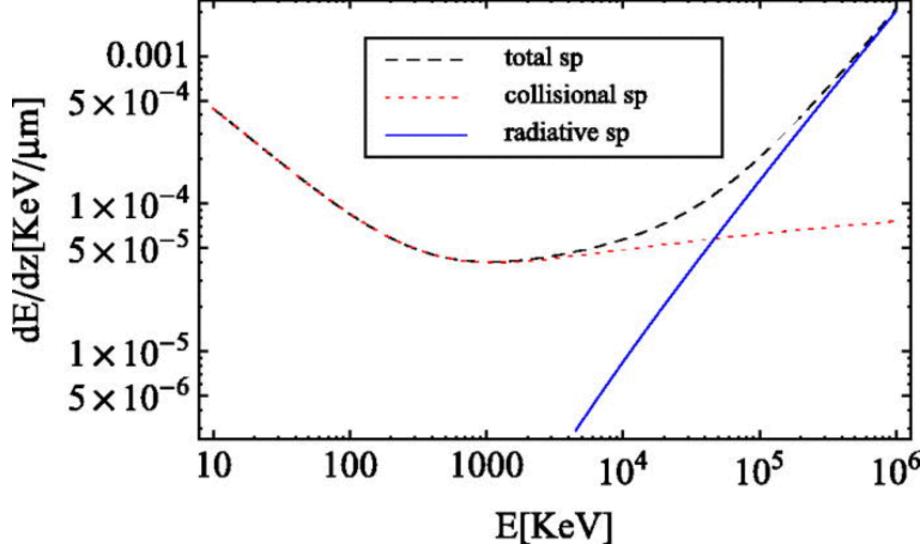
PENELOPE performs Monte Carlo simulations of coupled electron-photon transport in arbitrary materials in the energy range of 100 eV to 1 GeV. It uses a mixed simulation method that treats soft interactions (that is, those involving small angular deflections) with a multiple-scattering approach while individually simulating hard interactions. It is paired with a geometry-definition program, PENGEO, that allows defining samples with volumes of different material composition separated by arbitrary quartic surfaces. [48]

#### **2.1 Types of interactions**

In this section we consider the interactions that must be simulated to accurately model the spatial distribution of energy in a nanostructured target material heated by x-ray photons with energy on the order of 10 keV. PENELOPE simulates the following interactions: electron scattering (elastic and inelastic), Bremsstrahlung emission, photon scattering (both elastic (Rayleigh) and inelastic (Compton)), photoelectric absorption and Auger emission, x-ray fluorescence, and pair production and annihilation. Figs. 2.1 and 2.2 show the energy dependence of the relative strengths of the above electron and photon interactions, respectively. Several of the processes have negligible or nonexistent roles on the  $< 10$  keV energy scale considered in the current work, allowing us to limit our scope to the electron scattering and photoabsorption (with consequent fluorescence and Auger emission).

In what follows we introduce the physics of photoabsorption and elastic and inelastic scat-

Figure 2.1: Collisional and radiative electron stopping powers as a function of energy [49]

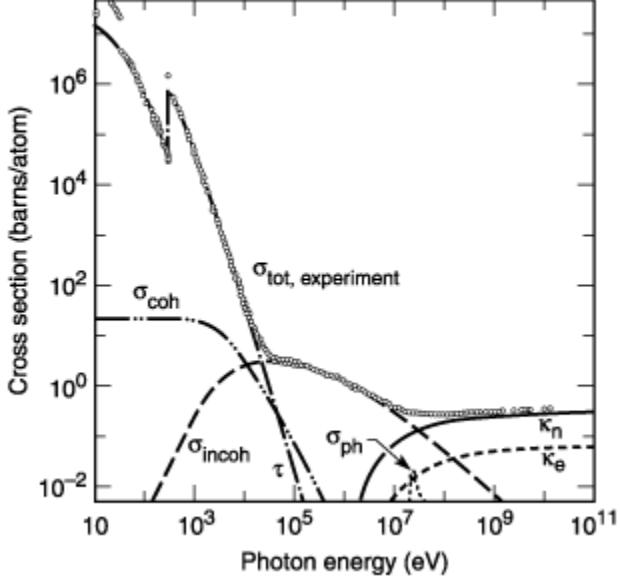


tering with attention to each process's contribution to the spatial distribution of deposited energy in a relaxation cascade beginning with photoionization by a hard x-ray photon. We discuss standard modeling approaches relevant to the 100 eV–10 keV regime, with a focus on the aspects of PENELOPE's treatments most relevant to our regime of interest.

### 2.1.1 Fluorescence

Fig 2.3 illustrates the photoionization of inner atomic shells and introduces the notation used to describe atomic energy levels and transitions between them. Both the photoelectric effect and secondary (Auger) emission resulting from high-energy atomic excitations can be accurately modeled using established treatments that combine theoretical calculation of atomic states via self-consistent modeling with experimental data.[51] Associated quantities are compiled in existing public databases; PENELOPE uses tabulated ionization energies from Carlson and photoelectric cross sections from the LLNL Evaluated Photon Data Library (EPDL). The EPDL additionally provides emission probabilities for fluorescence photons and Auger electrons in the relaxation of ionized atoms to the ground state.

Figure 2.2: Photon cross section components in C as a function of energy [50]



### 2.1.2 Assumptions

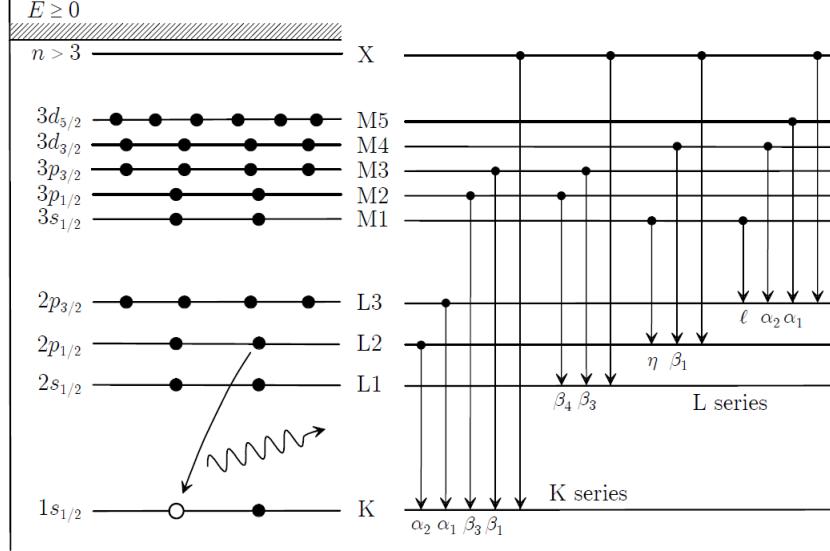
The above data sources are known to be accurate to the 1% level above 1 keV, under the condition (assumed by PENELOPE) of low incident photon densities, such that only single-electron transitions occur.[47]

PENELOPE assumes that incident photons are unpolarized and consequently fails to reproduce the polarization-dependent angular distribution of emitted electrons. We note that it does incorporate the angular distribution from Sauter's treatment of relativistic photo-electron emission—which, however, reduces to isotropic emission in the nonrelativistic regime covered here.[52]

### 2.1.3 Elastic scattering

Elastic scattering of electrons refers to interactions that do not alter target atoms' states. The simplest widely-used model for elastic scattering of electrons in a solid is the semi-

Figure 2.3: Atomic energy levels of the first three principal quantum numbers (left) and corresponding allowed radiative transitions (right). [47]



classical approach of Wentzel and Lenz, known as the Lenz model, which uses the Yukawa potential for the interaction between a fast electron and a target atom:

$$V(r) = \alpha^2 \frac{e^{-r/r_0}}{r} \quad (2.1)$$

The first Born approximation gives the amplitude for a particle's scattering off of a spherically symmetric potential as

$$f(\theta) \simeq -2 \frac{m}{\hbar^2 q} \int_0^\infty r V(r) \sin(qr) dr \quad (2.2)$$

Substituting (2.1) into (2.2) yields

$$f(\theta) \simeq -2 \frac{m \alpha^2}{\hbar^2 q} \int_0^\infty e^{-r/r_0} \sin(qr) dr = -\frac{2m \alpha^2}{\hbar^2 (r_0^{-2} + q^2)}, \quad (2.3)$$

therefore giving the following differential scattering cross section:

$$\frac{d\sigma}{d\Omega} = |f(\theta)| = \frac{4Z^2}{a_0^2 k_0^4} \frac{1}{(\theta^2 + \theta_0^2)^2},$$

where  $k_0 = m_0 v$  is the momentum of the incident electron,  $\theta_0 = (k_0 r_0)^{-1}$  is the characteristic angle for elastic scattering and  $a_0 = 4\pi\epsilon_0\hbar^2/m_0 e^2$  is the Bohr radius.

Using the Thomas-Fermi model, Wentzel and Lenz obtain  $r_0 = a_0 Z^{-1/3}$ . [53, 54] Doing this substitution and integrating over scattering angles gives

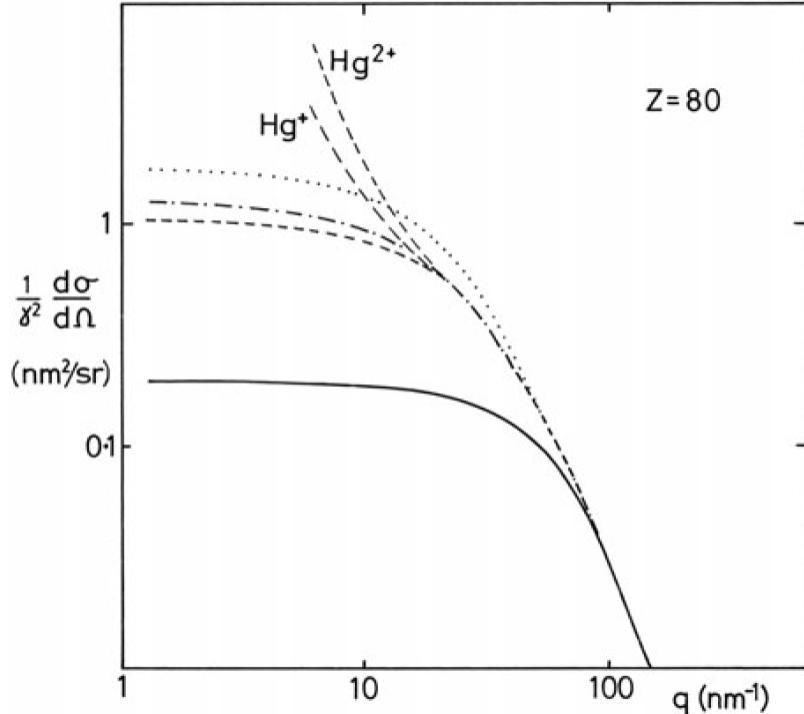
$$\sigma_e = \int_0^\pi \frac{d\sigma}{d\Omega} 2\pi \sin \theta d\theta = \frac{4\pi}{k_0^2} Z^{4/3} \quad (2.4)$$

We thus see that the angular deflections of elastic scattering decrease with increasing energy. For 10 keV electrons,  $\theta_0 \simeq 0.1$  rad and  $\sigma_e = 4.2 \times 10^{-20} \text{ m}^2$ . The elastic mean free path, an alternate measure of the collision frequency, is equal to  $\lambda_e = 1/(\sigma_e n)$ , where  $n$  is atomic number density. As an example, inserting  $\sigma_e = 39 \text{ \AA}^2$  and  $n = 8.5 \times 10^{25}/\text{m}^3$  for Fe yields  $\lambda_e = 300 \text{ \AA}$ . The product of expected numbers of elastic collisions on typical transport length scales (whose values exceed 10 nm) and the characteristic scattering angle are therefore at least of order unity (in radians), demonstrating that elastic scattering has a substantial influence on the propagation of below-10 keV electrons.

Despite its simplicity, the Lenz model gives total cross sections to within 10 % for light elements.[55] For heavier species it underestimates the small-angle differential cross section (Fig. 2.4) but correctly reproduces the large-angle DCS.

More accurate approaches use iterative (e.g. Hartree-Fock) solutions to the Schroedinger or Dirac equations to solve for the atomic potential.[57] Additionally, partial wave approaches can be used to avoid the Born approximation in regimes in which it fails (low electron energy and high-Z species). PENELOPE combines the above approaches: it solves the partial-wave expanded Dirac equation with a potential based on the Dirac-Fock electron density of Desclaux and exchange interaction of Furness and McCarthy. [58, 59] We will elaborate on PENELOPE's modeling of elastic scattering only within the narrow concern of assessing its accuracy within the physical regimes that we have interest in simulating; for more detail the reader may refer to Chapter 3 of the PENELOPE manual.

Figure 2.4: Angular dependence of elastic DCS of 30 keV electrons from a Hg atom under the Lenz model using the Wentzel potential (solid), and based on Hartree-Fock (dotted), Hartree-Slater (dot-dashed) and Dirac-Slater (dashed) wavefunctions. [56]



## 2.2 Inelastic scattering

We now discuss the treatment of inelastic collisions, which are the dominant mechanism for energy loss of electrons up to above 10 keV (Fig. 2.2). In an atomic system, the differential cross section for a transition from initial state wavefunction  $\psi_0$  to final state wavefunction  $\psi_n$  is

$$\frac{d\sigma_n}{d\Omega} = \frac{m_0}{2\pi\hbar^2} \frac{k_1^2}{k_0} \left| \int V(r) \psi_0 \psi_n^* \exp(iqr) d^3\vec{r} \right|^2 \quad (2.5)$$

where  $\mathbf{k}_0$  and  $\mathbf{k}_1$  are the wave vectors of the incident electron before and after scattering and  $\vec{q} = \hbar(\mathbf{k}_1 - \mathbf{k}_0)$  is the corresponding momentum transfer.[60]

At nonrelativistic velocities the potential between electron and atom may be expressed as the following sum of Coulomb potentials of the nucleus and atomic electrons:

$$V(r) = \frac{Ze^2}{4\pi\epsilon_0 r} - \frac{1}{4\pi\epsilon_0} \sum_{j=1}^Z \frac{e^2}{|\mathbf{r} - \mathbf{r}_j|} \quad (2.6)$$

Substituting the second term of equation 2.6 into 2.5, we note that the nuclear potential is independent of the coordinates of the atomic electrons and can therefore be removed from the integral. The orthogonality of the wave functions  $\psi_n$  implies that the nuclear potential does not contribute to inelastic scattering; the expression for the differential cross section of inelastic scattering is therefore:

$$\frac{d\sigma_n}{d\Omega} = \left( \frac{4}{a_0^2 q^4} \right) \frac{k_1}{k_0} |\epsilon_n(q)|^2, \quad (2.7)$$

where

$$\epsilon_n = \int \psi_n \sum_j e^{iqr_j} \psi_0 d^3\vec{r}. \quad (2.8)$$

The generalized oscillator strength (GOS) is an important related quantity:

$$f_n(q) = \frac{E_n}{R} \frac{|\epsilon_n(q)|^2}{(qa_0)^2}, \quad (2.9)$$

where  $R = (m_0 e^4 / 2)(4\pi\epsilon_0\hbar)^{-2}$ , the Rydberg energy, and  $E_n$  is the energy change of the transition. The GOS is in general continuous and therefore better expressed as a density with dimensions 1/energy, i.e.  $df(q, E)/dE$ , where  $E$  is energy loss. This allows us to re-express the double-differential cross section of inelastic scattering as follows:

$$\frac{d^2\sigma}{d\Omega dE} = 4REq^2 \frac{k_1}{k_0} \frac{df}{dE}(q, E). \quad (2.10)$$

### 2.2.1 Dielectric function

While this formulation makes it possible to calculate the GOS and associated quantities starting from atomic models, in solid state systems the scattering cross section of outer-shell

electrons is influenced by collective effects and chemical bonding. It's therefore preferable to describe the inelastic scattering of an electron from a solid using the solid's dielectric response function,  $\epsilon(q, E)$ .

Ritchie showed, using Poisson's equation and Fourier transforms, that an electron moving in the z-direction in an infinite medium experiences a force of the following magnitude opposite its direction of motion:

$$\frac{dE}{dz} = \frac{2\hbar}{\pi a_0 m_0 v^2} \int \int \frac{q_y E \operatorname{Im}[-1/\epsilon(q, E)]}{q_y^2 + (E/\hbar v)^2}, \quad (2.11)$$

where  $q_y$  is the component of the momentum transfer vector perpendicular to  $v$  and  $\omega = E/\hbar$ .[61] This quantity is referred to as the stopping power. It can be expressed in terms of the previously-defined DDCS:

$$\frac{dE}{dz} = \int \int n E \frac{d^2\sigma}{d\Omega dE} d\Omega dE, \quad (2.12)$$

where  $E$  is energy loss and  $\Omega$  is solid angle. By equating equations 2.11 and 2.12 in the small-angle limit it can be shown, by comparison with the atomic treatment, that

$$\frac{df}{dE}(q, E) = \frac{2E}{\pi E_a^2} \operatorname{Im}\left[\frac{-1}{\epsilon(q, E)}\right],$$

thus demonstrating the equivalence of the atomic and dielectric approaches.

Note, finally, that the GOS fully determines the value of equation 2.10 within the first Born approximation. As such, given the potential of equation 2.5 all modeling of the inelastic scattering of electrons at intermediate energies (1 keV – 300 keV) reduces to construction of a GOS model.

### 2.2.2 Modeling the generalized oscillator strength

Analytical expressions for the GOS are known for only the two simple cases of the free electron gas and hydrogen atom. In practice, however, it has been shown that the physics

of inelastic scattering is mostly determined by a few global features of the GOS and that relatively simple models are therefore adequate in most situations.[62]

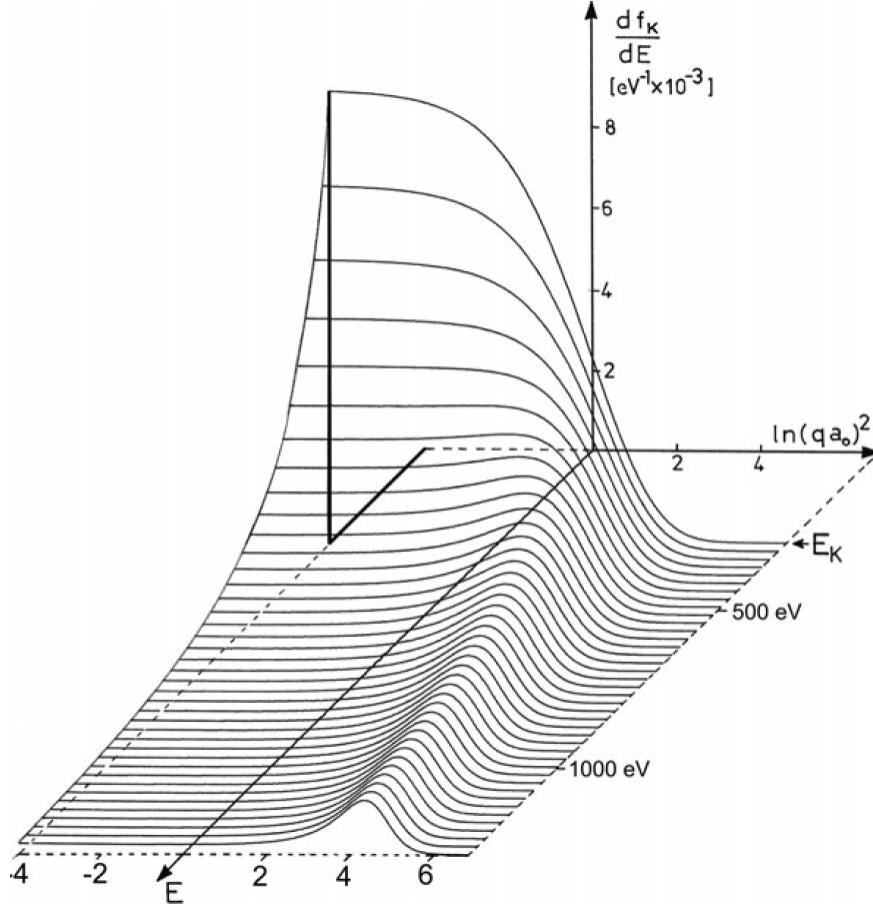
The GOS is conventionally represented as a two-dimensional surface plot called the Bethe surface (Fig. 2.5). We identify two constraints on the behavior of the Bethe surface which any GOS model must reproduce. First, in the limit  $Q \rightarrow 0$ , the GOS of the dielectric formulation becomes proportional to the optical oscillator strength  $\text{Im}[-1/\epsilon(0, E)]$ , which is experimentally constrained. Second, in the limit of large momentum transfer the most probable energy loss is equal to the kinematically-determined value for collision between two free electrons,  $E = \hbar^2 q^2 / 2m_e$ , where  $m_e$  is the electron mass.[63] The corresponding trace in energy and momentum is a feature of the Bethe surface known as the Bethe ridge.

As in Compton scattering, the shape of cuts through the Bethe surface (i.e. spectra of scattered intensity as a function of energy at fixed momentum transfer) is determined by the momentum distribution of atomic electrons. Certain models, such as that of Sorini et al, derive a value for the width of the Bethe ridge from Fermi velocity calculations.[63] PENELOPE adopts a simpler form based on the ‘ $\delta$ -oscillator’ model of Liljequist which splits the GOS into contributions from generalized ‘shells’ (each corresponding to either an atomic shell or a collective excitation).[65] The total GOS under this model is a sum over indices  $k$  of the shells:

$$\frac{df(q, E)}{dE} = \sum f_k [\delta(E - E_k)\Theta(q_k - q) + \delta(E - q)\Theta(q - q_k)],$$

where for the  $k$ th shell  $f_k$  is the shell’s number of electrons,  $q_k$  is the cutoff recoil energy, and  $E_k$  is the shell’s resonance energy.  $q_k$  is equal to the shell’s binding energy  $U_k$  (excluding the conduction band, for which it is set to 0), and  $E_k$  is computed from  $U_k$  and the material’s mean electron density, following Sternheimer.[66] Within this model the GOS is fully determined by the shells’ occupations and cutoff (binding) energies  $U_k$ , which PENELOPE obtains from Carlson. [67] It is possible, optionally, to direct PENELOPE to fit its GOS model to experimental stopping power data provided in material input files. It performs this fit through reweighting of the GOS model’s oscillators .

Figure 2.5: Bethe surface for ionization of the K shell in C, based on a hydrogenic GOS model.[64]



Substantial additional detail on the construction and interpretation of PENELOPE's GOS model can be found in its manual.

### 2.3 Accuracy and useful regimes

In the context of simulation of nanostructured materials, errors in PENELOPE's DCSs for electron scattering originate from both (1) the limited range of validity of PENELOPE's physical models with respect to the bulk properties PENELOPE seeks to reproduce, and (2) the difference between scattering DCSs of ambient-condition bulk materials on the one hand

and high-temperature nanostructured materials on the other. We address these two issues separately.

### *2.3.1 Nanophase dielectric functions*

As mentioned previously, a material's inelastic scattering DCS is fully determined by its loss function, the imaginary component of the dielectric function. Any difference between the responses of bulk and nanophases arises from the contribution to the loss function of collective electronic excitations, i.e. plasmons. Plasmon modes in nanostructured materials are widely studied, but there has been little prior work in the context of high-temperature dense matter.[68] The question of collective electronic excitations in heated nanophase materials thus manifests itself as both a problem and an opportunity. On the one hand, the lack of experimental data and accurate modeling makes it impossible to fully quantify the inaccuracy of simulations of ambient, bulk materials. On the other hand, XFEL heating experiments could be used to discriminate between computed dielectric response functions and their underlying finite-temperature electronic structure modeling—to the extent that alternative models generate experimentally measurable differences in the inelastic DDCS. We thus suggest that XFEL heating of nanostructured materials could enable a joint modeling/experimental program to validate WDM electronic structure theory.

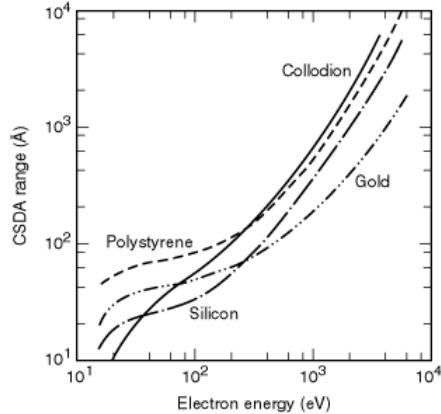
### *2.3.2 Numerical bound on low-energy loss DCS uncertainties*

In the current situation, wherein the plasmon contribution to the loss function is not known, we can take advantage of the fact that plasmon resonance are confined to energy losses smaller than approximately 100 eV. The influence of the low-energy region of the loss function on the spatial distribution of deposited energy can therefore be bounded using the continuous slowing down approximation (CSDA) of 100 eV electrons. The CSDA for electrons of energy  $E_0$  is the following integral over stopping power:

$$l_{CSDA} = \int_{E_{final}}^{E_0} \left( \frac{dE}{dz} \right)^{-1},$$

where  $E_{final}$ , the final energy of the electron, is usually taken to be 10 eV. For elements heavier than boron,  $l_{CSDA} < 10$  nm for  $E = 100$  eV. We therefore conclude that inaccuracy in treatments of collective excitations affect the spatial distribution of energy deposited by electrons only at a length scale below 10 nm (Fig. 2.6)

Figure 2.6: CSDA range as a function of energy for several materials, based on computed low-energy stopping powers. [69]



### 2.3.3 Energy cutoffs

PENELOPE stops simulation of an electron's motion once its energy drops below a prescribed cutoff value; at the endpoint of an electron's simulated track all of the electron's final energy is deposited at its final position. The resulting distortion in the spatial distribution of deposited energy can be bounded, as above, using the CSDA. PENELOPE's cutoff energy can be set as low as 50 eV. Assuming this value is chosen, the resulting error is smaller than the bound established in section 2.3.2 on error attributed to inaccuracy in the low-energy dielectric function. Simulation error due to PENELOPE's energy cutoff can therefore be safely neglected.

### 2.3.4 Elastic scattering

PENELOPE's use of the static field approximation in its elastic scattering model introduces a low-energy error in the DCS due to the effect of the polarizability of atomic charge.[70] The size of this error is 20% at 1 keV and 50% at 100 eV. [47] The CSDA range at 1 keV, where uncertainty at the level of the DCS is considerable, ranges from 10 nm for high-Z elements to over 100 nm for low-Z ones. Because the results of the PENELOPE simulations discussed in Chapter 3 are sensitive to errors on the 10 nm - 100 nm length scale, the CSDA does not usefully constrain the elastic DCS model's contribution to uncertainty in the spatial distribution of deposited energy.

The magnitude of uncertainty in the elastic DCS may be calculated by modeling elastic scattering of an electron as a correlated random walk defined by an elastic collision mean free path  $\lambda_e$  and energy-dependent distribution of scattering angles. Cursory consideration suggests that closed form solutions for transport distances are available only under restrictive assumptions; implementing this calculation as a Monte Carlo simulation appears straightforward, but we have not done so. It is worthwhile pursuing in the future, since until then one cannot fully quantify total uncertainties in PENELOPE's energy transport predictions.

## 2.4 Inelastic scattering

Inelastic scattering has much smaller characteristic angles than elastic scattering scattering but comparable total cross sections. As a result the influence of angular deflections by inelastic scattering on the propagation of electrons is relatively small. The effect of uncertainties in the inelastic scattering DDCS can thus be neglected, and we confine our attention to uncertainty at the level of the stopping power, a more coarse-grained quantity.

Fig 2.7 compares PENELOPE's computed stopping powers and inelastic mean free paths for Al to several experimental datasets. [47] The level of disagreement between different datasets is of the order 2 in the 1 keV - 10 keV energy loss range; the discrepancy between PENELOPE's modeled stopping power and the experimental datasets is also of this order.

Because all transport lengths are proportional to stopping power we must thus contend with a factor of 2 uncertainty in the length scale of computed spatial distributions—far larger than any of the other uncertainties we have considered until now.

The conclusions of Chapter 3 can nevertheless be conserved, with one modification, if we consider PENELOPE’s error in modeling the 1 - 10 keV stopping power as an unknown constant-factor scaling in stopping power. Such an uncertainty corresponds to an unknown scaling of both (1) the length scale of spatial distributions of deposited energy and (2) the flux magnitude of nonlocally-transported energy crossing a given material interface. To give a simple illustration, consider a one-dimensional configuration consisting of an infinite extent of source material from  $x = -\infty$  to  $x = \infty$ . When the sample receives x ray illumination of magnitude unity at position 0 the density distribution  $\rho(x)$  of deposited energy is given by a response function  $f(x)$  (fully determined by the sample material’s stopping power and incident x-ray spectrum):  $\rho(x) = f(x - x_0)$ . If the material is uniformly illuminated by x rays in the region spanning  $x = 0$  to  $x = \infty$  then (in arbitrary units):

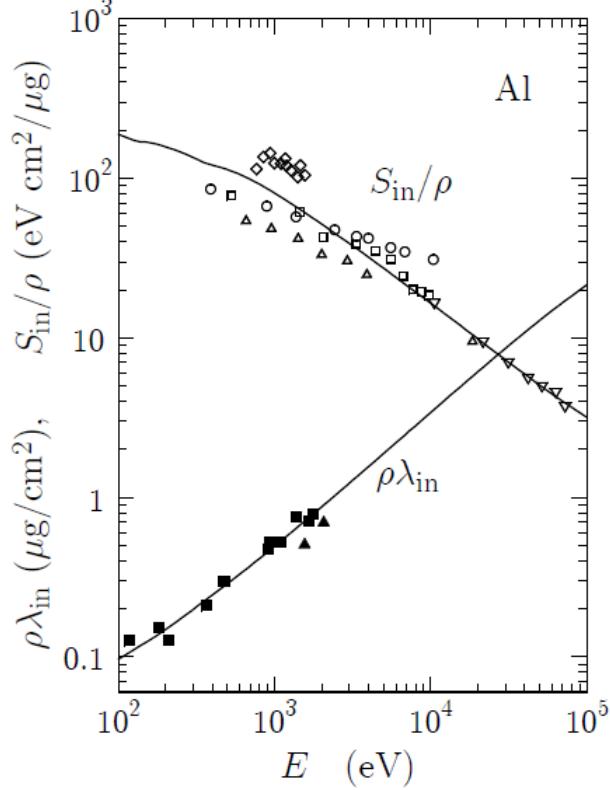
$$\rho(x) = \int_0^\infty f(x - x')dx'.$$

Under the substitution  $f(x) \rightarrow g(x) = f(cx)$  (equivalent to scaling  $dE/dz \rightarrow (1/c)dE/dz$  of the stopping power), and maintaining normalization of the response function, the distribution becomes:

$$\rho'(x) = \int_0^\infty cf((c(x - x')))dx = \int_{cx}^\infty f((u))u.$$

Therefore constant-factor scaling of the stopping power is equivalent to a change in units of length, implying that, under our assumed form of the uncertainty in  $dE/dz$ , and adding the assumption that the unknown scaling factor  $c$  is equal for all materials, the simulated spatial distributions of deposited energy density are correct up to a uniform scaling of the sample geometry.

Figure 2.7: Stopping power and inelastic mean free path for electrons as a function of energy in Al calculated by PENELOPE and from several experimental datasets.[71]



## 2.5 Dosimetry

PENELOPE's dosimetry includes both linear energy transfer from radiation to matter and the contribution of particle track ends, as mentioned in section 2.3.3. At the energy scales of interest the former contribution may be neglected, and the distribution of energy deposited by a particle shower is entirely dependent on simulated inelastic scattering events. PENELOPE's dosimetry calculation is tied to the termination of electron tracks: when an electron's energy drops below the (previously-defined) cutoff value its simulation ceases, and its entire energy is deposited at the track's endpoint. Similarly, the energy loss of soft inelastic collisions (ones having energy loss greater than the cutoff energy  $W_{cc}$ ) is deposited

locally (whereas hard inelastic collisions generate secondary electrons that are individually tracked).

Coarse-graining of the dose distribution is done by dividing the simulation volume into a three-dimensional grid of cells, in each of which PENELOPE calculates the total dose of deposited energy. This grid is defined by the parameters GRIDX, GRIDY, GRIZ and GRIDBN in PENELOPE's input.

These spatial dose distributions are the output data of interest in the simulations of Chapter 3.

## Chapter 3

### **NONLOCAL HEAT TRANSPORT AND IMPROVED TARGET DESIGN FOR X-RAY HEATING STUDIES AT X-RAY FREE ELECTRON LASERS**

*(This is a reproduction of a manuscript in review: Oliver Hoidn and Gerald Seidler, Physical Review B, submitted April 2017 )*

The extremely high power densities and short durations of single pulses of x-ray free electron lasers (XFELs) have opened new opportunities in atomic physics, where complex excitation-relaxation chains allow for high ionization states in atomic and molecular systems, and in dense plasma physics, where XFEL heating of solid-density targets can create unique dense states of matter having temperatures on the order of the Fermi energy. We focus here on the latter phenomena, with special emphasis on the problem of optimum target design to achieve high x-ray heating into the warm dense matter (WDM) state. We report fully three-dimensional simulations of the incident x-ray pulse and the resulting multielectron relaxation cascade to model the spatial energy density deposition in multicomponent targets, with particular focus on the effects of nonlocal heat transport due to the motion of high energy photoelectrons and Auger electrons. We find that nanoscale high-Z/low-Z multicomponent targets can give much improved energy density deposition in lower-Z materials, with enhancements reaching a factor of 100. This has three important benefits. First, it greatly enlarges the thermodynamic parameter space in XFEL x-ray heating studies of lower-Z materials. Second, it allows the use of higher probe photon energies, enabling higher-information content X-ray diffraction (XRD) measurements such as in two-color

XFEL operations. Third, while this is merely one step toward optimization of x-ray heating target design, the demonstration of the importance of nonlocal heat transport establishes important common ground between XFEL-based x-ray heating studies and more traditional laser plasma methods.

### **3.1 I. Introduction**

Dense matter under extreme conditions of pressure (P), temperature (T), or both, is a topic of classic and growing interest across multiple subfields of contemporary science. [1, 26, 72–74] We focus here on the very specific case of femtosecond-scale x-ray heating of crystalline matter, in which there is growing evidence that the lattice often has limited opportunity to structurally relax during the incident x-ray pulses [6–8] and that the loss of crystallinity during the x-ray pulse may have only modest scientific impact. [75] Such studies hold a significant and, we propose, unique position for discovery, because they encompass the case in which the consequences that traditional condensed phase electronic structure theory has on the structure of partially-ionized plasmas will be strongest and most easily interrogated. Hence, the study of crystalline matter at ambient density but highly elevated electronic temperature holds high potential for directly testing foundational issues in finite-T density functional theory, especially including the proper treatment of T-dependent functionals. [76–78]

This point has recently been made by Valenza and Seidler [78], who demonstrated that finite-T DFT makes strong, initially counter-intuitive predictions about the evolution of the absolute and relative Bragg peak intensities in x-ray diffraction (XRD) from crystalline matter as a function of electronic temperature on the 1 – 50 eV scale. The key point is that XRD provides a more detailed interrogation of the population of electronic states for crystalline matter than it does for the more amorphous states interrogated after, e.g., laser shock heating. Furthermore, it is this temperature dependence that is a key *microscopic observable* of all finite-T DFT approaches: the central quantity calculated in DFT is, after all, the spatial distribution of electron density. Therefore, careful characterization of the

real-space charge density at elevated electronic temperatures in a cool lattice gives a direct path to evaluating different DFT implementations. This is particularly significant as regards the temperature-dependent exchange functional, which is essential to predictions of bulk thermodynamic and elastic properties. [76, 77, 79]

However, in such a research program there is a confounding detail. The most effective heating by x-rays will occur with lower-energy photons (that are more strongly absorbed) whereas any detailed interrogation of the real-space charge distribution by XRD requires the use of higher energy x-rays to obtain information over a wide momentum transfer range. [12] This dilemma raises a question that is new in the XFEL community but old in the broader plasma physics community: *Given the incident pulse characteristics and the desired sample material, how does one design a target to achieve optimal energy density deposition?*

The most comprehensive treatment of this question would include a fully spatio-temporal treatment of radiative transport as well as electronic dynamics and electron-atom interactions wherein, again because of the short time scales, lattice relaxation can be ignored or at least is secondary. Within this framework, the temporal evolution of electron-electron and electron-atom interaction includes several stages. First, the atomic physics of the core levels gives rise to an initial population of high-energy Auger electrons and photoelectrons that decay into low-energy (< 50 eV) electronic excitations (both collective and single-particle) on the scale of a few femtoseconds. The resulting collective excitations decay by generating electron-hole pairs on the time scale of tens of femtoseconds. Subsequent electron-electron thermalization occurs on the scale of 100 fs – 1 ps for ambient matter [14-17], but in general has a strong eV-scale temperature dependence, thus requiring a self-consistent treatment at high incident flux levels. [80]

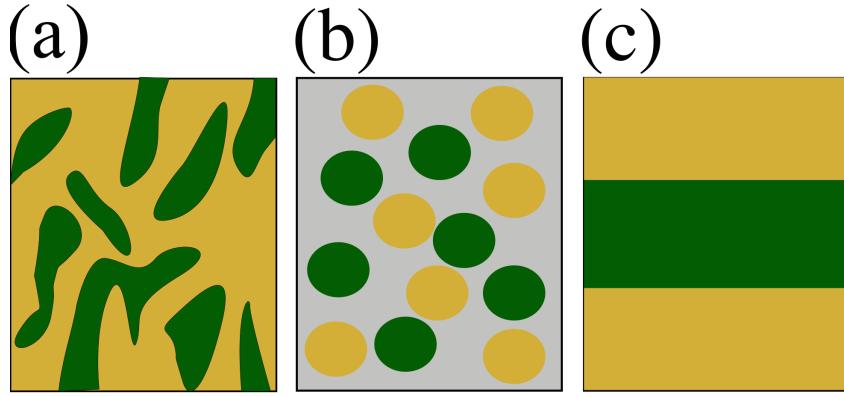
Here, we take a simpler approach with the goal of identifying and illustrating the most important contributors to x-ray heating and how their spatial extent strongly influences optimum x-ray heating target design, in the limited sense of optimizing the deposited net energy density in the desired sample phase. Specifically, we address the key questions surrounding nonlocal energy transport by hot electrons. This topic has a long history in plasma physics,

especially for inertial confinement fusion target design, but enters here with typically lower-energy electrons, i.e., keV-scale, than are important in ICF and in direct-drive laser-heating studies. This causes the energy deposition length of the hot electrons to decrease from the 100-1000 m scale for MeV electrons in laser experiments to instead only  $\sim$ 50-200 nm, depending on the atomic number of the species present in the XFEL x-ray heating target.

It is this much shorter length scale that brings us to consider multicomponent nanoscale targets for x-ray heating so that the influence of nonlocal energy transport by the hot electrons can be usefully engineered. While the importance of nanoscale energy transport has not previously been discussed in the context of XFEL heating target design, it has been studied and exploited in other experimental contexts. For example, there exists a significant body of literature in the medical physics community concerned with using gold nanoparticles for dose enhancement in radiotherapy treatment. [81, 82] A contrasting application of nonlocal energy transport is found in the macromolecular crystallography community, where there is interest in the use of submicron incident x-ray beams so that a large fraction of high-energy electrons escape the beam spot before slowing down, thus reducing radiation damage in the probed sample volume. [83–87]

With the above context established, we consider here a nanostructured target design that enhances energy deposition in a sample material using nonlocal heat transport from a more strongly x-ray absorbing material in contact with the sample – we refer to this second material as a ‘cladding’ as a matter of convenience, for closer contact to the terminology of laser-shock target design, even when the geometry may not strictly be cladded. Fig. 3.1 sketches several corresponding geometries, but in the current paper we concentrate on the particularly simple one of Fig. 3.1 (c), consisting of a single thin film of sample material clad with Au. We use the Monte Carlo code PENELOPE to simulate three-dimensional electron-photon transport and the corresponding spatial distributions of deposited energy to demonstrate two benefits to the design: first, it significantly enhances in-sample energy deposition, and second, it relaxes constraints on XFEL pump photon energy in a way that substantially increases the information content of XRD measurements in certain experimental contexts.

Figure 3.1: Representations of three types of multicomponent targets composed of sample material (green) and heater cladding (yellow). (a): A porous substrate filled with sample material; (b): a mixture of cladding and sample nanoparticles embedded in a solid matrix; (c): a multilayer film.



We proceed as follows. In section II, we describe the methods used to simulate photoionization and electron transport in a nanostructured target and discuss the simplifying approximations on which we rely. In section III, we present and discuss simulation results of multilayer targets consisting of sample material clad on one or two sides with gold. We find that such a cladding configuration significantly increases deposited energy density in a sample material, with the largest enhancement in low-Z samples. We argue that this enhanced effect in low-Z samples opens the door to wide-angle x-ray diffraction (wide-angle XRD), with significant utility for studying the time dynamics of the energy relaxation cascade for both electronic and lattice/ion degrees of freedom in such materials. These observations are particularly relevant in the context of two-color x-ray pump x-ray probe experiments at XFELs [88–91], but also serve more generally to establish the importance of nanoscale nonlocal heat transport in high-intensity XFEL studies. Finally, in section IV we conclude.

### 3.2 II. Methods

The simulation of electron transport in condensed matter is an area of ongoing research. In addition to continuing development of well-established codes in the high-energy experimental particle physics community [92], new developments include incorporation of *ab initio* band structure calculations in order to accurately model the electron mean free paths of interband transitions and plasmon excitations from relativistic energies down to a few eV. [93, 94]

In the regime relevant to the present study, calculation of the spatial distribution of deposited energy caused by absorption of a hard x ray requires accurate treatment of the processes that describe scattering of photo- and Auger electrons at the 100 eV to 10 keV scale (generation of secondary x-ray photons, though present, plays a negligible role in energy transport). The simplest atomic treatments of elastic and inelastic scattering demonstrate that, for mid- and high-Z elements, the ratio of elastic to inelastic total cross sections is of order unity and that characteristic elastic scattering angles are sufficiently large (for instance, of order 1 rad for  $\sim 1$  keV electrons) to influence deposited energy distributions. [95] Both components, therefore, must receive accurate treatments to adequately model spatial energy deposition distributions in a nanostructured target.

The spatial distribution of deposited energy is determined by the electron stopping power  $\frac{dE}{dz}$ , which in a classical treatment is related to a material's dielectric function  $\varepsilon(q, \omega)$  by

$$\frac{dE}{dz} = \frac{2^2}{\pi a_0 m_0 v^2} \iint \frac{q_y \omega \operatorname{Im}[\frac{-1}{\varepsilon(q, \omega)}]}{q_y^2 + (\frac{\omega}{v})^2} dq_y d\omega, \quad (1)$$

where  $\omega$  is angular frequency,  $q$  is momentum transfer (with  $q_y$  the magnitude of the component for momentum transfer perpendicular to the z-direction),  $a_0$  is the Bohr radius,  $m_0$  is the electron mass, and  $v$  is the electron velocity. [95] In the case of electron showers generated by 5-10 keV photons, the electron stopping power's dependence on  $v$  causes nonlocal energy transport to be dominated by the highest-energy Auger and photoelectrons. Though the slower time evolution of the subsequent electronic and lattice dynamics may be neglected in the present context of simulating fsec-scale energy transport, the possibility of interrogating

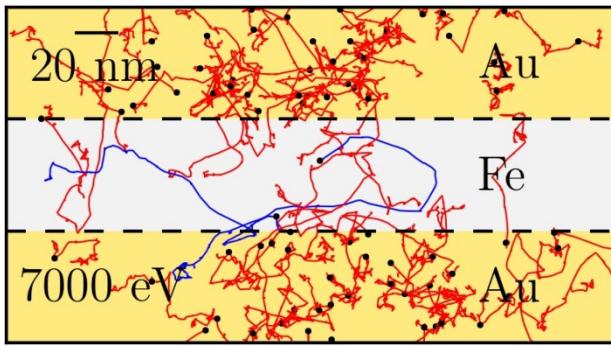
it by time-resolved XFEL pump-probe measurement is an interesting topic in its own right. [88]

To model the above physics we used the code PENELOPE, which implements particle-tracking Monte Carlo simulations of electron showers generated by x-ray photoionization. PENELOPE uses total and differential cross sections based on several physical models. Briefly, it derives elastic and inner-shell inelastic cross sections from strictly atomic wave functions, while the valence contribution to the inelastic double differential cross section is based on the Born approximation and generalized oscillator strength model of Liljequist [65], with an energy loss-dependent normalization that allows the model to replicate empirical stopping power data (provided as program input). Although the inelastic scattering cross section is dominated by low-energy loss collisions, inner shells contribute the majority of the stopping power for several-keV electrons, which account for the longest-range energy transport. For electrons of those energies the stopping power of a compound may be approximated within five percent by a stoichiometric sum based on atomic treatments of its constituents (an observation referred to as Bragg's rule). [96] Consequently we employed material data files generated by the PENELOPE 2011 program MATERIAL, which applies this approximation to infer stopping powers of arbitrary compounds using data from the NIST ESTAR database. [97]

### **3.3 III. Results and discussion**

We now present results for several realizations of our nanostructured target design, all of which consist of thin films clad with Au on one or both sides. The heating of an Fe thin film via nonlocal heat transport by hot electrons is illustrated in Fig. 3.2, which shows a two-dimensional projection of electron trajectory traces in an Au-Fe-Au trilayer stimulated with 7 keV incident photons. The color-coding of the tracks shows that, due to the much larger number of photoexcitations in the Au cladding compared to Fe inclusion, most hot electrons propagating in the Fe are part of a photoionization relaxation cascade originating in the cladding. Inelastic scattering of these hot electrons is the dominant contribution to

Figure 3.2: Visualization of a 3-D Monte Carlo simulation of electron transport in an Au-Fe-Au target heated by 7 keV photons, incident normally from the top of the page. Electron tracks are projected onto the plane of the page; showers resulting from photoexcitation of Au and Fe atoms are red and blue, respectively. Note that most of the electron tracks in the Fe are due to absorption events in the Au.



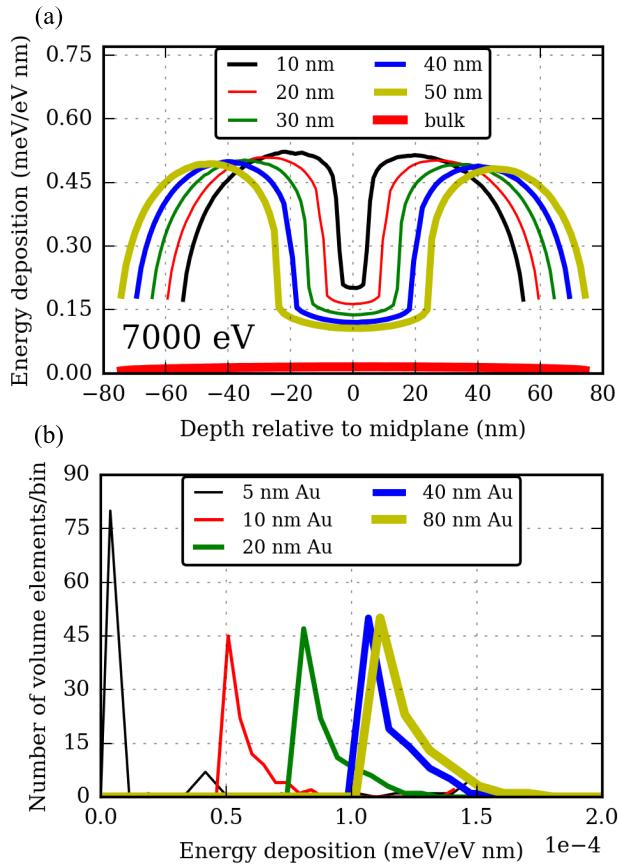
energy deposition in the central Fe region, as quantified by Fig. 3.3, which compares the linear energy deposition of several Au-Fe-Au trilayer configurations to that in bare Fe.

Photoionization by 7 keV photons yields mean energy deposition lengths  $l$  of 15.0 nm and 35.3 nm, respectively, in simulated bare Fe and bare Au targets, where  $l = \int_{z=0}^{\infty} z(\vec{r}) \rho(\vec{r}) d^3\vec{r}$ , with  $\rho(\vec{r})$  the volume density of deposited energy and  $z$  the magnitude of the projection of  $\vec{r}$  onto a fixed, arbitrary unit vector. Consistent with the above characteristic lengths, we found that absorbed energy density in the Fe inclusion saturates beyond an Au cladding thickness of 50 nm. Fig. 3.3 (a) shows the deposited energy distribution in a bare  $\text{Fe}_3\text{O}_4$  target and in several Au- $\text{Fe}_3\text{O}_4$ -Au trilayers with varying thicknesses of the  $\text{Fe}_3\text{O}_4$  inclusion. An interior layer thickness of 50 nm results in a factor of five enhancement in deposited energy density relative to the bare  $\text{Fe}_3\text{O}_4$  target. The increase in deposited energy density in a clad sample compared to a bare one is significantly larger for lower-Z materials, reaching a factor of 100 for an Au-C-Au target of the same geometry (Fig. 3.4).

These enhancements in energy deposition increase the accessible thermodynamic param-

eter space in all XFEL heating experiments, which is particularly significant for experimental diagnostics that require deviation from optimal pump pulse characteristics and are therefore normally incompatible with heating studies, for instance XRD. We illustrate this in Fig. 3.5, which compares the energy deposition in Au-Fe-Au and Au- $\text{Fe}_3\text{O}_4$ -Au targets stimulated with photons below the  $K$ -edge of Fe to that in a bare Fe target heated by photons above the edge. Nonlocal heating of the former samples compensates for the reduction in sample heating caused by lowering the incident photon energy below the Fe  $K$ -edge; the multicomponent targets thus allow improving the ratio of signal to (fluorescence) background while—in the more favorable case of  $\text{Fe}_3\text{O}_4$ —maintaining an energy deposition density comparable to the highest level possible with an equivalent monolithic target. However, Fig. 3.6 also demonstrates a tradeoff of the cladding’s presence: the diffracted signal from Au is stronger than that from the sample, making the described reduction in background worthwhile only assuming sufficient separation between Bragg peaks of the sample and cladding.

Figure 3.3: (a) Linear energy deposition density generated by 7 keV photons incident on an Au- $\text{Fe}_3\text{O}_4$ -Au target, displayed for several thicknesses of the central  $\text{Fe}_3\text{O}_4$  layer and a fixed Au cladding thickness of 50 nm. (b) Histograms of energy deposition density in volume elements of the  $\text{Fe}_3\text{O}_4$  inclusions in Au- $\text{Fe}_3\text{O}_4$ -Au targets, displayed for several thicknesses of the Au cladding and a fixed  $\text{Fe}_3\text{O}_4$  layer thickness of 50 nm.

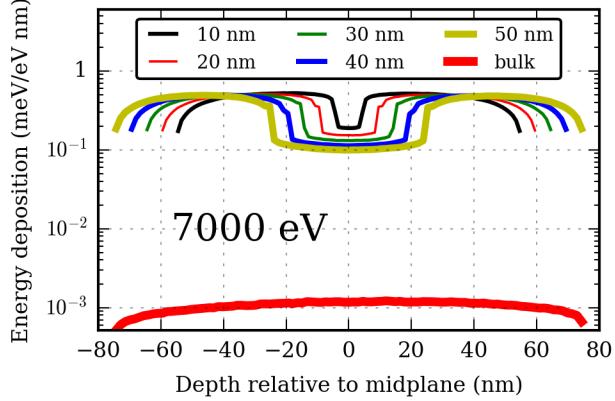


Low-Z sample materials provide a separate, independently interesting, case for the use of structured target design in XRD studies. In such materials, nonlocal heat transport is effective over a much wider range of incident photon energies compared to direct x-ray absorption. Until now, x-ray heating studies of low-Z materials, such as graphite, have required incident photon energies below 3 keV to reach HED conditions ( $> \sim 1$  eV temperatures) due to these materials' small photoelectric cross sections in the hard X ray (photon energy  $> 5$  keV) regime. This restriction limits the kinematically accessible range of momentum transfers in XRD, which correspondingly reduces available information on real-space charge density.

This creates an experimental dilemma with scientific consequences. For example, Hau-Riege et al. [98] showed evidence for ultrafast melting of graphite during a 40 fs-long XFEL pulse but were limited, for the reason described above, to using 2 keV incident photons, yielding diffraction from only the 002 Bragg reflection of graphite. The authors interpreted quenching upon heating of the 002 peak as evidence of nonthermal lattice melting. However, Valenza *et al.* [78] questioned this conclusion based on simulated diffraction using frozen-core finite-T DFT calculations, which predicted strong quenching of the graphite 002 reflection due to purely electronic reorganization in crystalline graphite at 10 eV electronic temperature. In graphite and other low-Z systems, the only means of unambiguously separating lattice disorder from electronic heating in the XRD signal is to probe several Bragg peaks, including the lowest-order reflections and their harmonics. [12]

It is therefore interesting to ask whether high energy-densities can be achieved in graphite when using photons suitable for wide-angle scattering. In Fig. 3.4 we show the deposited energy densities in Au-C-Au trilayers of several interior thicknesses, once again using 7 keV incident photons (sufficient to probe the 006 reflection of graphite). The deposited energy density in the interior layer is at least a factor of 100 greater compared to an unclad sample with the same incident photon energy, and a factor of two greater compared to an unclad sample stimulated with 2 keV photons. Indirect heating via high-Z cladding thus eliminates the constraint of selecting incident photon energies near a low-Z material's small core binding energies, making wide-angle XRD possible. In the context of carbon, the

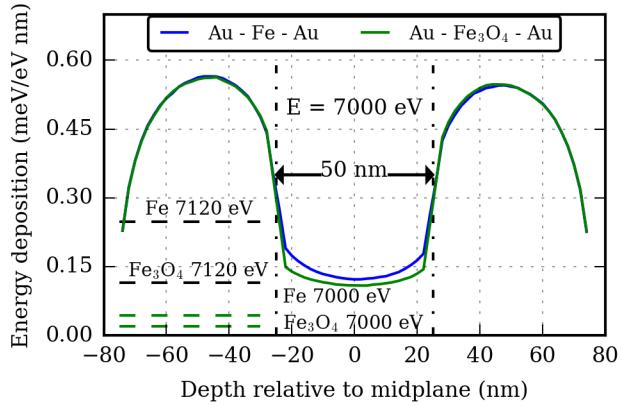
Figure 3.4: Linear energy deposition due to 7 keV photons incident on an Au-C-Au target displayed for several thicknesses of the central C layer and a fixed outer cladding thickness of 50nm.



weakness of the XRD from C compared to Au can be uniquely compensated with a highly-oriented pyrolytic graphite (HOPG) sample, whose high-reflectivity  $00l$  peaks yield much higher signal to background ratios than the powder-like Bragg and thermal diffuse scattering of polycrystalline Au. Similar configurations exploiting mosaic or single-crystal samples may enhance wide-angle XRD on a variety of low-Z systems, offering a much-improved ability to experimentally test predictions of finite-T DFT-based modeling of electronic structure in low-Z condensed matter, where finite-T effects are easiest to identify because of the relatively large valence-electron contribution to the XRD signal. [78]

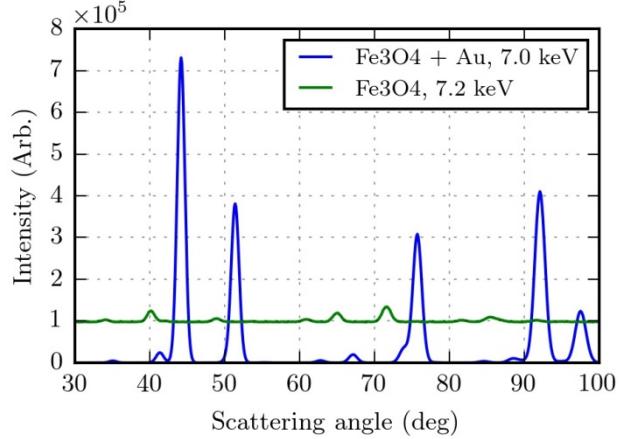
The simulations presented in this paper constitute a first demonstration of a particularly simple implementation of structured target design. One can imagine several improved designs that achieve the same level of nonlocal sample heating while averting some of the disadvantages of our multilayer approach. For example, a uniform mixture of small ( $< 50$  nm diameter) sample and heater nanoparticles would show similar mean deposited energy densities to a multilayer target and can be prepared by, e.g., spin coating or drop-casting. Such targets would have more homogeneous heating and would additionally allow preparation of

Figure 3.5: Linear energy deposition in layered Au-Fe-Au and Au- $\text{Fe}_3\text{O}_4$ -Au targets of 150 nm total thickness stimulated by 7 keV photons. Dashed lines indicate energy deposition in bulk  $\text{Fe}_3\text{O}_4$  and Fe at photon energies of 7.12 keV (above the iron K-edge) and 7 keV (below the edge). The multilayer configuration sufficiently enhances energy deposition so as to partially compensate for the difference between pre- and above-edge x-ray photoelectric cross sections. The benefit is particularly pronounced in  $\text{Fe}_3\text{O}_4$  due to its much lower density and photoelectric cross-section.



much thicker targets and give much higher scattered intensities. A similar result may be possible using electrochemical or vapor deposition to embed sample materials inside porous high-Z metal substrates. [99, 100] Two-color XFEL experiments may also lend themselves to lithographically patterned designs with concentric cylindrical volumes of (inner) sample and (outer) cladding materials, wherein the more tightly-focused probe pulse would be inscribed in a volume free of cladding material. Such a configuration would have the intention of reducing (cladding) background relative to signal, which would be particularly useful for weakly-diffracting low-Z samples.

Figure 3.6: Simulated powder diffraction of 50 nm Au-50 nm  $\text{Fe}_3\text{O}_4$ -50 nm Au stimulated by X-rays below the Fe K-edge (blue) compared to that resulting from photons above the edge incident on bare  $\text{Fe}_3\text{O}_4$ , including fluorescence background(green).



### 3.4 IV. Conclusion

We model the spatial distribution of deposited energy in nanostructured targets for hard x-ray XFEL heating experiments using the Monte Carlo code PENELOPE. We find that two-component targets consisting of a sample material and high-Z cladding achieve substantial nonlocal heating of the sample via the relaxation cascade following transport of multi-keV Auger and photoelectrons. We argue that this target design approach will bring substantial benefits to XFEL heating experiments in the following ways: first, by enlarging their accessible thermodynamic parameter space and second, by improving the capability of x-ray diffraction diagnostics to characterize finite-temperature electronic structure and to distinguish between thermalization of the electronic and lattice degrees of freedom in crystalline warm dense matter systems.

### ***Acknowledgements***

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## Chapter 4

### A PHOTOMETRIC STUDY OF ENERGY-DISPERSIVE X-RAY DIFFRACTION AT A LASER PLASMA FACILITY

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The low repetition rates and possible shot-to-shot variations in laser-plasma studies place a high value on single-shot diagnostics. For example, white-beam scattering methods based on broadband backlighter x-ray sources are used to determine changes in the structure of laser-shocked crystalline materials by the evolution of coincidences of reciprocal lattice vectors and kinematically-allowed momentum transfers. Here, we demonstrate that white-beam techniques can be extended to strongly-disordered dense plasma and warm dense matter (WDM) systems where reciprocal space is only weakly structured and spectroscopic detection is consequently needed to determine the static structure factor and thus the ion-ion radial distribution function. Specifically, we report a photometric study of energy-dispersive diffraction (ED-XRD) for structural measurement of high energy density systems at large-scale laser facilities such as OMEGA and the National Ignition Facility. We find that structural information can be obtained in single-shot ED-XRD experiments using established backlighter and spectrometer technologies.

#### **4.1 I Introduction**

In addition to their centrality for inertial confinement fusion studies, [101, 102] laser-shock experiments play a growing role at the interface between plasma physics and condensed mat-

ter physics, geosciences, and laboratory astrophysics. [103–114] However, for experiments reaching the highest energy density states the technical challenges extend beyond the creation of such states: the low repetition rates, limited facility access, and significant shot-to-shot variations each place a special emphasis on single-shot x-ray diagnostics of the structural and electronic properties of the compressed, heated target. [115–121] An important case-in-point is provided by the determination of the ion-ion radial distribution function,  $g_{ii}(\vec{r})$ , or equivalently the static structure factor  $S(\vec{k})$ . Knowledge of  $g_{ii}(\vec{r})$  fulfills an interesting variety of roles. First, it is necessary, if only at the level of mean density and average ionization state, for investigation of any equations of state (EOS) and of molecular dynamics simulations or other structural calculations performed in support of EOS calculations. Second, it is also a critical input parameter to any fine treatment of electronic structure. The electronic structure of dense crystalline systems and plasmas, in turn, is a quantity of fundamental interest but also of a certain pragmatic interest: some sufficient knowledge of electronic structure is needed for reliable determination of the target temperature and ionization state in dense plasma and warm dense matter (WDM) experiments [26, 122], and this capability is in turn needed for campaigns to experimentally measure the EOS in the WDM regime [3, 33, 123].

For targets that retain substantial medium- or long-range order upon shock compression, broadband backscatterer x-ray sources enable white-beam angle-dispersive x-ray diffraction (AD-XRD) in which substantial structural detail can be inferred from Kossel rings [124] and other fine scattering patterns dictated by the coincidence of reciprocal lattice vectors and kinematically-allowed momentum transfers [125]. However, white-beam AD-XRD is only applicable to systems that are substantially single crystalline: any statistically isotropic system, whether a polycrystalline fine-powder sample or a dense, partially ionized plasma, when illuminated by a broad-band source will show an angularly-featureless signal when observed on, *e.g.*, an image plate. For high atomic number ( $Z$ ) systems, single-shot white-beam extended x-ray absorption fine structure (EXAFS) has seen some applications [41]; the situation has proven more challenging for lower- $Z$  WDM and dense plasmas, as a result of the mutually-exclusive target thickness requirements of the x-ray measurement (soft x-ray

penetration lengths of order 1 micron or less) and laser ablation (necessary thicknesses of tens of microns) [126]. Consequently, the first determination of  $g_{ii}(r)$  for disordered, dense lower-Z plasma systems [39] instead used multi-shot, quasi-monochromatic AD-XRD, *i.e.*, ‘traditional’ XRD.

Here, we investigate whether single-shot, white-beam XRD can be performed on *strongly disordered*, laser-shocked solids and WDM using spectral information at the detector location to parameterize the momentum transfer of the quasielastic scattering event, *i.e.*, we consider purely energy-dispersive x-ray diffraction (ED-XRD). Some context is needed to fully define this term and to distinguish it from XRD methods already in use in the laser-plasma community. The differential scattering cross section per atom for coherent scattering of x rays (ordinary diffraction of incoherent incident photons) from an isotropically disordered, elemental material such as a powder sample, liquid, or dense laser-shock heated plasma of a single atomic species is

$$\frac{d\sigma_{coh}}{d} (k) = \sigma_t S(k) f(k)^2 \quad (1)$$

where  $\sigma_t$  is the Thomson cross section,  $S(k)$  is the directionally-averaged structure factor and  $f(k)$  is the spherically averaged atomic form factor. The structure factor  $S(k)$  is simply related by a sine transform to  $g_{ii}(r)$ ,

$$S(k) = 1 + (4 \pi \rho/k) \int_0^\infty dr r [g_{ii}(r) - 1] \sin(kr). \quad (2)$$

These well-known expressions establish the close connection between XRD and  $g_{ii}(r)$  while also demonstrating the need to measure the differential scattering cross-section (and hence  $S(k)$ ) at many different momentum transfers if any significant constraint on the form of  $g_{ii}(r)$  is to be obtained.

The  $k$ -dependence of  $d\sigma_{coh}/d\Omega$  can in principle be measured with any suitable combinations of scattering angle  $2\theta$  and photon energies spanning the needed momentum transfers:  $k$  is chosen by the combined effect of these two experimentally-selectable parameters,  $k = (2E/c)\sin 2\theta$ . In practice, however, XRD is measured in only two modes: angle-resolved XRD (henceforth ‘AR-XRD’) and energy-dispersive XRD (henceforth ‘ED-XRD’). Their distinction is best introduced kinematically. As illustrated in Fig. 4.1, any measurement of  $S(k)$

must follow a curve in  $E\text{-}2\theta$  space which crosses many of the shown contours of constant  $k$ . The parameter space probed by a typical AR-XRD experiment using  $\sim 8$  keV monochromatic incident photons is represented by the vertical curve in the figure. Experimentally, the necessary apparatus will include a monochromatic source and either an angle-scanning detector or a position sensitive detector (PSD), which we show schematically in Fig. 4.3 (a) and (b). On the other hand, a typical ED-XRD experiment instead resides on the horizontal curve in Fig. 4.1, *i.e.*, at a fixed scattering angle of 135 degrees but requiring both a broad incident source spectrum and an energy-resolving detector. An experimental schematic for ED-XRD is presented in Fig. 4.3(c). We note that ED-XRD has a long history in laboratory and synchrotron XRD studies, and plays an important role in high-pressure diamond anvil cell research where the limited angular access to the sample space substantially complicates AD-XRD. [127–131] There is then an obvious commonality with experiments at large-scale laser facilities; angular access at such facilities is strongly constrained by the beam paths of the laser light itself.

AD-XRD from laser-shock compressed, disordered Al has recently been reported by Ma, *et al.*, [39] and this first such study illustrates both the scientific benefits and technical drawbacks of AD-XRD for large-scale laser facilities. Specifically, concerning the latter, a few high-resolution spectrometers must be moved between different scattering angles for different shots so as to obtain a complete characterization of  $S(k)$  by pooling the results of many shots after suitable normalization or other characterization of shot-to-shot variations in the source or target. While the study of Ma, *et al.*, [39] has overcome these challenges and provides an interesting comparison of experiment to modern theoretical treatments of the structure of dense plasmas, it is still important to note that the use of a multi-shot technique has, at a minimum, decreased the range of phase space that can be studied subject to the strong constraints that exist on facility access. A single-shot alternative could therefore have high scientific impact and is likely the only way that  $S(k)$  will be measured on disordered dense plasmas at the National Ignition Facility, where the number of shots per scientific study is especially limited.

Consequently, with the above context established, we report here a photometric analysis of ED-XRD for laser-shock experiments illuminated by broad-band backlighter sources. This analysis makes use of known results for the spectrum of a broad-band backlighter, representative experimental results for  $S(k)$  for disordered systems, and representative, established technical characteristics of spectrally-resolving detectors available at large-scale laser facilities. We find significant benefits to ED-XRD for disordered systems, including single-shot determination of  $S(k)$ , and we propose that ED-XRD should become a standard diagnostic at large-scale facilities such as OMEGA and the National Ignition Facility.

We continue as follows. In section 2 we describe the methods used in the photometric analysis, including the reference target, modeled experimental geometry, and any assumptions about detector or spectrometer performance. In section 3 we present and discuss our results for ED-XRD using each of two different experimental configurations. These are, first, an x-ray CCD detector operating in single-photon mode as an energy-resolving solid-state detector and, second, a wavelength-dispersive spectrometer using a highly-oriented pyrolytic graphite (HOPG) mosaic crystal as the diffractive element. The CCD configuration is viable, but has some drawbacks associated with saturation and double-counting that require special care. We find that the HOPG-based spectrometer quite easily resolves the energy spectrum of the diffraction with excellent counting statistics for a broad-band backlighter that has been fielded at OMEGA, with the caveat that a single HOPG crystal analyzer covers a narrower energy range, and hence a more restricted  $k$ -range, than a CCD detector. Finally, in section IV we conclude.

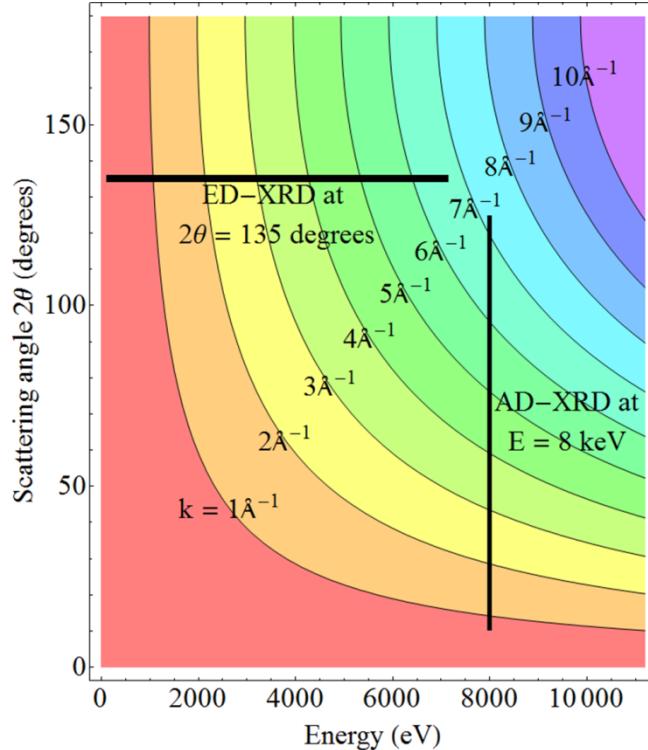
## 4.2 II Methods

### 4.2.1 II.A. Source and target

One readily available broadband source in laser shock experiments is the thermal spectrum from a laser-imploded polymer shell, usually filled with H<sub>2</sub>-D<sub>2</sub> gas [40, 132]. In Fig. 4.6 we show a typical spectrum collected at OMEGA. Because of the spectrum's supra-exponential

decay, an ED-XRD experiment with this source is preferentially conducted at low energy, between 2 and 6 keV, as shown in the ED-XRD curve at a scattering angle of 135 degrees in Fig. 4.1. Also shown in Fig. 4.6 is the spectrum for a typical narrow band backlighter source at OMEGA, where these sources have seen extensive use in x-ray scattering studies, both elastic (XRD) [39] and inelastic (usually called ‘x-ray Thomson scattering’) [26]. The narrow-band spectrum is obtained by scaling the spectrum of a Cu  $K$  target driven by a 10 J, 10 ps laser pulse at the MTW laser facility to a 2.5 kJ, 10 ps laser pulse at OMEGA, using a typical  $K$  photon yield of  $4 \cdot 10^{10}$  photons per J of laser energy. [133]

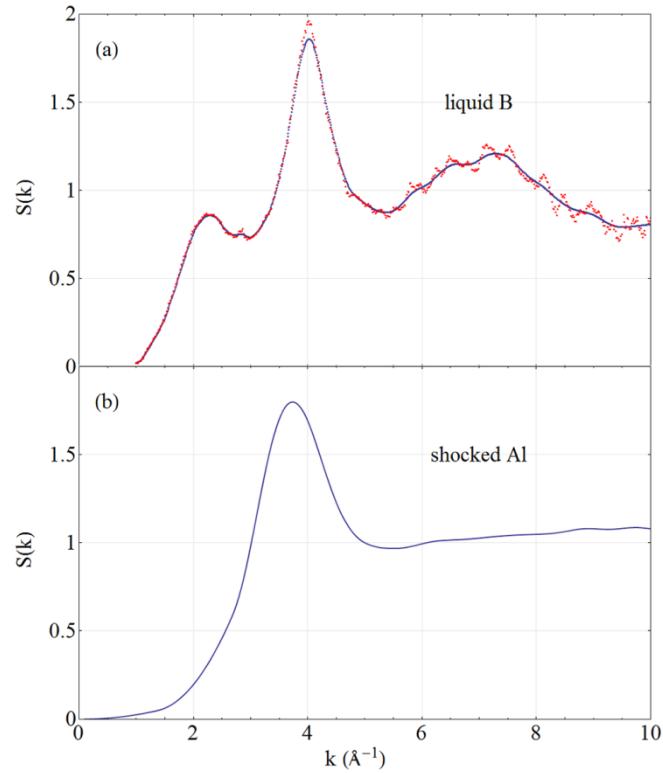
Figure 4.1: Contours of equal momentum transfer  $k$  (labeled in units of  $\text{\AA}^{-1}$ ) in energy and scattering angle. Angle-dispersive x-ray diffraction (AD-XRD) and energy-dispersive x-ray diffraction (ED-XRD) take vertical and horizontal cuts, respectively, to achieve broad coverage in  $k$  and thus obtain information about the radial distribution function.



We consider two target systems where experimental  $S(k)$  are available: liquid boron at

ambient pressure and shock-compressed aluminum. For liquid boron we use the experimental results of Krishnan *et al.* [73, 134], the data for which were taken at a synchrotron light source using hydrodynamically-levitated boron heated to 2400K by continuous illumination from infrared lasers. While this is not a WDM system *per se*, it is a reasonable surrogate. As shown in Fig. 4.2.1 (a), note the presence of a few broad peaks in  $S(k)$ , representative of a system with only limited, short-range information in  $g_{ii}(r)$ . For clarity in our photometric analysis, we will use a smoothed  $S(k)$  where the sharp (nonphysical) noise in the experimental  $S(k)$  has been filtered. On the other hand,  $S(k)$  for shock-compressed aluminum ( $n_e = 5.4 \cdot 10^{23} \text{ cm}^{-3}$ ;  $T_e = 10 \text{ eV}$ ) is based on results from Ma *et al.* [39], who have recently reported the first AD-XRD measurement of a shock-compressed, disordered WDM system.  $S(k)$  was recovered from Ma *et al.*'s theoretical calculation of an elastic scattering profile for triply-ionized shock-compressed aluminum, to which they fit their data. We note that only an approximate atomic form factor, that of ambient aluminum, was used to calculate  $S(k)$  from the scattering profile; however, the resulting error in  $S(k)$  is expected to be negligible above  $k = 3A^{-1}$ , and hence does not affect the location of any coordination peaks. As shown in Fig. 4.2.1 (b), note again that the presence of only short-range order in the target results in a simple form for  $S(k)$ . In this case, the information content is largely limited to the location and intensity of the obvious first coordination peak.

Figure 4.2: (a): Liquid structure factor of B at 2400K. The original data (red) of Krishnan *et al.* [73] contains sharp unphysical noise; we therefore use the filtered interpolation (blue) of the data for  $S(k)$  throughout this paper. (b): Equivalent theoretical curve for shock-compressed Al at electron density  $n_e = 5.4 \cdot 10^{23} \text{ cm}^{-3}$  and temperature  $T_e = 10 \text{ eV}$  based on Ma. [39] The curve is based on an approximate treatment of this system's atomic form factor (see the text for details).



#### 4.2.2 II.B. Photon-electron interactions and numerical modeling

For the targets considered here, the experiment is conducted in an energy region far above any atomic fluorescence from the targets and also far above any soft x-ray blackbody radiation from the surface or bulk of the target, each of which is easily attenuated in practice with a thin plastic or Be shield. Consequently, we need only consider the coherent and incoherent scattering of the x-rays as direct contributors to the measured scattering signal; the photoelectric interaction appears only in its contribution to absorption coefficient in the energy range of interest. Note that by coherent here we refer to the quasielastic scattering process itself, *i.e.* “ordinary” diffraction, with no expectation of coherence of the incident beam (such as is used in diffraction experiments at XFEL facilities).

Given a backlighter source with fluence  $I_{\text{source}}(E)$  (units of photons/eV, integrated over 4 steradian) at a distance  $d_{\text{source}}$  from the target, the areal flux incident in the target is  $I_{\text{incident}}(E) = I_{\text{source}}(E) / 4\pi d_{\text{source}}^2$ . The contribution of coherent scattering to the measured energy spectrum at a scattering angle  $2\theta$  is then

$$I_{\text{coh}}(E, 2\theta) = I_{\text{incident}}(E) \frac{d\sigma_{\text{coh}}}{d}(k) d\Omega_{\text{det}} \eta_{\text{det}}(E) \tau_{\text{coh}}(E, 2\theta), \quad (3)$$

where  $k$  is implicitly determined by  $E$  and  $2\theta$ ,  $d\Omega_{\text{det}}$  is the solid angle subtended by the detector,  $\eta_{\text{det}}(E)$  is the net efficiency of detection of photons of energy  $E$  that arrive in  $d\Omega_{\text{det}}$ , and  $\tau_{\text{coh}}(E, 2\theta)$  includes the necessary corrections to the measured XRD due to the target’s geometry and energy-dependent absorption coefficient [34]. When operating near to a backscattering geometry, for example,  $\tau_{\text{sample}}(E, 2\theta) \sim \rho A(1 - e^{-2\mu(E)d})/2\mu(E)$  where  $\rho$  is atomic (number) density,  $A$  is the cross-sectional area of the portion of the backlighter beam that illuminates the target region of interest,  $d$  is the target thickness, and  $\mu(E)$  is the x-ray absorption coefficient. For present purposes,  $d\sigma_{\text{coh}}/d\Omega$  includes all elastic and quasielastic scattering; it integrates over all ion-ion correlation dynamics [135].

The incoherent contribution to the measured signal is somewhat more complex to model. The microscopic physics of the incoherent scattering processes, wherein one must address both momentum transfer ( $k$ ) and energy transfer ( $\omega$ ), results in the need for a double dif-

ferential cross-section  $d^2\sigma_{\text{incoh}} \frac{(k,\omega)}{d\Omega} \Omega$ . The detected intensity from incoherent scattering is then

$I_{\text{incoh}}(E, 2\theta) = d\Omega_{\text{det}} N_{\text{atoms}} \frac{d\sigma_t}{d\Omega} \int_0^\infty dE' I_{\text{incident}}(E') S_{\text{incoh}}(k, \omega) \tau_{\text{incoh}}(E', E, 2\theta)$  (4), where  $N_{\text{atoms}}$  is the number of atoms in the target,  $k$  is again implicitly determined by  $E$ ,  $E'$ , and  $2\theta$  and  $\tau_{\text{incoh}}(E', E, 2\theta)$  includes the influence of attenuation for an incident photon of energy  $E'$  that scatters through an angle  $2\theta$  and departs the incoherent interaction with energy  $E$ . In the first Born approximation,  $d^2\sigma_{\text{incoh}}/d\omega d\Omega = (d\sigma_t/d\Omega) S_{\text{incoh}}(k, \omega)$ , where  $d\sigma_t/d\Omega$  is the Thomson differential scattering cross section and  $S_{\text{incoh}}(k, \omega)$  is the inelastic component of the dynamic structure factor. In the independent-electron approximation [27, 136],  $S_{\text{incoh}}(k, \omega)$  may be expressed as a sum over electrons and matrix elements between the initial and final states of the system:

$$S_{\text{incoh}}(k, \omega) = \sum_j \sum_{f \neq i} \left| \langle i | e^{i \mathbf{q} \bullet \mathbf{r}_j} | f \rangle \right|^2 \delta(E_f - E_i - \omega). \quad (5)$$

At sufficiently high  $k$ ,  $S_{\text{incoh}}(k, \omega)$  is peaked at the Compton shift  $\Delta E = ^2k^2/2m$ . In the high- $k$  (non-collective) scattering regime the total inelastic portion of the dynamic structure factor is constructed using equation (5) evaluated as a sum over individual valence and core electrons. In our modeling procedure this consists of truncated valence and core Compton profiles generated in the impulse approximation [36, 136] where  $S_{\text{incoh}}(k, \omega)$  depends only on the ground state electronic density and kinematics of the scattering process. The first moment of  $S_{\text{incoh}}(k, \omega)$  was normalized after truncation according to the Bethe  $f$ -sum rule [37]. For boron our approximation yields incoherent scattering cross sections which exceed experimental values by up to 30 percent, making our approximate treatment of the incoherent background conservative. In the relevant range of momentum transfers the Compton shift is sufficiently small that we substitute  $\tau_{\text{coh}}(E, 2\theta)$  for  $\tau_{\text{incoh}}(E, E', 2\theta)$  without introducing appreciable systematic error, allowing  $\tau$  to be factored out of the integrand in equation (4). Similarly, the FWHM of  $S_{\text{incoh}}(k, \omega)$  (which, in the impulse approximation, is directly related to the width of the momentum distribution of the electronic ground state) is small compared to our required energy resolution, such that we can define a Compton-shifted energy variable  $E^* = E + \Delta E$  and re-express (4) in approximate form:

$$I_{\text{incoh}}(E, 2\theta) = d\Omega_{\text{det}} N_{\text{atoms}} \frac{d\sigma_t}{d\Omega} \tau_{\text{coh}}(E, 2\theta) I_{\text{incident}}(E^*) \int_0^\infty dE' S_{\text{incoh}}(k, \omega). \quad (6)$$

The total scattered intensity, in units of photons/sr, is then

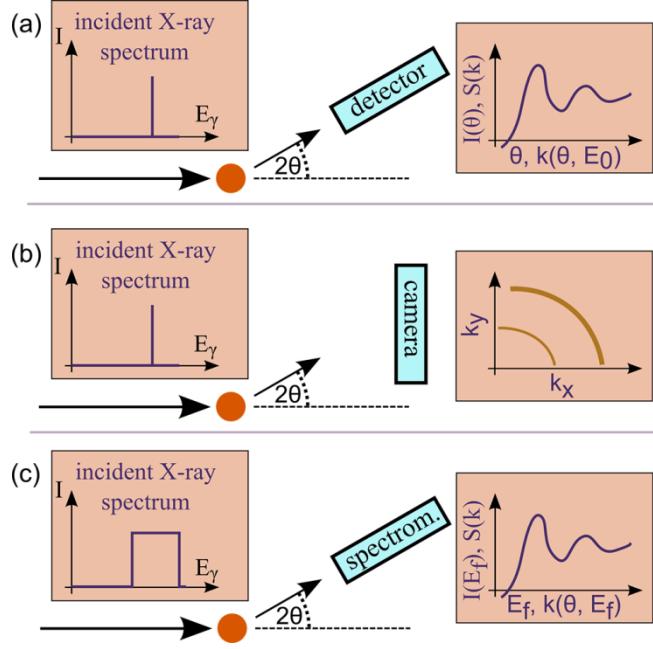
$$\mathbf{I}_{\text{total}}(\mathbf{E}) = d\Omega_{\text{det}} N_{\text{atoms}} \tau(E, 2\theta) \frac{d\sigma_t}{d\Omega} [\mathbf{I}_{\text{incident}}(\mathbf{E}) f(\mathbf{k})^2 \mathbf{S}(\mathbf{k}) + \mathbf{I}_{\text{incident}}(\mathbf{E}^*) \int_0^\infty dE' S_{\text{incoh}}(k, \omega)]$$

Note that  $\int_0^\infty dE' S_{\text{incoh}}(k, \omega) = N$  (the atomic number of the scattering species) in the high- $k$  limit of the impulse approximation [36] and takes on smaller values at lower momentum transfers; by comparison,  $f(0)^2 = N^2$ , and  $S(k)$  is of order unity. Therefore the first (coherent) term in  $I_{\text{total}}(E)$  dominates for heavier elements or for sufficiently small momentum transfers. In Fig. 4.7 (a) and (b) we compare  $f(k)^2$  to the incoherent background scattering for the above-described model. These results lead us to expect that the background in an ED-XRD experiment will not substantially limit the ability to observe the desired coherent scattering.

#### 4.2.3 II.C. Spectrometers for detection of ED-XRD

We now consider two different detection options. As shown in the schematic of Fig. 4.3, one or both of an x-ray CCD and a HOPG-based spectrometer may be used as energy-sensitive detectors. Simulated spectra for both follow in section III. Throughout the remainder of the paper the following experimental parameters are used:  $d_{\text{source}} = 1 \text{ cm}$ ; target dimensions (for both B and Al): 0.25 mm 0.25 mm 0.1 mm; scattering angle  $2\theta = 135$  degrees. These choices will be motivated below.

Figure 4.3: Schematic representations of (a) and (b) angle-dispersive x-ray diffraction, compared to (c) energy-dispersive x-ray diffraction (ED-XRD).

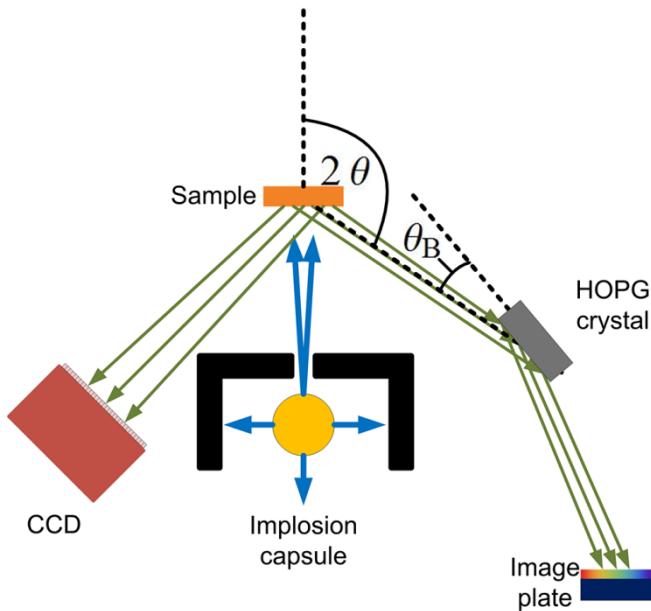


The modeled CCD has a 2-dimensional square grid of 2200 x 2200 pixels, with a pixel edge length of 13.5 microns. A quantum efficiency of 1 is assumed. The optimal distance between the detector and the target is determined by the competing demands of high signal collection and high rejection of two-photon events on single pixels. We find it reasonable to balance these demands by selecting a single photon-hit regime with an expectation value  $p$  of 0.1 photon hits per pixel. At a given scattering angle and in the absence of addition of any special absorbers between the target and the CCD other than a Be filter for low-energy photon rejection,  $p$  is determined by the working distance of the CCD and the scattered intensity off the target. The working distance is not a highly-constrained parameter; it must merely be sufficiently large that backgrounds from the high neutron flux and other stray radiations are likely to be substantially suppressed. An upper bound on target intensity arises from signal broadening due to the finite angular size subtended by the target relative to the backlighter. We require this geometrical broadening in momentum transfer,  $\delta k$ , to

satisfy  $\Delta k/k < 0.05$ , such that it is sufficiently small compared to the intrinsic scale of structure in  $S(k)$ . We label the angle subtended by the target  $\Delta\theta_t$  and express the geometrical broadening in terms of it:  $\Delta k/k = \cot \theta_t$ . At  $2\theta = 135$  degrees the maximal  $\Delta\theta_t$  is approximately 0.1 radians, which corresponds to a sample length of 1 mm.

The task of presenting a modeled HOPG spectrum in a non-configuration-specific manner is complicated by the significant dependence of the spectrometer's energy range on several geometric parameters. Using the labeling of Fig. 4.4 and, as an example, the spectrometer geometry described by Fig. 4.5 (a), the differential in  $k$  for scattering from the target is

Figure 4.4: Experimental configuration for ED-XRD at a laser shock facility. A long pulse-driven CH capsule emits a broad thermal spectrum. Scattering from the target is observed using an HOPG spectrometer or a CCD in the single-photon hit regime.



$$dk = \frac{k}{E} dE + \frac{k}{\delta(2\theta)} d(2\theta) = \frac{E}{c} (\sin(\theta) \cot \theta_B - \cos(\theta)) d\theta. \quad (9)$$

As a crystal of length  $l$  located a distance  $F$  from the target subtends an angle of approximately  $(l/F) \sin \theta_B$ , we can directly use (9) to calculate the range  $k$  covered by an analyzer crystal as a function of  $k$ ,  $2\theta$ , and the choice of HOPG reflection. Fig. 4.5 illustrates this.

Salient features of  $\Delta k(k, 2\theta)$  are that it is asymptotically linear in  $k$  and depends weakly on  $2\theta$  everywhere except at low  $k$ .

That said, we can choose a typical configuration for an HOPG spectrometer and generate a detected spectrum that spans the entire range of  $k$  with which we are concerned. Conceptually, this is done by repeatedly rotating the crystal to different central  $\theta_B$  to acquire narrow spectra in different ranges of  $k$  and then stitching together the resulting spectra. This spectrum, which is henceforth referred to as the “HOPG source spectrum”, does not represent a realistic data set, since acquiring it in a single shot would require prohibitively many analyzer crystals, but it does serve as a convenient compilation of the ensemble of possible experimental configurations; the exact choice of spectrometer configuration for a given experiment depends on some prior knowledge of the desired  $k$  range, as we discuss below.

The modeled HOPG spectrometer is qualitatively similar to several instruments that have previously been fielded for x-ray Thomson scattering studies at OMEGA [137, 138]. For our modeled instrument, the HOPG diffractive element operates on the 002 reflection, has a mosaic spread of 0.3 degrees, is taken to be a flat square with side length  $l = 12$  cm, and is located at a distance  $F = 25$  cm from the target. The energy-dependent integral reflectivity of the HOPG is based on computed reflectivity curves [139] for an HOPG crystal having a mosaic spread of 0.3 degrees. Denoting  $r$  as the peak reflectivity and  $\omega$  as the FWHM of the reflectivity curve, the angular integral reflectivity,  $\Delta\theta_B$ , is approximately  $r$ ; equivalently, the integral reflectivity in energy units is  $\Delta E = E \cot \theta_B \Delta\theta_B$ . We define  $E_{\max}$  and  $E_{\min}$  as the maximum and minimum energies diffracted by the crystal. For isotropically-scattered photons with a fixed energy  $E$  between  $E_{\max}$  and  $E_{\min}$  the probability of reflection is  $\eta = \Omega_0 \Delta E / (4 \pi (E_{\max} - E_{\min}))$ , where  $\Omega_0 = (l/F)^2 \sin \theta_B$  is the solid angle subtended by the crystal relative to the source (units of sr). Correspondingly, the detected spectrum resulting from  $I_{\text{incident}}$  on the target is  $I_d(E) = 4\pi\eta dI_{\text{incident}}(E)/d\Omega = \Delta\theta_B(l/F)dI_{\text{incident}}(E)/d\Omega$ . For reference,  $\Delta\theta_B l/F = 7 \times 10^{-4}$  at 4 keV. It will be seen in the next section that the resulting net collection efficiency in a given achievable energy band is several orders of magnitude

higher than that of the CCD.

### **4.3 III Results and discussion**

There is good reason to believe, heuristically, that the above-described experimental configurations for ED-XRD should determine  $S(k)$  with adequate statistics. Numerous past x-ray Thomson scattering experiments at laser plasma facilities have measured the inelastic portion of  $S(k, \omega)$  using narrow pulse backscatterers for illumination [26, 33, 38, 123, 140–142]. Above 2 keV, a broad-band thermal backscatterer has approximately 100 times the photon conversion efficiency of a short-pulse Cu  $K$  backscatterer (Fig. 4.6); additionally, the elastic scattering cross section is typically larger than the Compton cross section, as discussed in section II and shown in Fig. 4.7 (a) and 5 (b). Thus, ED-XRD should offer vastly higher signal intensity than (quasi-monochromatic) x-ray Thomson scattering using a metal-foil backscatterer, and therefore better statistics.

Figure 4.5: Range  $k$  in momentum transfer of scattering off the target probed by a small HOPG crystal per degree of its maximum subtended angle,  $\theta_{\max}$ , for three spectrometer geometries that involve the same position (but different rotations) of the HOPG crystal: (a) the detector located in the target scattering plane and away from the axis passing through the backlighter and target, (b) the detector located in the target scattering plane and near the axis passing through the backlighter and target, and (c) the detector located such that it, the target, and the HOPG crystal define a plane perpendicular to the scattering plane.  $\theta_{\max}$  denotes the maximum possible subtended angle of the HOPG crystal given a fixed spectrometer working distance  $F$ ; *i.e.*, for a crystal of length  $l$ , the maximum subtended angle is  $\theta_{\max} = l/F$ .

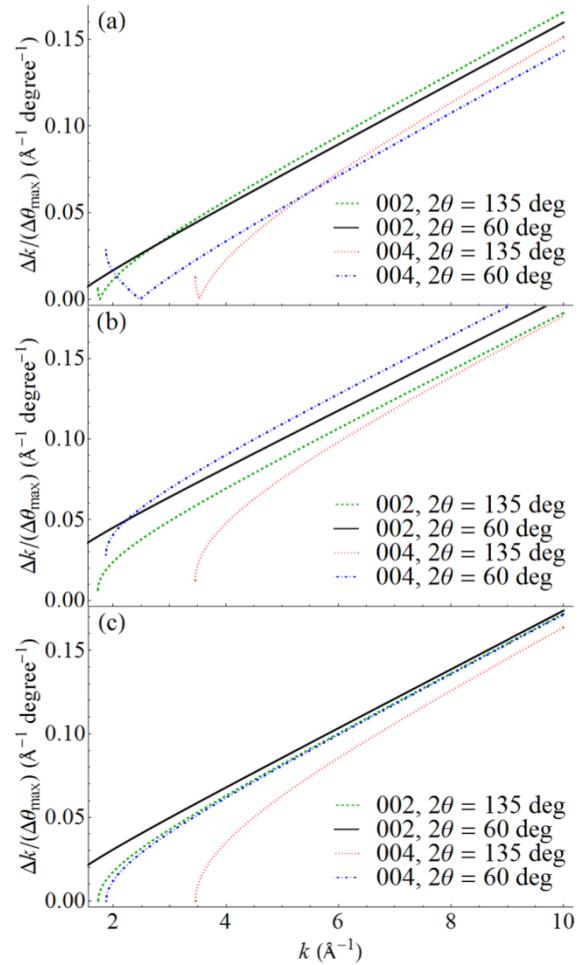


Figure 4.6: Red: experimental thermal backscatter spectrum from OMEGA <sup>43</sup>. Blue: a short-pulse Cu *K* backscatter spectrum, based on scaling of results from a lower energy laser system to a 2.5 kJ, 10 ps laser shot at OMEGA <sup>44, 45</sup>.

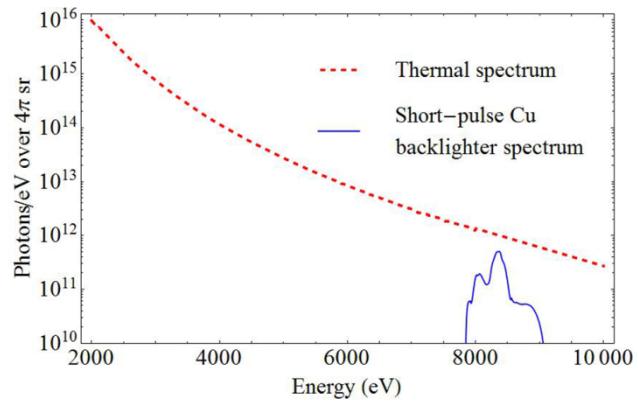
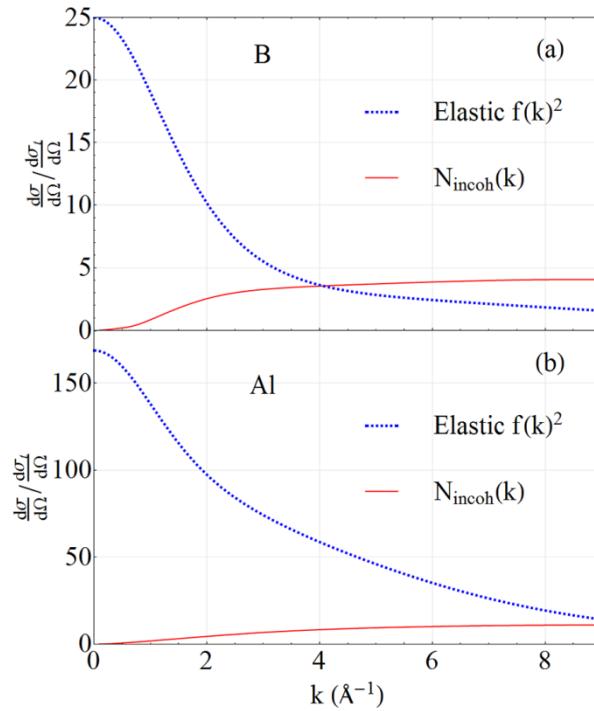


Figure 4.7: Elastic and inelastic contributions to the differential cross section of (a) boron and (b) aluminum. The elastic cross sections are based on tabulated values of  $f(k)$ . The inelastic differential cross sections, defined by  $N_{\text{incoh}}(k) = \int_0^\infty dE' S(k, \omega')$ , are based on  $S(k, \omega')$  generated from  $f$ -summed, truncated Compton profiles in the impulse approximation. See the text for further details.



In Fig. 4.8 we present  $I_d(E)$  defined in section II, filtered by a 20 m Be foil (to reject low-energy photons) for liquid boron acquired on a CCD alongside the equivalent HOPG source spectrum. The highlighted region of the HOPG source spectrum shows the energy range covered by a specific configuration: a 12-cm long HOPG crystal at distance  $F = 25$  cm from the target, oriented such that the detected spectrum is centered on the main correlation peak in  $S(k)$ . This crystal size results in a solid angle subtended by the crystal similar to that in existing high-efficiency HOPG spectrometers. [143] Figure 4.9 shows the CCD and HOPG spectra for shock-compressed Al in this same format.  $S(k)$  reconstructed for B and Al is presented in Figs. 4.10 and 4.11, respectively. In both these figures the  $k$ -range probed by the specific spectrometer configuration is highlighted. All reconstructed  $S(k)$  curves, including those without background subtraction, show a well-defined correlation peak. Note that the uncorrected curves overshoot the experimental  $S(k)$  at large  $k$ ; this is a result of the monotonically-increasing Compton background (as well as double-counts, for the CCD). This background decreases relative to the XRD signal for larger atomic numbers, as seen by comparison of Figs. 4.10 and 4.11. The HOPG source spectrum exhibits excellent statistics (error bars < 2 percent) relative to the CCD over the entire plotted energy range. While deteriorating at high energy, the CCD spectrum also has good statistics (error bars < 5 percent) below 4.5 keV.

The relative merits of the two detectors are dictated by particular features of the ED-XRD configuration and the spectrum probed. Despite the substantially better energy resolution of an HOPG spectrometer compared to a Fano-noise limited CCD, energy resolution is a poor criterion for comparison: at 135 degrees scattering angle, the  $k$ -width of features in  $S(k)$  corresponds to a width in energy greater than 500 eV, substantially larger than the resolution of both the CCD and the HOPG spectrometer. Instead, the leading limitation on data quality is shot noise at high  $k$  due to the sharp decay of the source spectrum intensity with increasing energy.

The latter limitation is severe only for the CCD, (1) because of vastly lower overall counts and especially (2) because the intense low-energy portion of the incident spectrum

is ‘echoed’ as double-counts at higher energy. In simulated CCD spectra the double-count contribution to the detected spectrum outweighed the single-count contribution above 5 keV. This double-count noise cannot be reduced by varying  $p$ : in the single photon-hit regime, the number of double-hits on single pixels scales as  $p^2$ ; the associated Poisson noise scales as  $p$ . Single photon counts also scale as  $p$ ; as a result, above 5 keV varying  $p$  has little effect on the signal-to-noise (*i.e.* single-to-double-count) ratio. It is instead highly preferable to carry out an ED-XRD experiment in near-backscatter geometry, such that the range of  $k$  in which  $S(k)$  has structure is probed by a lower-energy region of the backscatter spectrum. In fact, the only means of significantly improving data quality on a single hit CCD are (1) using a detector with more pixels to improve statistics, and (2) moving the detector closer to backscatter.

Figure 4.8: Photon-energy histograms for energy-dispersive diffraction spectra of liquid boron on CCD and HOPG spectrometers. The expectation value of photon counts/pixel on the CCD is  $p = 0.1$ . The energy range of a specific HOPG configuration using a 12-cm long HOPG analyzer is denoted by the shaded region, the width of which corresponds to the spectrometer configuration of Fig. 4.5 (a). The spectrometer's focal length is 25 cm, and the length of the crystal in the non-energy dispersive orientation is 12 cm; both spectrometers are positioned at  $2\theta = 135$  deg. A 20-m thick Be foil is used to reject low-energy photons. Error bars in the HOPG histogram are smaller than the size of the symbols.

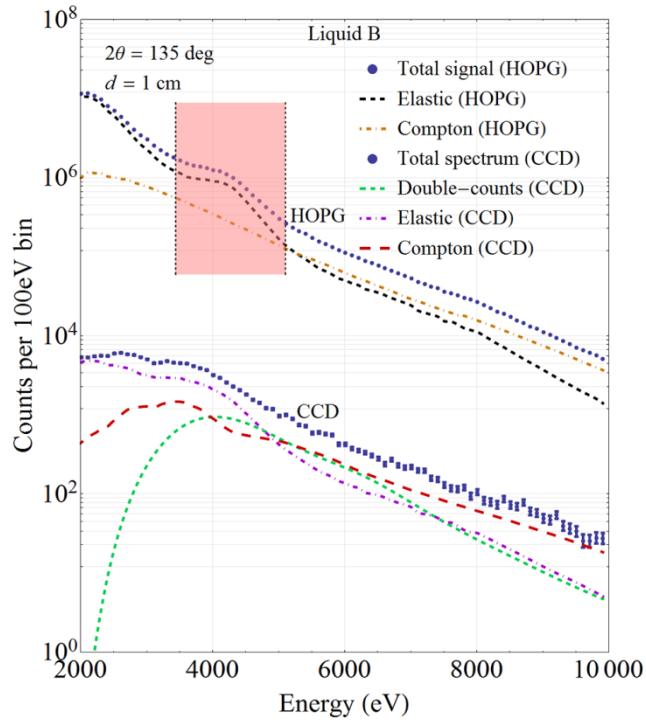
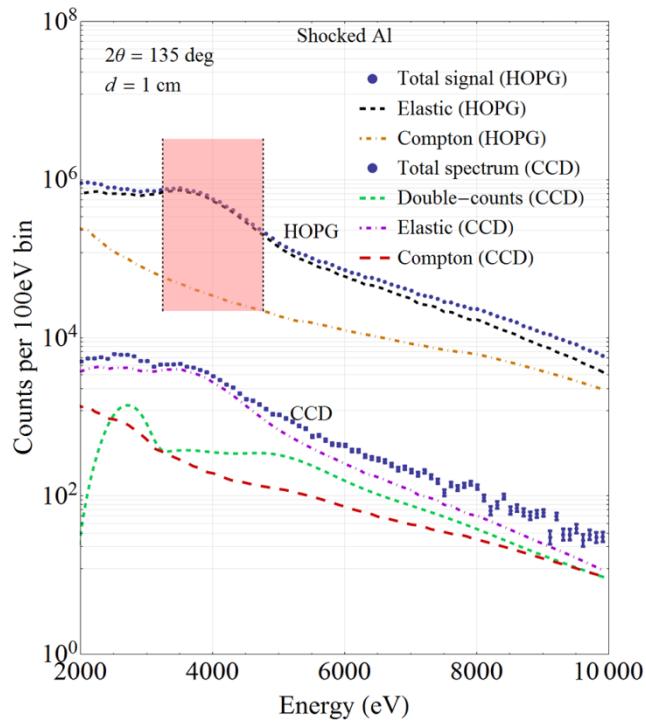


Figure 4.9: Photon-energy histograms on CCD and HOPG spectrometers for shock-compressed Al at electron density  $n_e = 5.4 \cdot 10^{23} \text{ cm}^{-3}$  and temperature  $T_e = 10 \text{ eV}$ , using Ma *et al.*'s best-fitting theoretical model to their experimental results for  $f(k)^2 S(k)^{35}$ , and assuming  $f(k)$  of ambient Al. The expectation value of photon counts/pixel on the CCD is  $p = 0.1$ . The energy range of a specific HOPG configuration using a 12-cm long HOPG analyzer is denoted by the shaded region, the width of which corresponds to the spectrometer configuration of Fig. 4.5 (a). The spectrometer's focal length is 25 cm, and the length of the crystal in the non-energy dispersive orientation is 12 cm; both spectrometers are positioned at  $2\theta = 135 \text{ deg}$ . A 20-m thick Be foil is used to reject low-energy photons. Error bars in the HOPG histogram are smaller than 1% (not shown).



The two spectrometer types offer a variety of configurations adapted to experimental situations in which different  $k$ -ranges need to be probed. If the goal is to locate the main correlation peak in  $S(k)$ , a single-HOPG crystal spectrometer is a viable option (illustrated, as mentioned above, in Figs. 4.10 and 4.11). On the other hand, if the scientific goal requires a significantly wider  $k$ -range, then a CCD detector in single photon counting mode, multiple HOPG analyzer crystals, or both are necessary. Despite the CCD's relatively poor signal to noise ratio, there is substantial motivation for performing ED-XRD using both spectrometer types if the full  $k$  range is desired. In such a dual configuration the CCD would provide low-noise data up to approximately 4.5 keV with one or more HOPG spectrometers covering the remainder of the energy spectrum, corresponding to a reduced range of  $\theta_B$  from 21 to 49 degrees, for which a modest number of analyzer crystals would be required.

The above results establish single-shot ED-XRD as a viable method for use at OMEGA, even for systems with only liquid-like, isotropic short-range order; this observation clearly extends to fine, isotropic polycrystalline systems where the structure in  $S(k)$  can only be sharper. We note that pump laser energy is 30 times larger at NIF than at OMEGA and that the ratio of backlighter fluences exceeds that factor due to the higher backlighter electron temperature at NIF. [132] Consequently, ED-XRD is also viable at NIF where the higher backlighter fluence may allow a substantial reduction in solid angle subtended by an HOPG spectrometer, compared to present calculations. This would in turn allow incorporating a larger number of spectrometers in a single diagnostic module. CCD-based studies at NIF are also, in principle, viable but may run into technical difficulties related to neutron backgrounds or difficulty in shielding from electromagnetic pulses.

Figure 4.10:  $S(k)$  for liquid boron reconstructed from simulated energy-dispersive spectra of Fig. 4.8 for (a) an HOPG spectrometer and (b) a CCD, with and without subtraction of Compton background and photon double-counts. Data bin size is 100 eV. The shaded  $k$ -range in the HOPG spectrum corresponds to the spectrometer configuration described in the text, and is centered about the main correlation peak in  $S(k)$ .

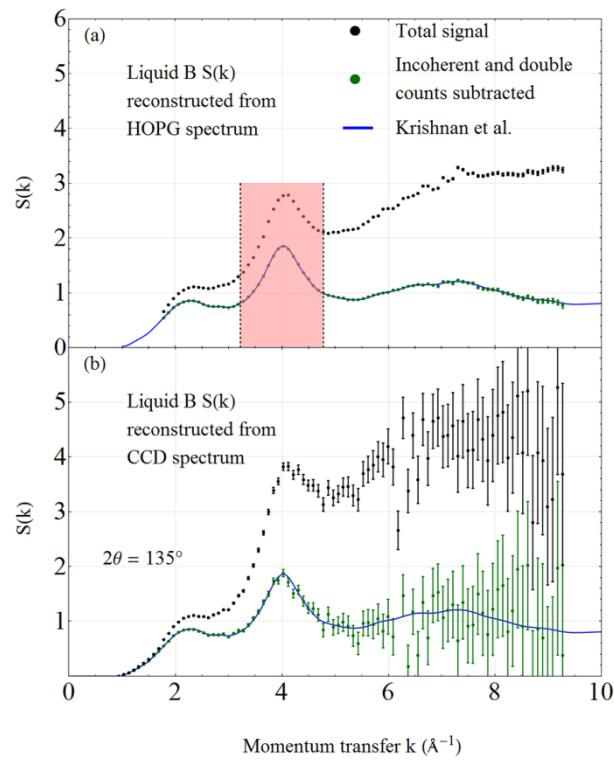
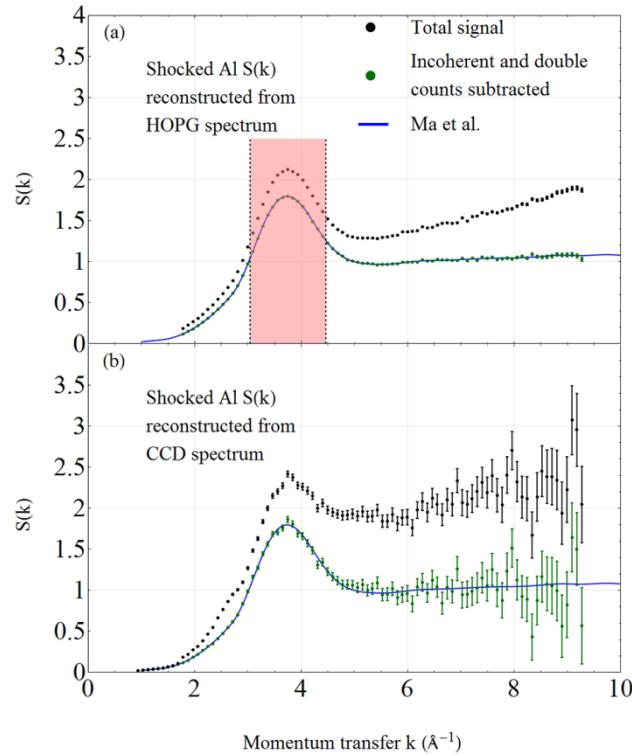


Figure 4.11: In blue: X-ray structure factor  $S(k)$  for shock-compressed Al computed from Ma, *et al.*<sup>35</sup>. Overlaid with  $S(k)$  reconstructed from the spectra of Fig. 4.9 for (a) an HOPG spectrometer and (b) a CCD. The data bin size is 100 eV. The shaded  $k$ -range in the HOPG spectrum corresponds to the spectrometer configuration described in the text and is centered about the main correlation peak in  $S(k)$ .



#### 4.4 IV. Conclusions

We report a photometric study of the viability of single-shot investigation of the isotropic static structure factor  $S(k)$  in experiments using a broadband x-ray backlighter as the source for energy-dispersive x-ray diffraction (ED-XRD). The results are extremely favorable, and indicate that single-shot ED-XRD can be used at OMEGA or NIF. A standard scientific-grade x-ray CCD camera operating in single-photon counting mode suffices for many studies, but exhibits degraded performance at high momentum transfers due to the rapid decrease of

incident flux at higher photon energy. On the other hand, a typical HOPG-based wavelength dispersive spectrometer has exceptional count rates in any selected  $k$  range, but its limited energy range may require either the use of multiple spectrometers or of a single compound spectrometer having multiple analyzer crystals.

### ***Acknowledgements***

We thank Brian Mattern, Tilo Doeppner, Philip Nilson, Barukh Yaakobi, Christian Stoeckl, Yuan Ping, Justin Wark, and Andrew Higginbotham for helpful discussions. This work was supported by the US Department of Energy, Office of Science, Fusion Energy Sciences and the National Nuclear Security Administration, through grant DE-SC0008580.

## Chapter 5

# X-RAY FREE ELECTRON LASER-BASED STUDIES OF WDM

### 5.1 *X-ray Free Electron Lasers*

XFELs produce radiation of unprecedented brilliance (10 orders of magnitude higher than undulator radiation from third-generation synchrotron sources), full transverse coherence, and pulse durations as short as 10 fs. This combination of capability far exceeds that possible with third-generation light sources and opens new frontiers in imaging and the interrogation of ultrafast processes in materials science and biology. In this section we give an overview of the technology and its range of applications in the study of HED states of matter.

#### 5.1.1 *Physics of XFELs*

To describe the FEL interaction, we first consider the generic case of radiation emission from undulators, the type of insertion device used in both XFELs and the highest-brilliance beamlines at third-generation synchrotron light sources.

A simple time-of-flight argument may be used to obtain an intuitive understanding of radiation by a single electron in an undulator. A radiation wavefront co-propagating with an electron undergoing forced transverse undulation with a (longitudinal) period  $\lambda_u$  will move ahead of the electron. Constructive interference of the radiation field produced by successive undulations of the electron will occur at discrete values of the electromagnetic wavelength,  $\lambda_n$ , satisfying  $\lambda_n = \lambda_1/n$ , where  $\lambda_1$  is defined as the fundamental resonant wavelength. The time  $t$  taken for an electron to propagate one undulator period  $\lambda_u$  at speed  $v_z$  ( $t = \lambda_u/v_z$ ) is equal to that needed for a resonant wavefront travel the distance  $\lambda_u + n\lambda_n$ . Equating the propagation times for the wavefront and electron yields the relation [144]

$$\lambda_n = \frac{\lambda_u}{n} \left( \frac{1 - v_z/c}{v_z/c} \right). \quad (5.1)$$

More detailed treatment shows that, in the case of a helical undulator, only the fundamental mode has strong on-axis emission. [145]

This describes the narrow spectral width of undulator radiation and the coherent addition of radiated wave amplitudes by a single electron over the length of an undulator. This constructive interference accounts for the much higher brilliance of radiation produced by an undulator, compared to a wiggler or bending magnet.

At a synchrotron light source electrons in a bunch have uncorrelated positions, and the undulator spectrum is therefore a simple incoherent sum of the emission of all individual electrons passing through it. An XFEL improves on this by creating a positional ordering electrons into ‘micro-bunches’ separated from one another by the radiation field wavelength. The coherent emission from multiple micro-bunches with  $N_b$  electrons each would be equivalent, in an idealized case where the micro-bunch dimension were much smaller than the x-ray wavelength, to that from point-like charges of magnitude  $eN_b$ , with a resulting factor of  $N_b^2$  enhancement in brilliance relative to that from an incoherently-emitting electron bunch.

Electrons in an undulator experience a longitudinal force from the radiation field that is modulated by its period. The consequent bunching of electrons with a period equal to the X-ray wavelength is a self-reinforcing process referred to as self amplified stimulated emission (SASE). [146] Crucially, the occurrence of SASE requires a sufficiently strong initial radiation field, [147] which third-generation synchrotron storage rings—having 100 ps-duration electron bunches—are not capable of producing. The key feature of an XFEL is its use of a linear accelerator to produce very compact electron bunches with sufficient electron density to bootstrap SASE.

### 5.1.2 XFELs and WDM generation

Single-shot flux densities available from focused XFEL beams exceed  $10^4 \text{ J/cm}^2$ , sufficient to produce HED states with per atom energy deposition over 100 eV with uniform, volumetric heating. Because XFEL radiation is monochromatic it can be used as a probe for nearly all X-ray diagnostics useful for determination of the state variables of WDM, with the notable exception of XAS. Taken together, these characteristics make XFELs ideal for both producing and probing short-timescale dynamics of HED matter.

One of the most significant recent advances in XFEL technology is the generation of two-color pairs of hard X-ray pulses. This is done by production of time-delayed twin electron bunches (achieved either by illuminating the source cathode with a train of two laser pulses, or using an emittance spoiler) and the addition of magnetic chicanes that introduce a time-energy correlation in the electron beam before the bunches' entry into the undulator. [148] At the LCLS, two color X-ray pulse energies up to the mJ level—approaching the values of single-pulse SASE—have been demonstrated. [149] X-ray arrival time delays are variable between 30 and 125 fs, and maximum color separations of up to 1.9 % of the photon energy have been demonstrated. [150]

Operating an XFEL in two-color mode opens up significant possibilities for truly time-resolved probes of WDM. In single-pulse operation the time evolution of an XFEL-heated target can, to some extent, be studied by variation of pulse duration. However, such a study yields a signal that, for each XFEL configuration, is a convolution over all intermediate states of the target as it heats throughout each pulse's duration. In contrast, two-color operation offers two advantages:

- Temporal resolution: by choosing pulse energies that straddle an absorption edge of a chemical filter (in the case of an XRD probe), or of the target itself (in the case of an XES probe), signal from the pump pulse can be rejected. Varying pump-probe delay thus allows measuring the sample's temporal response to the pump.

- Uniformity of probed state: By additionally reducing the intensity of the probe relative to the pump, one can ensure that the probe is only a weak perturbation to the heated state generated by the pump.

The possibility of clean time-resolved studies of XFEL-generated WDM is quite attractive, given that the electronic relaxation cascade in a heated solid consists of several partially-overlapping stages of uncertain durations: i.e. collisional ionization by hot electrons; stimulation of long-wavelength collective excitations; and damping of large- $q$  excitations through production of electron-hole pairs. Lack of prior information in the physics under scrutiny emphasizes the need for the highest-information diagnostics available.

## **5.2 HED physics at XFEL facilities**

### *5.2.1 Prior work*

Initial efforts at FLASH and LCLS, the first free electron lasers operating at short wavelengths, have been focused on the creation of exotic states and the exploration of interactions of high-intensity hard X rays with matter. Thomas et al. and others have studied the Coulomb explosion of noble gas clusters, including the dynamics of nanoplasma formation. [151] Using intense XFEL radiation Young et al. demonstrated the production of fully-stripped Ne atoms as well as induced X-ray transparency in ‘hollow’ atoms, a manifestation of ‘beating’ the Auger clock though ionization rates faster than the recombination times of core electrons. [152, 153] Their modeling of x-ray/atom interactions using a rate-equation based approach yielded predictions of atomic populations consistent with electron spectroscopy, providing an early validation of the application of population kinetics codes such as SCFLY to the simulation of XFEL-matter interactions. [154]

Nagler et al. have similarly demonstrated saturable absorption of an L-shell transition in Al, where the long lifetime of 2p vacancies allowed complete depopulation within a single XFEL pulse at incident intensities on the order of  $10^{16}$  W/cm<sup>2</sup> and 92 eV photon energy. [155] This experiment was one of the first demonstrations of a bulk, crystalline material in

a high-energy density (and highly non-thermal) electronic configuration.

Finally, a significant subset of XFEL-based studies of WDM rely on optical or infrared pump to produce HED conditions. The Matter in Extreme conditions (MEC) endstation at the LCLS is largely dedicated to this type of experiment. Its combination of short- (40 fs pulse duration) and long- (2 to 200 ns pulse duration) laser systems (each with per-pulse energies exceeding 1 J) renders accessible a significant range of laser-generated HED systems. Highlights of early experiments in this regime include diffraction and phase contrast imaging of shocked materials—studies that require both a laser drive and x-ray probe sources with one or more of the high flux, brilliance, and coherence of an XFEL.

### **5.3 Scientific Directions**

#### *5.3.1 Time dynamics of WDM states*

The ability of XFELs to produce such transient HED states invites basic questions about the creation of these states and their temporal evolution. Population kinetics codes such as SCFLY are well-established tools to simulate the electronic evolution of an XFEL-heated material, but such codes are based on atomic physics treatments and cannot be all-encompassing, as they omit solid-state electronic structure as well as the interaction of electrons with the lattice of a solid-density system. Hau Riege et al. have examined electron-ion dynamics during heating by a single XFEL pulse, using comparison of Bragg diffraction from heated graphite with molecular dynamics simulation to quantify perturbation of the atomic lattice. They have identified melting of the graphite lattice within 40 fs pulses—far shorter in duration than the ps-timescale of electron-phonon coupling indicating an ultrafast phase transition. We revisit Hau-Riege’s conclusions in a different light in Chapter 6, but their work pertinently demonstrates that the characterization of even coarse-grained quantities such as lattice thermalization timescales gives insight into the new physical regimes that XFELs are capable of producing and probing.

Similar observations apply to electron-electron thermalization in a solid, where damped

collective excitations (ie. plasmons) may play a significant role as a bottleneck stage between absorption of XFEL photons and eventual thermalization of atomic electrons.[63, 64]

As alluded to above, two-color XFEL operation is a promising potential means of addressing these questions.

### *5.3.2 Tests of Finite-T electronic structure*

The output quantity of a density functional theory (DFT) simulation is real-space charge density. At the same time, the real-space charge distribution of a crystalline XFEL target material can be interrogated via X-ray diffraction, which samples the unit cell structure factor at momentum transfers corresponding to vectors of the reciprocal lattice. Because a material's lattice typically does not have sufficient time to respond to the changing electronic configuration over the duration of an XFEL pulse, XRD from WDM states produced by an XFEL can be directly compared to predictions of frozen-lattice finite-temperature DFT calculations.

Figure 5.1: Operation of an x-ray free electron laser.[144] Electrons enter the undulator with random phases and originally emit incoherent radiation at the undulator's resonant wavelength. As the electrons propagate, random fluctuations in the radiation field causes them to bunch at the resonant wavelength and emit coherently.

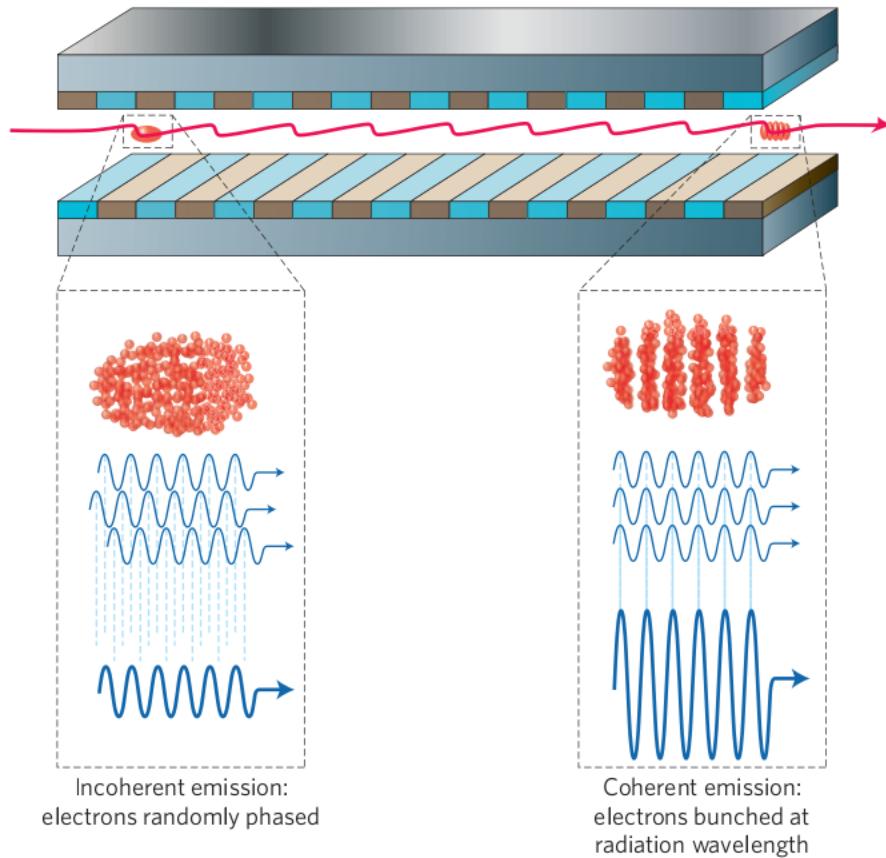


Figure 5.2: Schmematic representation of a two-color XFEL x-ray diffraction measurement wherein a chemical filter is used to reject pump photons.

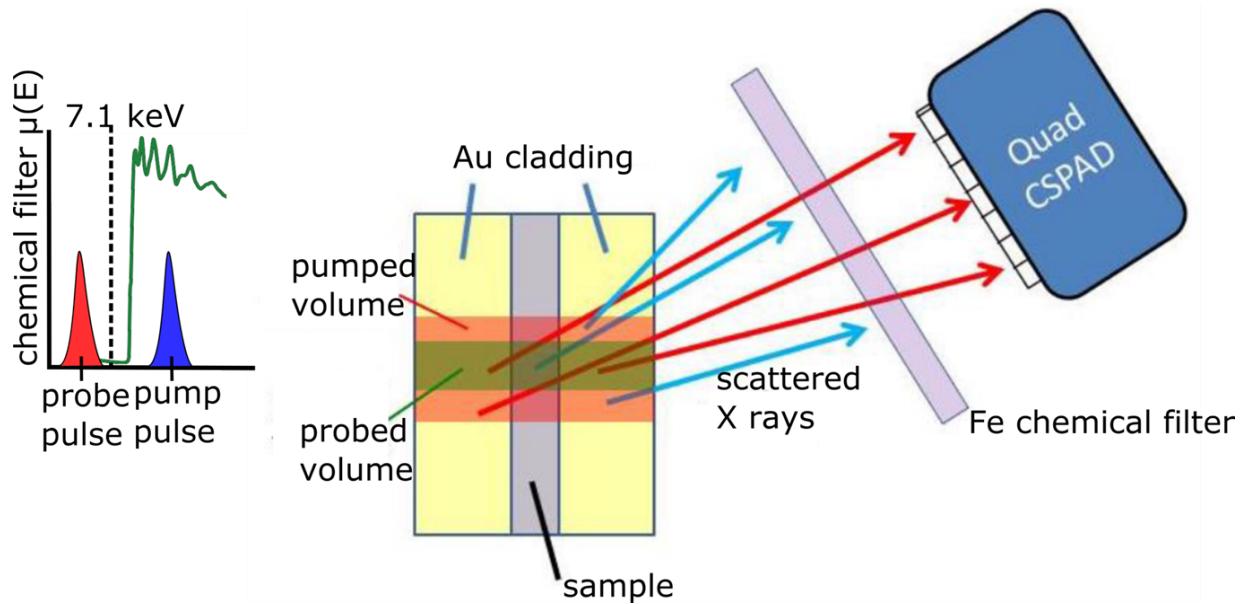
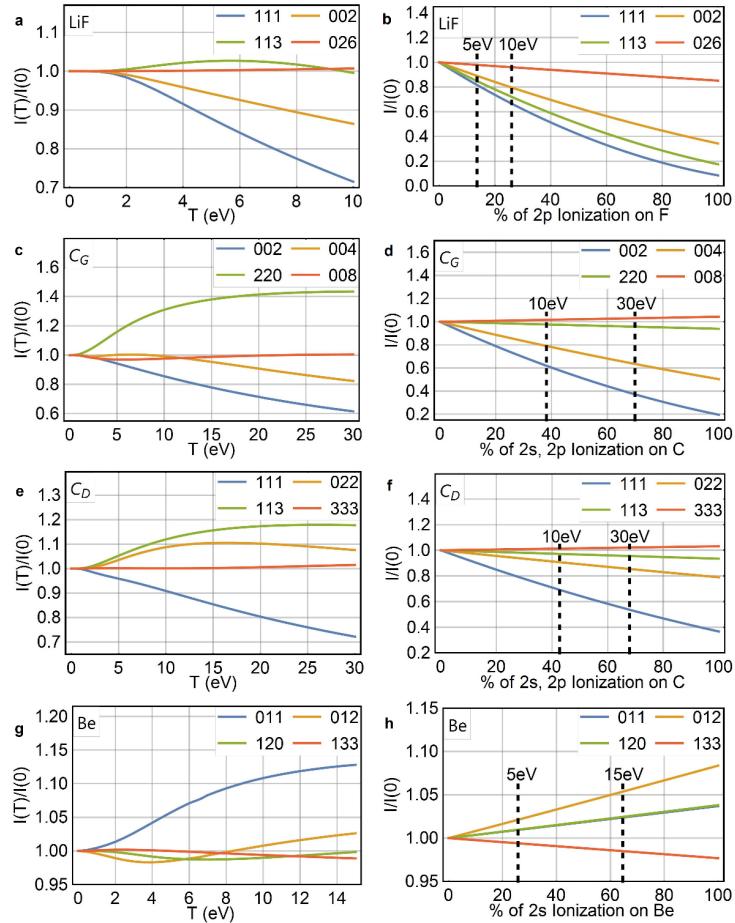


Figure 5.3: Left: intensity of diffraction peaks as a function of temperature, using finite-temperature DFT calculations in VASP; right: intensity of diffraction peaks as a function of ionization, using an atomic form factor-based model of ionization. The four simulated compounds are (from top to bottom) LiF, diamond, graphite, and Be. Taken from Valenza et al.[78]



This observation has led Valenza et al. to generate predictions of the consequences of XFEL heating on the intensities of Bragg peaks in several materials using DFT calculations in VASP. [78] They have shown that the information in the XRD signal is sufficient for discrimination between competing theoretical predictions, provided the XRD measurement is performed over a sufficiently wide range of momentum transfers. Valenza et al. demonstrate strong testable signatures of condensed-phase effects in each of LiF, graphite, diamond, and Be as a result of heating to temperatures on the order of 10 eV. A summary of their results is reproduced in Fig. 5.3.

The capability to test predictions of finite-temperature electronic structure models is a unique feature of XFEL-based experiments. We will explore the topic in some more detail in chapter 6, where we have the opportunity to apply it to experimental data.

#### **5.4 Design of an XFEL heating experiment**

One can identify several experimental desiderata shared by the majority of XFEL-based studies of WDM wherein the primary probe is X-ray diffraction:

- Maximization of information in the XRD signal
- Effective target heating so as to maximize the accessible range of energy densities
- Time resolution

Each of these can be achieved in one or more ways. Respectively:

- As alluded to in section 5.3.2, better-constrained estimates of real space charge density can be obtained by sampling a larger number of Bragg reflections. This requires probing a large momentum transfer range, made possible by using a high incident photon energy.

- In bulk samples, a high density of deposited energy requires matching the incident photon energy to a value at which the photoelectric absorption cross section is large. In Chapter 3 we will introduce an alternate approach based on the design of structured targets that relaxes this constraint on incident photon energy.
- Wherever a single XFEL pulse is used to both heat and probe a sample, a limited degree of sensitivity to the time-evolution of transient states can be had by varying time duration. Two-color XFEL operation, however, is much more attractive. However, it suffers from tradeoffs: most notably experimental complexity and reduced signal, due to the need for attenuation of the probe pulse relative to the pump.

These goals, and the tradeoffs that accompany them, are important context for both the experimental work described in the next section and the modeling-based exploration of the experimental technique discussed in section 3.

## **5.5 Experimental Work**

In the following I describe several experimental results arising from two beam runs at the Matter of Extreme Conditions (MEC) endstation at the Linac Coherent Light Source (LCLS) in June of 2014 and January of 2016. The studies conducted addressed questions about the relative magnitudes, and time scales, of lattice and electronic heating in various solids, mainly metal oxides. The primary diagnostic was XRD, with which we measured changes in electronic charge distribution as a function of incident flux, with the eventual goal of comparison to finite-T condensed matter electronic structure theory, as described in 6. The secondary diagnostic—used in a subset of the studies—was a von Hamos X-ray emission spectrometer with a highly annealed pyrolytic graphite (HAPG) analyzer crystal and 9 eV energy resolution, with which heating-induced line shifts and changes in valence-level emission were measured.

Throughout these measurements the XFEL beam was brought to a focus at the sample location using a stack of Be lenses. Flux incident on-sample was altered through a combi-

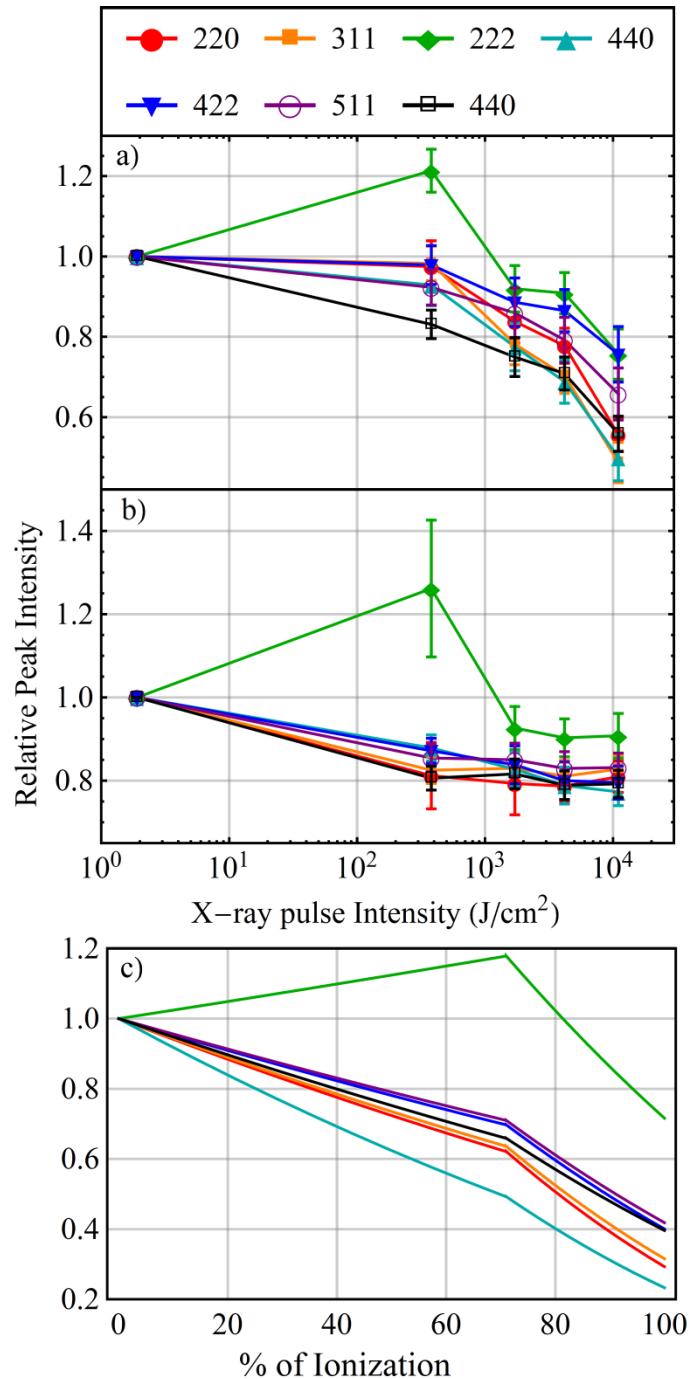
nation of beam attenuation and variation of the focal spot diameter between minimum and maximum values of 2 and 58 microns. XRD data was collected on a quad CSPAD solid state detector downstream from the sample. [156]

In samples wherein the signal was weak compared to time variations in the area detector pedestal values, additional processing was performed in order to reconstruct signal incident on the detector. This is described in more detail in Chapter 6, which details analysis and modeling of electronic heating based on an XRD dataset of XFEL-heated MgO.

### *5.5.1 Testing Lattice Thermalization in XFEL-heated Solid State Systems*

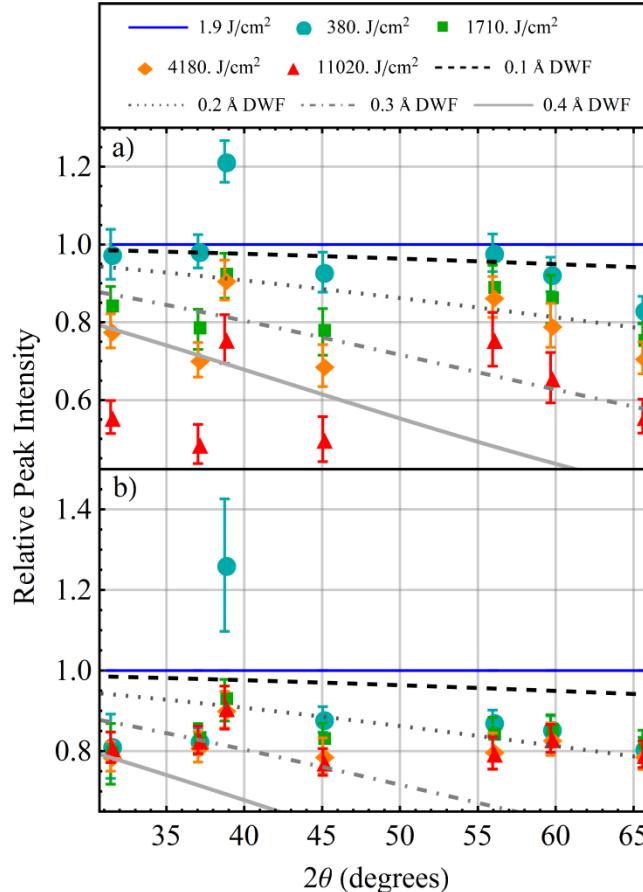
Fig. 5.4 (a, b) displays the progression of Bragg peak intensities as a function of incident flux for two different  $\text{Fe}_3\text{O}_4$  targets heated by 45 fs XFEL pulses. It demonstrates monotonic declines in the intensities of all Bragg peaks as a function of flux density, with the exception of the (222) peak, which rises to a maximum at the second-lowest flux density point before declining.

Figure 5.4: Progression of Bragg peak intensities as a function of incident x-ray flux density for (a) microphase and (b) nanophase  $\text{Fe}_3\text{O}_4$ , normalized to the intensity of the lowest-flux density point. (c) displays the progression of Bragg peak intensities as a function of electron ionization in an atomic form-factor based model wherein the Fe 3d and O 2p electrons are first ionized, followed by the more tightly-bound Fe 4s and 3p, and O 2s electrons. [157]



It is straightforward to evaluate the relative contributions of thermalization of electronic and lattice degrees of freedom to the XRD signal's evolution as a function of heating. The main distinguishing feature between these two components is that the latter causes Debye-Waller quenching of Bragg peak intensities that is approximately proportional to  $e^{-q^2\langle u^2 \rangle}$ , where  $q$  is momentum transfer and  $u$  is atomic displacement. Fig. 5.5 compares the experimental data to this Debye-Waller progression for several different values of RMS atomic displacement. The experimental data shows a complete lack of Debye-Waller-like  $q$ -dependence in Bragg peak intensities at high levels of heating, signifying that the XRD response is strongly dominated by reorganization of electronic charge density within a unit cell.

Figure 5.5: Same data as Fig. 5.4 plotted against Bragg angle and compared with the Debye-Waller factor for several values of RMS atomic displacement. [157]



The electronic response of  $\text{Fe}_3\text{O}_4$  to XFEL heating can be further interpreted through comparison of the data to a simple atomic form factor-based model of ionization (the model is described more specifically in Chapter 6. We find that the model reproduces the anomalous rise in intensity of the 222 reflection (Fig. 5.4) via a loss of destructive interference between the valence wavefunctions of O and Fe as both are simultaneously ionized. [157]

## Chapter 6

### MAPPING SPECIES-SPECIFIC IONIZATION IN WARM DENSE CRYSTALLINE MGO UNDER EXTREME X-RAY HEATING

*(This is a reproduction of a manuscript in preparation: Oliver Hoidn, Ryan Valenza, Gerald Seidler, Alexander Ditter, William Holden, Evan Jahrman, Samuel Vinko, Josh Kas, Fer Vila, Alison M. Saunders, Luis Avila, Galen O’Neil, Hae Ja Lee, and Bob Nagler, Physical Review B, 2017 )*

X-ray heating by x-ray free electron laser (XFEL) pulses is emerging as an important method to create matter under extreme conditions. Many prior reports of XFEL heating have focused on achieving extremely high levels of ionization, and then have used advanced x-ray methods to with the goal of evaluating the use of traditional plasma-theoretic approaches to the resulting warm dense matter (WDM) where such approaches may, or may not, be perturbatively applicable. Here, we adopt a complementary strategy wherein we use more modest XFEL heating to create more weakly ionized, ‘tepid’ dense matter so as to investigate the earliest stages of ionization and elucidate the boundaries of applicability of traditional solid state physics ideas upon the breakdown of its assumptions of, e.g., high electronic degeneracy and coincident long range order of ion cores and valence charge density. Specifically, we choose to study the early stages of XFEL heating of MgO because of its large ground state bandgap, whose existence is a direct consequence of such long range order, and because the rocksalt structure of MgO holds special benefits in that its x-ray diffraction (XRD) pattern can be used not only to look for changes in average ionization of the unit cell but also for

differential ionization between Mg and O sites. We find an anomalously low onset for valence-level O 2p ionization that requires the presence a large density of states within the ground state band gap, despite the strong evidence that no ion core motion has occurred during the x-ray pulse itself and despite the fact that the O 2p ionization is still much too small for screening effects to cause ionization potential depression. We propose that this may instead be a consequence of the destruction of long-range order of the electronic potentials due to site-disorder of the ionization, an effect that would be an extreme manifestation of the Lifshitz tail effect that is well-known in semiconductor physics.

### **6.1 I. Introduction**

The ‘warm dense matter’ (WDM) regime resides in an important and theoretically interesting middle-ground between the conditions typical of high-pressure studies in condensed matter physics and those instead of great interest to traditional plasma physics, where atoms are fully ionized. WDM is defined by partial ionization, solid-like or higher densities, substantial Fermi degeneracy ( $T \leq E_F$ ), and values for the plasma coupling parameter of order unity or larger. [158] The collective properties of WDM—such as its equations of state (EOS), opacities, and viscosities—are of fundamental importance in geophysics, planetary and stellar astrophysics, and inertial confinement fusion (ICF). [159]

However, the very intermediacy of WDM between condensed matter and plasma physics conditions poses new challenges to fundamental theoretical treatment of this state of matter because, on the one hand, high degrees of ionization and incomplete Fermi degeneracy are poorly treated even at a perturbative level by solid state physics electronic structure methods and, on the other hand, the importance of the ion core potentials, possible long-range order, and exchange interactions between valence and core electrons pose unsolved challenges to adaptations of theories intended for dense, more-completely ionized plasmas. In this context, WDM created by electronic heating from x-ray free electron laser (XFEL) pulses holds special promise, and has led to interesting results for the electronic structure of matter at solid

density and relatively extreme degrees of valence-level ionization. [160, 161] Such results are enabled not only by the creation of the WDM state by the x-ray pulse but also by the experimental diagnostics enabled by those same pulses, such as x-ray diffraction (XRD) and different implementations of x-ray spectroscopies. [144, 162–164]

However, we choose here a complementary paradigm for the scientific opportunity provided by XFEL heating of dense matter. In contrast to extreme ionization and inquiry into the perturbative persistence of theories from the dense plasma physics literature, we instead seek to finely interrogate the earliest stages of XFEL heating with an eye toward seeing how far methods of solid state physics can find new, extended relevance in a ‘tepid dense matter’ regime where plasma-theoretic approaches to electronic structure, such as screening approaches to ionization potential depression, will not be applicable because of choice of material or degree of ionization. In particular, we report here a wide-angle XRD study of XFEL heating of the wide-bandgap semiconductor MgO. The choice of method and material are intertwined and are motivated by our overall scientific mission via two main considerations.

First, a novel perspective on the use of elastic x-ray scattering, i.e., XRD, in the study of crystalline WDM has recently been presented by Valenza and Seidler. [78] While all early XRD studies of WDM were performed in laser-shock studies where long-range crystalline order of the target is destroyed, [39] those authors instead address the question of XRD from WDM created by heating of crystalline targets by the extremely fast pulses created by x-ray free electron lasers (XFELs). One key result of Valenza and Seidler is the large contribution to XRD of the nominally ‘free’ electrons for low-Z systems, but there are two more overarching perspectives in that work that are more relevant for the present study. To begin, XRD from crystalline WDM provides an important testing ground for finite-T electronic structure theory, giving direct measurement of the fundamental quantity predicted in DFT approaches, i.e., the spatial distribution of charge density. For example, for low-Z systems, finite-T studies of XRD might give an especially salient inquiry into exchange functional effects under intermediate degeneracy of the unbound electrons. [77, 165, 166] Next, and of greater relevance here, XRD from a WDM state where the ion cores are at least

effectively stationary is a rich experiment that, through the careful choice of target material crystal structure, can be designed to have far higher information content about microscopic parameters, such as species-specific ionization states, than has been the case in studies of disordered WDM or simple elemental metal targets. In particular, we show here that species-specific ionization state sensitivity can be obtained by judiciously selecting a crystalline compound whose diffraction peaks express a combination of destructive and constructive interference between different atomic sites in the unit cell. The rock-salt structure taken by MgO is a classic textbook example of exactly this effect. Of relevance here, the (200) and (220) Bragg peaks have perfect constructive interference between charge density at the Mg and O sites in the unit cell, whereas the (111) peak instead has perfect destructive interference.

Second, the choice of MgO is particularly appropriate here because of its ground state electronic structure. MgO is a strongly ionic, very wide-band gap insulator. As such, unlike with an elemental metal target such as Al or Cu, the valence electronic charge density is quite spatially localized and has a strong contribution to the XRD that must rapidly change upon ionization. For example, prior study of strongly electronically excited KH<sub>2</sub>PO<sub>4</sub> using optical bandgap excitation and XRD diagnostics found clean signatures of the resulting changes in real space charge distribution. In the present case, with an ionic rather than molecular crystal, it is important to recognize that the wide bandgap of MgO, 7.8 eV, is a special manifestation of the ground state crystalline symmetry and long-range order of both the atomic positions and the local electronic structure. As such, the large ground-state band gap provides a special, potentially very sensitive, opportunity to see the initial consequences of the breakdown of the ground-state symmetries.

With background complete, we summarize our results. During the single-shot studies, where heating and diffraction occur simultaneously, we find no signatures of long-range lattice disorder, such as either Debye-Waller or ‘Bragg gating’ effects, across a range of energy deposition densities reaching 150 eV per unit cell. However, we measure a monotonic rise in normalized intensity of the (111) peak of MgO with increasing XFEL flux density.

This effect is the fully expected signature of a loss of destructive interference within the MgO unit cell as the valence electrons progressively delocalize from their O 2p-like ground state locations. This is an observation of short-range, purely electronic charge reorganization in a solid-density, partially-ionized plasma that constitutes an initial demonstration of the general type of ‘warm dense crystallographic’ effect predicted by Valenza, et al. [78] The observed onset for strong O 2p ionization is, however, anomalously low when compared to constraints that would be imposed by the large ground-state band gap of nearly 8 eV. We propose that the site-disorder of ionization that is a hallmark of x-ray heating is likely introducing a significant density of states within the ground state band gap, thus giving a new mechanism, independent of, e.g., traditional ionization potential depression (IPD), for enhanced ionization effects in WDM. Such ‘Lifshitz tails’ are well known in the theory of semiconductor physics but have not previously been discussed in the context of WDM. Although the lack of local thermal equilibrium (LTE) in the present study limits the utility of comparisons to theory, the experiment validates wide-angle XRD as an effective probe of local real-space electronic reorganization in crystalline warm dense matter. It thus presents the appealing prospect of future XRD studies on XFEL-heated WDM and solid-density plasmas designed to empirically constrain DFT-based predictions of finite-temperature electronic structure, especially for experiments performed using two-color x-ray pump, x-ray probe methods where many limitations of the present study will be ameliorated.

We continue as follows. First, in section II we describe experimental methods. In section III we discuss approaches for modeling variations in the Bragg diffraction signal as a consequence of XFEL heating. This includes ground-state, molecular, density functional theory, and species-by-species radiative combination calculations. In section IV we present and discuss experimental and modeling results, the most consequential of which is that the presence of valence disorder substantially complicates interpretation of WDM structure by invalidating ground state-based treatments of the electronic structure and providing a new route for effective enhancement of ionization effects that is specific to crystalline dense plasmas. Finally, in section IV we conclude and discuss future directions.

## 6.2 II. Experimental Methods

### 6.2.1 II. A. Experimental Details

The experiment was performed at the matter of extreme conditions (MEC) endstation of the Linac Coherent Light Source (LCLS), where XFEL pulses were used to excite MgO samples consisting of a 100 nm-thick layer of PMMA with embedded MgO nanoparticles (Sigma Aldrich, typical size 50 nm) on an 8 m-thick polyimide substrate. We used self-amplified stimulated emission (SASE) pulses of 45 fs mean duration, average pulse energies of 2 mJ, and a nominal x-ray energy of 9 keV. Variations in the mean photon energy of each pulse are monitored by a downstream dispersive spectrometer. We controlled the flux density incident on the sample via a stack of Be lenses, with which we varied the focal spot diameter of XFEL pulses at the sample position from 2 to 60 m; these diameters were determined using an ablative imprint method to measure the spatial profile of the focused XFEL beam. Using the full available range of focal spot sizes and the unattenuated beam, we obtained incident flux densities ranging from 30 to 2000 J/cm<sup>2</sup>.

During data collection the sample's position was rastered at a rate of 100 m between the XFEL pulses, whose repetition rate was 120 Hz. At every XFEL pulse the Bragg scattering signal was collected and read out from a quad CSPAD solid state detector having 800 x 800 resolution and a pixel pitch of 100 μm. [167] The 8 x 8 cm<sup>2</sup> active area of the detector subtended the range of scattering angles from 10 to 58 degrees, encompassing the (111), (200), and (220) Bragg reflections of MgO (located at 33.5, 38.8, and 55.9 degrees, respectively, for 9 keV incident photons).

### 6.2.2 II.B. Data Reduction and Analysis

Several steps of processing and event selection were performed prior to generating powder diffraction patterns. For each event the quad CSPAD readout was corrected by subtracting pixel pedestals (measured using previously-collected dark exposures) as well as common-mode noise in each of the detector's 16 individual tiles. [167] Due to the small number of

photon hits in a single shot residual ADC noise often dominated the Bragg scattering signal. To address this we made use of a standard component of the analysis pipeline for CSPAD data in low-photon count rate experiments at the LCLS, such as macromolecular imaging and crystallography, which identifies clusters of spatially-concentrated signal resulting from x-ray photon hits, rejecting the output of noise-dominated pixels. [168]

For each LCLS pulse a powder diffraction pattern is generated from the quad CSPAD frame by the summation of elliptically-shaped strips of pixels at equal scattering angle. The mapping of pixel coordinate to scattering angle is calculated from the CSPAD's location and orientation relative to the sample and incident XFEL beam; this geometry is in turn obtained from the conic section parameters of powder diffraction peaks in data from a known reference material measured in the same source-detector geometry. After generation of a powder pattern, two corrections are made. First, the each peak is shifted to correct for angular offsets caused by imperfect flatness of the sample substrate and also event-to-event jitter in the mean photon energy of the XFEL. Second, a linear fit is made to the background of each peak, and this background is subtracted from the peak signal. The signal-to-background ratio for this peak is then computed by comparison of the background level derived from the linear fit to a simple integration of the background-subtracted peak. Events in which any of the peak signal-to-background ratios fall below a threshold (chosen to be 0.2) are rejected in subsequent summation over data from multiple events.

Bragg peak scattering intensity is the most significant derived quantity from each powder pattern in this study, but its estimation requires correcting the effect of variations in the total scattering signal caused by sample non-uniformity and temporal variation of the XFEL pulse energy. The latter contribution can be corrected using direct measurement of incident pulse intensities available from an upstream nitrogen detector; for comparison of Bragg peak intensities at different flux density values, however, we normalize each pattern to the integral intensity of its (200) peak in order to control for variations in sample thickness, or fluctuations in nanoparticle volume in the beam, such as from nonuniform aggregation..

### 6.3 III. Modeling Methods

Finally, the relationship between the incident flux density and the resultant energy density in the MgO nanoparticles requires some care. The small (100 nm) sample thickness requires that a significant portion of higher-energy electrons created in the relaxation cascade following, e.g., primary photoionization of the Mg 1s orbital, will necessarily escape into the surrounding low-Z substrate and surrounding binder, causing a reduction in the density of *locally deposited*, versus absorbed, energy from the incident XFEL pulse. This effect has recently been discussed in detail, and proposed to be especially important for the design of XFEL x-ray heating targets. [88] In the present case, using the methods described in [88] we use PENELOPE to perform Monte Carlo simulations for 9 keV incident photons striking a target consisting of a 50-nm thick MgO layer clad with graphite, where graphite is taken as representative of carbonaceous binder and substrate materials. This simulation implements particle-tracking simulation of electron showers in which elastic scattering differential cross sections are calculated from partial-wave solutions to the Dirac equation, while inelastic interactions (involving both impact ionization and collective excitations) are represented using a modified version of Liljequist's 'delta-oscillator' generalized oscillator strength (GOS) model. [88]

The average energy deposited per unit cell is then calculated on the basis of the incident pulse energy, the focal spot size, standard (cold) cross sections for x-ray absorption, which greatly dominates Compton and elastic scattering, and the above correction. This calculation is an upper bound, in that it assumes that long-wavelength electronic excitations, e.g., plasmons, are a minor contributor to the energy distribution at any moment in the relaxation cascade and will have decayed to simple electron-hole excitations during the time duration of the pulse.

To model the dependence of the XRD signal on the electronic configurations of the Mg and O ions we use the Hartree-Fock code of Cowan [169] to calculate the atomic form factors of Mg and O decomposed by subshell. The crystal's structure factor is subsequently calculated

as a sum over basis atoms and subshells; i.e.,

$$S(\vec{Q}) = \sum_j \sum_{n,l} N_{n,l} f_{j,n,l}(Q) e^{-i \vec{Q} \cdot \vec{r}_j}, \quad (1)$$

where  $f_{j,n,l}(Q)$  is the atomic form factor of the subshell  $n,l$  of the  $j$ th species, where  $n$  and  $l$  are principal and orbital angular momentum quantum numbers, and  $N_{n,l}$  is the subshell's population. The intensity of a given Bragg reflection (neglecting Debye-Waller quenching and the geometric dependence of scattering by a powder of crystallites) is then obtained by evaluating  $S(h \mathbf{a}_1 + k \mathbf{a}_2 + l \mathbf{a}_3)$ , where  $\mathbf{a}_1$ ,  $\mathbf{a}_2$  and  $\mathbf{a}_3$  are the basis vectors of the reciprocal lattice and  $h$ ,  $k$  and  $l$  are Miller indices. Following standard practice in plasma physics modeling, we treat ionization of atomic electrons as a uniform (real-space) smearing of free electrons; thus, ionization of an atomic orbital simply corresponds to reduction of its weight  $N_{n,l}$ .

In the high-energy density regime, defined as having mean temperatures above 2 eV, we simulated the temporal evolution of the MgO charge state distribution (CSD) over the course of an XFEL pulse using a variant of the collisional radiative code SCFLY that Vinko et al. have modified to self-consistently support elemental mixtures. [161] The code implements a local density-based treatment of continuum lowering that Vinko et al. have demonstrated accurately reproduces experimental ionization potential shifts at high charge states in several solid-density plasma mixtures. Unlike other collisional radiative codes, SCFLY models the plasma's free electron energy density self-consistently with respect to XFEL heating and interaction with ions (e.g. impact ionization and Auger decay). Its principal caveat in the current setting, where the plasma is heated via photoexcitation by photons with energies far above the absorption edges of Mg and O, is its assumption of an instantly-equilibrating thermal distribution of free electrons. [22]

Our inputs to SCFLY were the sample composition and XFEL photon energy, flux density, and temporal profile (which we took as a Gaussian with a 45-fs FWHM duration); the main outputs were temporal profiles of the charge state populations of Mg and O during the XFEL pulse. With the help of a simplifying approximation (discussed in section III below) that relates Mg and O charge states to 2p ionization, we used the AFF ionization model to obtain

predicted Bragg peak intensity ratios for each simulated incident flux density.

In the low-energy density regime we instead adopt three alternate models that capture aspects of the condensed phase physics under contrasting assumptions and limiting conditions. First, we use the Vienna ab-initio Simulation Package (VASP) [170], a density functional theory (DFT) code, to compute the X-ray diffraction signal at finite temperature using the charge distributions of Kohn-Sham eigenstates populated by Fermi-Dirac Statistics. The relation between temperature and deposited energy density is derived from the zero-temperature density of states of MgO, which we compute using the code FEFF. [171] Under this model it is assumed that the potential landscape and density of states are not significantly altered by finite-temperature redistribution of charge. Additionally, the presence of local thermal equilibrium is implicit.

Second, we take a simplified picture of XFEL heating where all energy deposited in the MgO sample contributes to excitation of O 2p states. Departing from the ground state density of states (DOS), we assume that the energy required to delocalize an O  $2p$  electron is equal to the band gap, 7.8 eV. Under these assumptions a given XFEL dose therefore generates a known amount of O 2p ionization; from this, the AFF model is used to calculate the resulting XRD response. We term this approach the ground state model.

Third and finally, we consider the limit in which perturbation of the electronic structure creates a large density of states in the band gap and the O  $2p$  ionization potential is determined by local interactions alone. In this molecular model we approximate the ionization potential of O<sup>2-</sup>, embedded in a dielectric background mimicking bulk MgO, using a delta SCF (self-consistent field) calculation. [172] This approximation yields an ionization potential of 1.9 eV, from which the XRD response can be calculated in the same fashion as in the ground state model

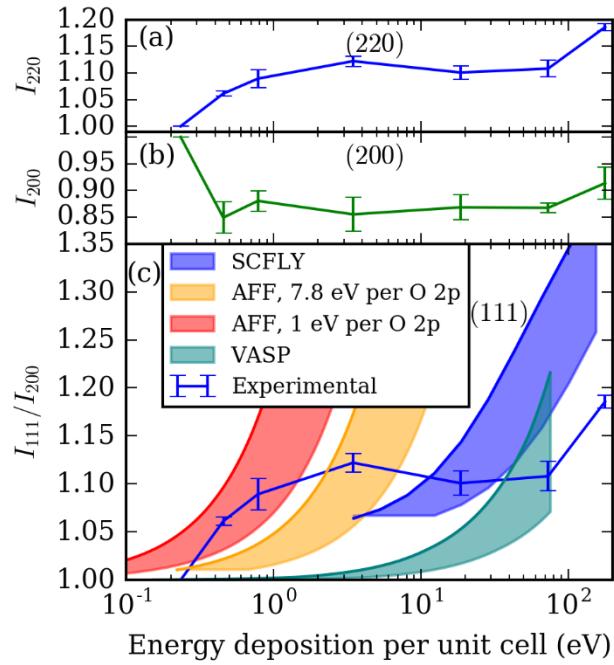
#### **6.4 IV. Results and Discussion**

To begin, in Fig. 6.4 (a), we show the experimentally measured intensity of the MgO (200) peak as a function of energy deposited per MgO unit cell. The ~15% scatter in the observed

scattering intensity upon increasing excitation is explained as being due to variations in MgO nanoparticle content across different regions of the sample. Consequently, our first result is clear: the MgO nanoparticles remained substantially, and possibly completely, crystalline for the duration of the XFEL pulse. There is no evidence for ‘Bragg-gating’ or other self-limiting diffraction signals that are known to be important in the context of macromolecular crystallography at XFELs. [75]

In Fig. 6.4 (b) we plot the normalized experimental intensity of the (111) and (220) Bragg peaks of MgO as a function of incident flux density (together with curves for several models, which we discuss below). Specifically, for each Bragg peak, the entire curve is normalized to the intensity of the “cold” (lowest-flux density) dataset and each individual data point is normalized to the (200) peak intensity for the corresponding flux density. The normalization to the intensity of the (200) peak helps to remove fluctuations in diffracted intensity due to sample thickness nonuniformity. We hereafter refer to intensities normalized in this fashion, for a given peak ( $hkl$ ), as  $I_{hkl}/I_{200}$ . Displayed error bars are estimated systematic errors due to background subtraction and peak integration; counting statistics-derived errors are negligible. The most salient feature is a 20% rise in the relative intensity of the (111) peak between the lowest and highest flux densities. In contrast, the relative intensity of the (220) peak fluctuates but does not display a monotonic progression. The behavior of both curves—and in particular the rise in relative intensity of the (111) peak—is strongly at odds with the any Bragg peak quenching that would result from a Debye-Waller thermal-like, uncorrelated, increase in the mean squared displacement of atoms from their lattice sites. The absence of any such signature further supports the crystallinity of the heated target and the isolation of the deposited energy in the electronic, rather than lattice, degrees of freedom.

Figure 6.1: (a): Experimental intensity of the (220) Bragg peak from a sample of MgO simultaneously heated and probed by 45-fs duration XFEL pulses, as a function of XFEL energy deposited per MgO unit cell, with no normalization across individual data points. (b): Equivalent data for the (200) peak. (c): Experimental intensities of the (111) peak, compared to several models. Each experimental data point is normalized by (1) its intensity at minimum flux density and (2) the (200) peak intensity. For each of the four displayed models, the shaded region corresponds to the locus of possible curves once the loss of in-sample energy deposition due to nonlocal heat transport by hot electrons is accounted for. See the text for discussion.

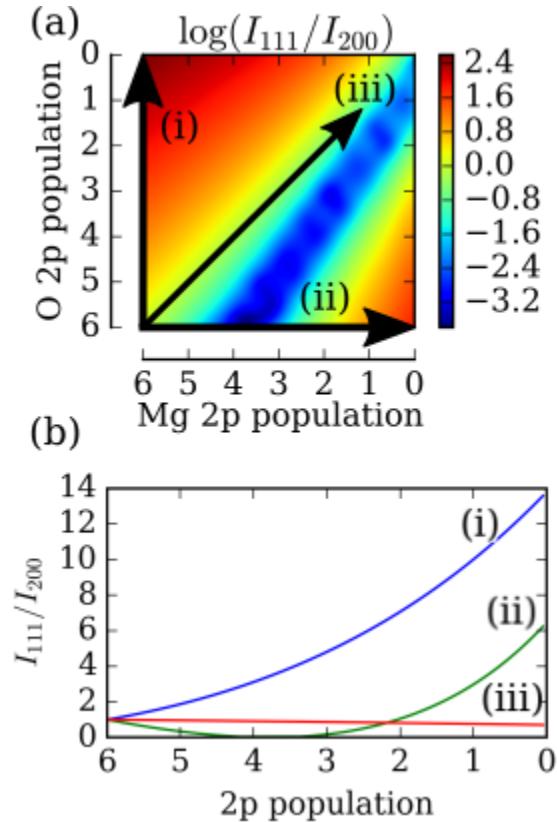


A first step toward understanding the increase in relative intensity of the (111) Bragg peak comes from consideration of the ground-state x-ray crystallography of MgO. MgO's rock salt-type crystal structure consists of two interpenetrating FCC lattices of Mg and O, with one of the lattices shifted by half of the FCC lattice constant in the direction of one of the lattice basis vectors. This has consequences for the dependence of the (200), (111), and (220) Bragg peak intensities on the characteristics of the ions on the two sites in the primitive basis, as is frequently discussed in introductory texts. [173] In particular, the (200) and (220) peaks result from perfect constructive interference between the two unit cell sites while the (111) peak, on the other hand, instead has perfect destructive interference between the two unit cell site. The nominal ground-state ionic species of MgO,  $Mg^{2+}$  and  $O^{2-}$ , have identical electron configurations and have only very slightly different ionic form factors for x-ray scattering as a secondary consequence of the different nuclear potentials on the spatial extent of the electronic wavefunctions. This offers an explanation for the small ground-state intensity of the (111) Bragg peak, as well as for its monotonic rise with increasing incident x-ray flux: as temperature increases electrons of the weakly-bound O 2p orbitals are ionized at a higher rate than those of Mg semi-core 2p orbitals, increasing the dissimilarity of the form factors of the O and Mg ions.

This relationship is illustrated by Fig. 8.2.2, which shows  $I_{111}/I_{200}$  as a function of O 2p and Mg 2p population under the AFF ionization model presented in section II. Three curves denoting different scenarios for the electronic configuration of Mg and O following x-ray heating are indicated in Fig. 8.2.2b, and the corresponding Bragg peak intensity progressions are plotted in Fig. 8.2.2b. First, trajectory (i) corresponds to progressive ionization of the O 2p electrons with a fixed (ground state) population of Mg 2p electrons; it encompasses possible states of the x-ray excited system following relaxation of all deeply-bound Mg 2p holes. Along trajectory (i), removal of O 2p charge density causes the (111) Bragg peak intensity to increase monotonically due to reduction in the O electrons' cancellation of the Mg charge density's scattering amplitude. Conversely, on trajectory (ii) only Mg 2p electrons are ionized; noting that the Mg K shell dominates the photoelectric cross section of MgO at hard

x-ray energies, this corresponds to the locus of possible initial states following instantaneous x-ray ionization. In this case, ionizing the Mg 2p orbitals (starting from the ground state) reduces the magnitude of the total scattering amplitude until total destructive interference is reached before the scattering factors differ again as Mg 2p ionization continues. The resulting intensity progression for case (ii) in Fig. 8.2.2b therefore has a local minimum (located at an Mg 2p population of approximately 3.5 electrons). Finally, trajectory (iii) represents an intermediate scenario wherein the levels of O and Mg 2p ionization are (artificially) equal. Here, the dominant effect is a slow decrease in intensity due to uniform reduction of the scattering amplitude contributions of all 2p electrons in the unit cell.

Figure 6.2: Dependence of  $I_{111}/I_{200}$  on population of the 2p orbitals of  $Mg^{2+}$  and  $O^{2-}$ , according to an atomic form factor (AFF) based model of ionization. This ratio reaches a maximum factor of 13.8 times the unperturbed value at full ionization of the O 2p electrons.



Referring back to the results of Fig. 6.4c for  $I_{111}/I_{200}$ , we see a more gradual enhancement than is the case for a thermalized system with only O 2p ionization and there is no evidence of initial decreases for states dominated by Mg 2p ionization. The resulting qualitative conclusion is then a trajectory intermediate between (i) and (ii), where any theoretical treatment will need to include both the lifetime of the Mg 2p core holes during the x-ray excitation and also the presence and significant, if incomplete, thermalization of O 2p valence-level electrons. Because of the counteracting effects of O and Mg 2p ionization in this regime, the value of  $I_{111}/I_{200}$  does not fully constrain the extent of either O or Mg 2p ionization. Trajectory (i) nevertheless delimits the minimum extent of O 2p delocalization as a function of  $I_{111}/I_{200}$ ; the largest experimental value of  $I_{111}/I_{200}$  corresponds to an O 2p ionization level of at least 5 %.

Hence, predicting the consequences of single-pulse XFEL heating on XRD requires separate calculation of an average of the probed Mg and O ionization states —both temporal (over the duration of an XFEL pulse) and spatial (over all probed unit cells). We begin with the low-energy limit. In the regime where energy deposition per unit cell is less than 1 eV, condensed matter physics and the details of valence-level electronic structure should be dominant. For example, prior work on the XRD from KH<sub>2</sub>PO<sub>4</sub> after strong optical excitation from the valence band to the conduction band could be well-interpreted in the general arena defined by the ground-state electronic structure of the crystalline phase. [174]

Here, the absence of local thermal equilibrium (LTE) is a challenge for modeling fs-scale electronic reorganization in the 0.1-1eV temperature regime because—unlike in the plasma limit, where the atomic kinetics are unambiguous (modulo treatment of the ionization potential depression)—there is a lack of established frameworks for calculating the time-evolved electronic structure. We thus forgo *ab initio* simulation and take a simple assumption of proportionality between the density of deposited energy and the level of O 2p ionization. Under this assumption, we then consider two idealized bounds on the excitation kinetics.

First, we consider the case where the ground state electronic structure is taken as a static venue that is unperturbed by even relatively high levels of ionization, i.e., where the energy

needed to excite an O 2p electron is equal to the band gap of MgO,  $E_g = 7.8$  eV no matter the level of O 2p ionization. The results of this nave ground state model are shown as a shaded region (orange) with label AFF 7.8 eV in Fig. 6.4 Under this condition, and defining  $\rho_E$  as the density of deposited XFEL energy, it follows that  $\rho_E/E_g$  is an upper bound on the concentration of O 2p excitations (i.e., corresponding to all XFEL energy coupled into O 2p excitation). The yellow shaded region of Fig. 6.4 shows the ground state model's predicted intensity progression of the (111) Bragg reflection as a consequence of a density of deposited energy equal to  $\rho_E/E_g$ . The measured onset of the (111) peak intensity's rise is much delayed compared to the model's prediction, from which we can infer that the experimental level of O 2p delocalization is significantly higher than that allowed by the ground state density of states of MgO – in other words, there must be a plethora of states in the band gap that occur as a consequence of the x-ray excitation, even while periodicity of the ion-core locations is preserved. This inconsistency is corroborated by comparison of the experimental progression with a more advanced calculation of the same ilk, a finite-temperature DFT-based calculation, which also fails to reproduce the (111) peak's early rise (teal region in Fig. 6.4, labeled VASP).

Second, as an alternative bounding case, one may consider an isolated, atomic O<sup>2-</sup> in an MgO-like dielectric background results in a much lower calculated ionization threshold of 1.9 eV. This limit would be representative of a complete breakdown of any band-like effects. The general, quadratic shape is still shown (color, label in overestimate of the onset for O 2p ionization. Hence, the dilute-plasma limit, modified only by ion-pairing for local neutrality, has omitted too much of the condensed phase physics.

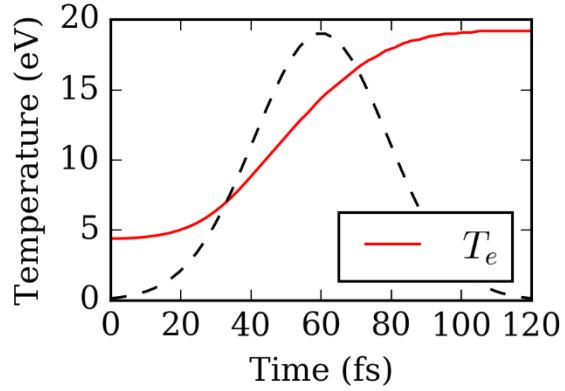
Given the above discussion, the question then arises as to possible explanations for the observed enhancement of O 2p ionization at lower incident energy densities. Prosailically, some part of this effect may be due to our choice of nanophase material. Unsurprisingly, the finite size of MgO nanostructures manifest surface states with energies inside the ground state band gap. However, the magnitude of the present effect requires a more intrinsically bulk-like behavior. Though the effect superficially resembles ionization potential depression

(IPD), conventional models of IPD inevitably fail in the low-energy density regime because they treat variations in the continuum level as a consequence of screening, with dependence only on the average ionization and ion density of a plasma, quantities that are showing only very small changes here compared to that needed for substantial changes in screening. [10, 161] Here, the key physics may instead be the fact that while long-range structural order persists, long-range *electronic* order has been significantly weakened by the site-randomness of ionization on both the O sites (by valence-level ionization) and on the Mg sites (due to the long lifetime of Mg 2p vacancies created during the relaxation cascade).. It is known that site disorder in an otherwise perfectly crystalline solid (for instance lattice vacancies, impurities, or, as in our case, randomly-distributed electron vacancies) can introduce localized states with energies inside the band gap, a spectral phenomena referred to as Lifshitz tails. [175] One particularly celebrated example of this is Anderson delocalization. [176] The possibility that this classic idea in solid state physics may find new application in dense plasma physics is an interesting result that can be further interrogated with, e.g., large-cluster quantum chemistry calculations or with other real-space DFT methods where site disorder of ionization state can be directly manipulated.

We now turn our attention to high energy deposition densities in Fig. 6.4. In this regime, treatment of the interaction between atomic and free electrons, which gives rise to plasmas physics effects such as continuum lowering, becomes necessary. The above atomic and solid state treatments become inappropriate—even for the purpose of establishing rough bounds on the concentration of excitations—and we instead turn to time-resolved collisional radiative simulation.

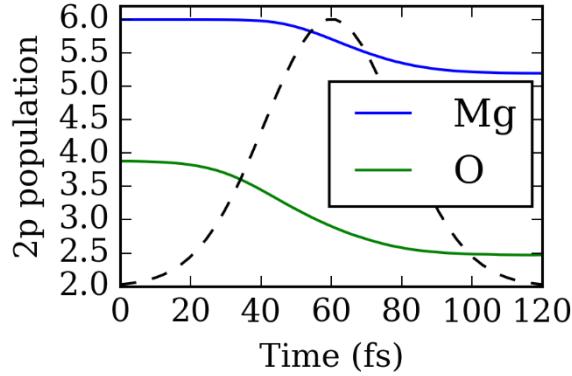
The principal outputs of such a simulation are temporal evolutions in electron temperature and atomic species charge states. Figs. 6.4 and 6.4 display these data for simulated XFEL heating of an MgO target,with an incident XFEL intensity equal to the highest experimental value using the code SCFLY. Notably, the charge state distribution is strongly athermal: the difference between the initial and final Mg 2p population levels is 0.8 electrons, which exceeds the equilibrium ionization level corresponding to the final temperature of 19

Figure 6.3: Electronic temperature evolution during an XFEL pulse simulated by the radiative collisional code SCFLY. The incident XFEL photon energy and flux density are 9 keV and  $2 \times 10^4$  J/cm<sup>2</sup>, respectively. The dashed line represents the temporal profile of the incident XFEL pulse.



eV by a large factor. One reason for the lack of LTE is readily apparent. The lifetime of Mg 2p holes is large compared to the 45 fs XFEL pulse duration [152, 177] and the simulated free-electronic temperatures are far below the Mg 2p binding energy. Consequently, the production of Mg 2p holes will be dominated by rates of 2p and 1s photoionization and electron impact ionization during the XFEL pulse.

Figure 6.4: Evolution of the mean charge states Mg and O of during an XFEL pulse simulated by the radiative collisional code SCFLY. The incident XFEL photon energy and flux density are 9 keV and  $2 \times 10^4$  J/cm<sup>2</sup>, respectively. The dashed line represents the temporal profile of the incident XFEL pulse.



The low value of the free electronic temperature relative to the  $K$  shell binding energies of O and Mg allows a simplification in application of the AFF ionization model to the output of SCFLY. Because only the  $2p$  orbitals of Mg and O are substantially ionized, the charge state of each species uniquely determines its electronic configuration under Eq. 1. Progressions of Mg and O charge states (or, equivalently, Mg and O  $2p$  populations) therefore contain sufficient information to compute Bragg peak intensities using the AFF model. Fig. 6.4c shows the output of the resulting SCFLY-based XRD calculation evaluated over the full range of flux densities simulated with SCFLY. At high flux density agreement between the experimental Bragg peak intensity data and SCFLY-based model is poor but shares a qualitative features with the experimental data, namely a rapid rise in intensity of the (111) peak beyond a 5 eV per unit cell energy deposition.

A few explanations can be proposed for the plateau in  $I_{111}/I_{200}$  at higher flux densities, although additional work will clearly be needed. First, the population of excitons may saturate at high flux densities due to dependence on the exciton recombination rate on deposited energy density. A robust modeling of the energy relaxation cascade that includes both

long-wavelength excitations (plasmons) and also point-like excitations (ionization) would be needed to better understand such a proposition. Alternatively, a reduction in the rate of ionization may arise from an increase in the  $2p$  ionization potential as more electrons enter excited states (though this effect competes with IPD).

### ***6.5 V. Conclusion and Future Directions***

We have explored the use of single hard x-ray XFEL pulses to simultaneously create and probe crystalline WDM via wide-angle x-ray diffraction. We present experimental results on the consequences of XFEL heating on the electronic structure of MgO as a function of deposited energy density, using a Hartree-Fock orbital-based model of ionization to infer electronic subshell populations from experimental Bragg peak intensities. We find that the experimental XRD signal is a sensitive measure of charge reconfiguration, allowing inference of valence ionization levels with a precision of under 0.1 electrons per unit cell. This sensitivity is in large part contingent on the structure of the system chosen: the odd-numbered Bragg reflections of MgO exhibit near-destructive interference in the ground state with a rapid, easily-measurable increase in intensity upon delocalization of electrons in the highest occupied molecular orbital (HOMO).

The experimental data shows a rapid delocalization of O  $2p$  electrons at deposited energy densities per unit cell far below the 7.8 eV band gap of MgO, which constitutes evidence for the creation of excitations within the ground state band gap. Significantly, we find no indication of a loss of long-range order in the positions of ion cores; we propose that the presence of states in the ground state band gap is instead a consequence of long-range disorder in the electric potential caused by ionization-derived site disorder.

Theoretical interpretation of the data is made difficult by the lack of LTE (a consequence of the presence of long-lived Mg  $2p$  holes), which renders comparison to finite-temperature DFT calculations impossible. Consequently, future experiments will aim for a closer approach to local thermal equilibrium in the probed system. One way of achieving this will be by studying systems free of long-lived excitations like those of the Mg  $2p$  core hole that

complicate the present analysis. Heavier rock-salt materials such as KCl are promising candidates as they exhibit shorter-lived  $p$  vacancies than MgO while sharing its most important features: namely, a large band gap and a diffraction signal with high sensitivity to site-specific charge delocalization. A closer approach to local thermal equilibrium can also be achieved by using time-resolved measurements under two-color pump-probe operation of the XFEL: specifically, a sufficient delay between pump and probe provides time for thermalization of electronic degrees of freedom. An additional benefit of two-color pump/probe configurations is the ability to interrogate temporally uniform states, instead of integration over a sample's evolution during XFEL stimulation (as is the case with single-pulse simultaneous pump/probe). Given the present hypothesis of strong changes in the density of states within the ground-state bandgap, it is also interesting to consider x-ray pump studies with optical (or UV) probe to directly evaluate changes to the electronic energy landscape on the energy scale of the band gap and ionization thresholds. In future studies it may be worthwhile, finally, to study non-rock salt compounds that similarly manifest a combination of destructive- and constructive-interference diffraction peaks. One possibility is layered binary dielectrics, in which one would expect strong sensitivity to interplanar charge reorganization effects.

## Chapter 7

# A DISPOSABLE X-RAY CAMERA BASED ON MASS PRODUCED CMOS SENSORS AND SINGLE-BOARD COMPUTERS

(Originally published as: Oliver R Hoidn and Gerald T Seidler, Review of Scientific Instruments **86.8** (2015), p. 086107. )

We have integrated mass-produced commercial complementary metal-oxide-semiconductor (CMOS) image sensors and off-the-shelf single-board computers into an x-ray camera platform optimized for acquisition of x-ray spectra and radiographs at energies of 2 – 6 keV. The CMOS sensor and single-board computer are complemented by custom mounting and interface hardware that can be easily acquired from rapid prototyping services. For single-pixel detection events, i.e., events where the deposited energy from one photon is substantially localized in a single pixel, we establish  $\sim$ 120% quantum efficiency at 2.6 keV with  $\sim$ 190 eV resolution and a 100 kHz maximum detection rate. The detector platform's useful intrinsic energy resolution, 5-m pixel size, ease of use, and obvious potential for parallelization make it a promising candidate for many applications at synchrotron facilities, in laser-heating plasma physics studies, and in laboratory-based x-ray spectrometry.

### 7.1 ***Introduction***

The performance of a wide range of contemporary applications of x-ray methods are contingent upon the capabilities of x-ray imaging sensors. Examples include radiographic imaging across the full span of spatial resolutions in addition to both energy-dispersive and

wavelength-dispersive spectroscopy in astrophysics, plasma physics [178], synchrotron science [179], and laboratory-based x-ray spectroscopies. The growing centrality of imaging detectors, especially those with significant single-pixel energy resolution, has led to a steady increase in commercial products and also niche-specific research efforts.

Here, we are most interested in a particular endpoint of these efforts, the possibility of mass-production of disposable x-ray spectroscopic cameras, i.e., those where each pixel has some significant energy resolution, having good performance for 2 – 6 keV photon energies. The ready availability of such sensors would be beneficial in several of the fields mentioned above while also serving as an easy test platform for new applications and as a convenient tool in education. We are not the first to consider these issues, and recent work in this subfield has demonstrated tantalizing potential for spectroscopic cameras based on standard, consumer-grade monochrome complementary metal-oxide semiconductor (CMOS) pixel arrays, [180, 181] such as regularly used in security cameras and other low-end imaging applications. This prior work establishes the viability of CMOS pixel arrays as spectroscopic imaging detectors of hard x rays and explores a host of performance characteristics, including linearity, radiation-hardness, and spatial response to single-photon interactions. The use of CMOS sensors, instead of charge-coupled devices (CCDs), is motivated by their lower cost due to chip-level integration of all sensor functions and the mature state of CMOS fabrication technology, as well as their typically much higher radiation hardness. These considerations are in some ways representative of other efforts where admittedly much more advanced and specialized CMOS sensors are making growing inroads.

## **7.2 Methods, Results, and Discussion**

Unlike prior work, here we investigate sensor performance below 6 keV photon energy. Our sensor platform design is driven by the goals of: (1) achieving a high saturation count rate, (2) generating single-photon spectra in real time, (3) ease of operation for new wavelength-dispersive spectrometer development in the laboratory setting [182] and (4) developing simple sensor exchange to make the camera viable as a disposable detector for use in plasma physics

experiments where experimental diagnostics are exposed to large electromagnetic pulses and to hazards from shrapnel from the laser-target interaction.

We consequently avoid commercial camera bodies and sensor evaluation boards, instead using a mass-produced CMOS sensor that can be easily and inexpensively replaced if damaged, a general-purpose single-board computer (SBC) having fast and flexible GPI/O capability as the principal hardware component, and a custom sensor board that has been designed in-house and fabricated by a rapid-prototyping printed circuit board service. To be specific, the sensor is an Aptina MT9M001 monochrome CMOS device with 1280 x 1024 resolution and a pixel size of 5.2 x 5.2 m<sup>2</sup>. The sensor was chosen primarily because of its high near-infrared sensitivity, which indicates a relatively thick active layer. Before the chip's installation its protective glass cover was removed, as it strongly absorbs x rays. The SBC is similarly a mass-produced component (BeagleBone Black SBC, Texas Instruments). The SBC is based on the AM3358 system on a chip, which contains an ARM Cortex A8 processor and a PRU-ICSS (Programmable Real-Time Unit Subsystem and Industrial Communication SubSystem) subsystem with two Programmable Realtime Unit (PRU) coprocessors. The SBC's software interface to the sensor board consists of two PRU programs (implemented in PRU assembler) that perform the readout and communicate with a Linux user space program (implemented in C) that concurrently processes the resulting data stream (see Fig. 7.2). The PRUs operate at 200 million instructions per second (MIPS) and are configured for single-clock access to the GPI/O pins on the SBC that interface with the sensor PCB. This is sufficient for readout at 30 frames per second (fps), near the MT9M001's maximum data rate. Our current implementation suffers from a memory bandwidth bottleneck that restricts frame rate to 10 fps, but this limitation can be removed by improving the PRU Linux kernel driver's allocation and management of the ARM/PRU DDR buffer so that it exploits the ARM core's CPU cache.

Figure 7.1: Block diagram of the CMOS camera design.

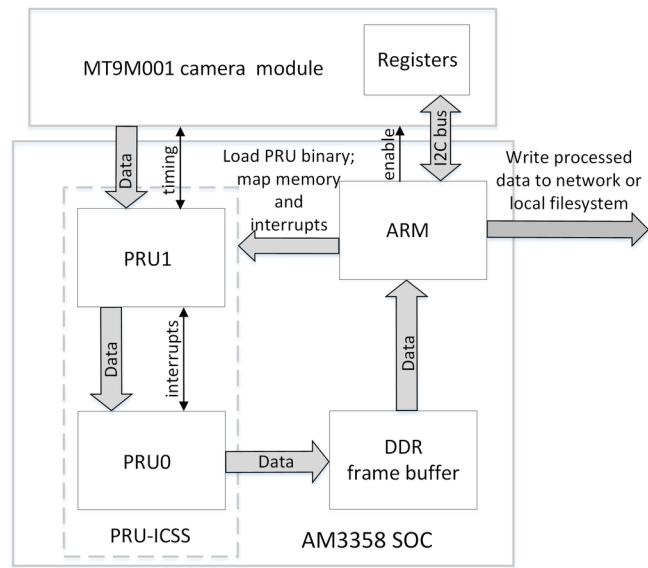
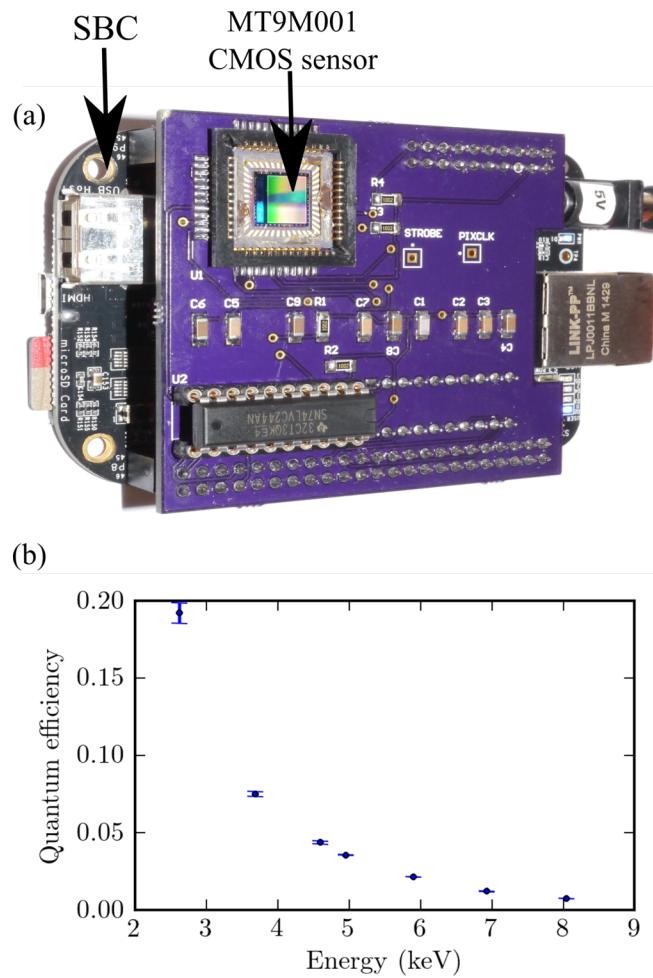


Figure 7.2: (a) An image of the camera, and (b) the camera's quantum efficiency in single-photon counting mode as a function of x-ray photon energy, as established by comparison with a commercial Si drift detector. The glass cover of the CMOS sensor has been removed to allow direct x-ray detection.



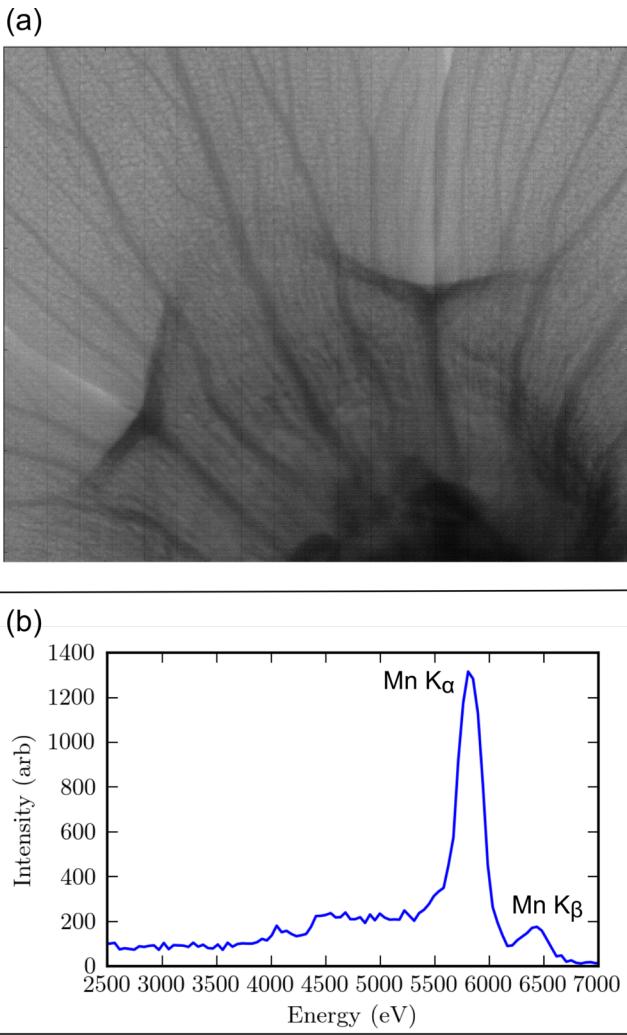
Multiple steps in processing are all performed on the SBC, and processed data is stored on the SBC's SD card before transfer to the control workstation. An exposure sequence accumulates the sum of all individual frames as a single image. Additionally, a spectrum is generated by binning the number of pixels per ADC channel. The finest energy resolution requires operating the sensor in the low-intensity single photon counting (SPC) regime where the mean period between photons incident on a given pixel is significantly larger than the frame time. Only x-ray events for which the entire charge cloud is concentrated in a single pixel are incorporated into the spectrum; this filtering step, which we refer to as cluster rejection, is well-established as necessary for optimal performance in pixel detectors used for SPC spectroscopy [180].

In cluster-rejection mode the sensor's saturation rate is 100,000 photons per second, but this can improved  $\sim$ 3-fold by resolving the aforementioned memory bottleneck. The quantum efficiency (QE) of the detector was characterized by measurement of the  $K$ -shell fluorescence spectra of chlorine, calcium, and several transition metals. This was done using a low-power laboratory x-ray tube source to excite  $1s$  core holes of these elements in various solid samples. The intensity of resulting  $K_\alpha$  and  $K_\beta$  emission registered by the detector was referenced to that recorded at the same position by a commercial Si drift detector (Amptek XR-100SDD) having known QE; results are presented in Fig. 7.2. Due to the small active layer thickness of the CMOS sensor, its quantum efficiency rapidly decreases from 19% at 2.6 keV (Cl  $K_\alpha$  emission) to  $\sim$ 1% at 8.0 keV (Cu  $K_\alpha$  emission). For imaging applications, such as use as a position-sensitive detector in wavelength-dispersive spectroscopy, it is clear that higher QE can be obtained by cluster identification, i.e., including information from events with some multipixel character. Our initial experience suggests a 50% increase in detected photon rate, but this requires further investigation. We expect that the QE will decrease below the Si  $K$ -edge because of the sudden increase in penetration length compared to the active layer thickness, but that some utility will remain below 1.5 keV. The present camera design is being modified for easier vacuum compatibility and the above issue will be investigated.

We now present detector performance in two representative applications. The radiograph in Fig. 7.2 (a) demonstrates the sensor's use as an imaging detector, while Fig. 7.2 (b) presents a spectrum of Mn  $K$ -shell emission. No dark-field corrections are used here: the dark counts are negligible in this bin range. The FWHM of the sensor's energy response function at Mn  $K_{\alpha}$  is 280 eV, approximately two times as large as in Fano noise-limited x-ray CCDs but still sufficiently small for the Mn  $K_{\alpha}$  and  $K_{\beta}$  emission peaks to be resolved. The resolution generally scales as  $\sqrt{E}$ , where  $E$  is photon energy, for example showing 190 eV resolution at Cl  $K_{\alpha}$  and 330 eV at Cu  $K_{\alpha}$ . The spectrum's background below the Mn  $K_{\alpha}$  peak energy is due to incomplete collection of charge from photon events, even after filtering for single-pixel events.

The camera's good QE below 4 keV suggests that few-keV x ray spectroscopy, whether in direct detection or as the position sensitive detector in a wavelength-dispersive instrument [179], would be a particularly favorable venue. In this regime, the smaller pixel dimension of CMOS sensors similar to the MT9M001 is a significant advantage relative to conventional x-ray CCDs, as it enables the combination of short working distance, high collection solid angle, and high energy resolution. [183–185] Additionally, such CMOS sensors' much smaller (1% or under) cost, while not in itself a technical innovation, makes them promising candidates for disposable direct-detection spectrometers in laser plasma experiments, for high-resolution radiography in educational (instructional) settings, and for versatile coverage of special scattering angles in synchrotron studies.

Figure 7.3: (a) Radiograph of a flower petal. The grayscale is a representation of raw incident intensity. Improved spatial resolution would be achieved by selection of single-pixel events. (b) X-ray emission spectrum of a Mn metal foil excited by a low-power laboratory x-ray tube source. The spectrum is based only on nominally single-pixel events.



### 7.3 Conclusions

We have reported the development of a flexible and surprisingly effective x-ray camera platform composed of standard commercial components merged with custom electronics that can be readily ordered from commercial prototyping services. The observed performance suggests an interesting range of future applications at photon energies of a few keV. This includes two aggressive possibilities: (1) large-area spectroscopic detectors formed by multiplexing large numbers of our cameras to reach net spectroscopic count rates useful for studies at the highest-intensity synchrotron beamlines or at x-ray free electron lasers, and (2) disposable detectors for use in the EMP-rich environments of laser plasma experiments.

### Acknowledgments

This work was supported by the U.S. Department of Energy, Basic Energy Sciences under Grant No. DE-FG02-09ER16106 and also by the Office of Science, Fusion Energy Sciences and the National Nuclear Security Administration thought Grant No. DE-SC0008580. We thank Bryan Venema for assistance with board assembly and for many useful discussions.

## Chapter 8

### A COLOR X-RAY CAMERA FOR 2-6 KEV USING A MASS-PRODUCED CMOS SENSOR

(*This is a reproduction of a manuscript in preparation: Oliver Hoidn, William Holden, and Gerald Seidler, Review of Scientific Instruments, 2017* )

We report here the development of a spectroscopic x-ray camera for 2 – 6 keV photons using mass-produced sensors and commercial control electronics. This instrument has several favorable characteristics for advanced x-ray spectroscopy studies in the laboratory, at synchrotron light sources, at x-ray free electron lasers, or using pulsed x-ray sources such as for laser plasma physics research. These characteristics include fine position and energy resolution for individual photon events; high saturation rates; easy user maintenance for damaged sensors; and software for real-time processing. We present results that evaluate this camera as an alternative to traditional energy-dispersive solid-state detectors, such as silicon drift detectors, and also illustrate its use in a dispersive x-ray emission spectrometer that has recently been reported elsewhere [Holden, et al., Rev. Sci. Instrum. 2017].

#### **8.1 I. Introduction**

The capabilities of a variety of x-ray techniques at the synchrotron, x-ray free electron laser (XFEL) and university-scale laboratory are heavily dependent on the characteristics of the x-ray detectors with which they are implemented. One technological regime of interest is that of pixel area detectors combining spectroscopic and spatial resolution with features such as high readout rate, large collection solid angle, and hardness to ionizing radiation and elec-

tromagnetic pulses (EMPs). The advent of time-resolved spectroscopy with pulsed photon sources, such as x-ray free electron lasers (XFELs), where it is often necessary to collect large numbers of signal photons quasi-instantaneously and with repetition rates exceeding 100 Hz, has greatly expanded the need for this class of detectors. Similar needs are also present in laser-plasma physics, where entire spectra for fluorescence, x-ray band thermal emission, or inelastic scattering must often be collected in truly single-pulse experiments.

While there is an impressive effort aimed at either improvement of existing state-of-the-art technology or *de novo* development of new ideas for truly advanced high-performance detectors, there is another route that requires consideration. Highly mass-produced, commercial multipixel sensors intended for primary use at optical wavelengths are, by the standards of x-ray science, already stunningly advanced sensors. For example, recent advances in the performance of mass-produced CMOS image sensors, including readout rates above 200 Mpix/second and optical-wavelength quantum efficiencies exceeding 80%, significantly increases their potential for scientific applications. The direct application of such sensors to the x-ray regime is limited mainly by the fact that their small pixel thicknesses lead to greatly decreased quantum efficiency for hard x-rays. That being said, the use of CMOS image sensors in the x-ray regime has been explored in prior literature, which has established them as viable spectroscopic imaging detectors having a favorable combination of low cost (a consequence of chip-level integration of all sensor functions), high framerates, and improved radiation hardness relative to comparable charge coupled devices (CCDs). [180, 181, 186, 187]. By ‘spectroscopic’, we mean that the camera output contains sufficient information for determination of both the energy and position of a photoabsorbed x-ray. Such devices are often referred to as ‘color x-ray cameras’.

In a prior publication we presented an x-ray camera platform for the 2-6 keV photon energy range based on a legacy CMOS image sensor, the Aptina MT9M001. Here, we introduce a new camera that incorporates a modern back-illuminated CMOS sensor with significantly improved readout rates and finer spectral and positional resolution compared to the previous model. Specifically, we find an energy resolution of  $\sim 150$  eV at 2 keV

with saturation rates above  $10^6$ /s at  $\sim 80$  Hz frame rate. These spectroscopic benefits are complemented by a spatial resolution of 2.9 m and real-time processing of all results, but are constrained by a  $\sim 60\%$  quantum efficiency at 2 keV that decreases to below 20% at 5 keV.

This manuscript continues as follows. First, in section II, we describe experimental details including the commercial hardware, and its modification used in the present instruments, and also the new software package that has been developed to support real-time spectral analysis or real-time energy-windowed imaging. A key point here is that it is not only the sensor, but also the entire camera read-out system that is commercially available because of the high demand for extreme low-light sensitivity imaging for, e.g., amateur astronomy. Next, in section III, we present results and discussion, demonstrating the cluster-binning methods and also both energy-dispersive and photon-counting modes for the camera. This includes representative data from a wavelength-dispersive spectrometer whose design has recently been described elsewhere. [188] Finally, in section IV we conclude and provide future directions.

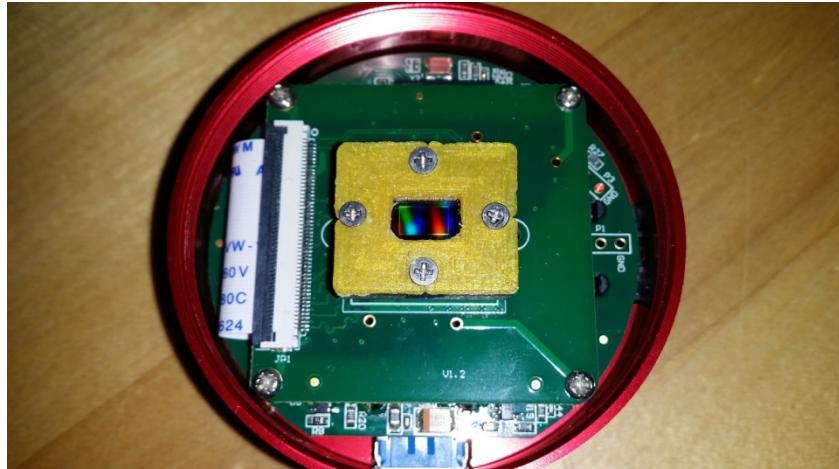
## **8.2 II. Experimental**

### *8.2.1 II.A. Hardware*

The hardware consists of a commercial amateur astronomy camera (ZWO Company) based on the Sony IMX291, a back-illuminated CMOS image sensor with a rolling shutter, pixel pitch of 2.9-m, pixel grid of 19361096, and maximum framerate of 170 fps. The sensor features high sensitivity and dynamic range, with a 12-bit A/D converter and readout noise of 1e- at maximum analog gain. The choice of vendor and model was driven by the manufacturer's provision of a software API allowing straightforward configuration and access to the sensor's uncompressed video stream; notably, however, other manufacturers offer products with similar feature sets.

We have modified the camera in two ways. First, the main camera board has been reworked by removing the IMX291 sensor and replacing it with a custom IC socket (Andon

Figure 8.1: Photograph of the modified camera. The original commercial product has been reworked to install an IC socket for the sensor and to remove the glass cover of the sensor.



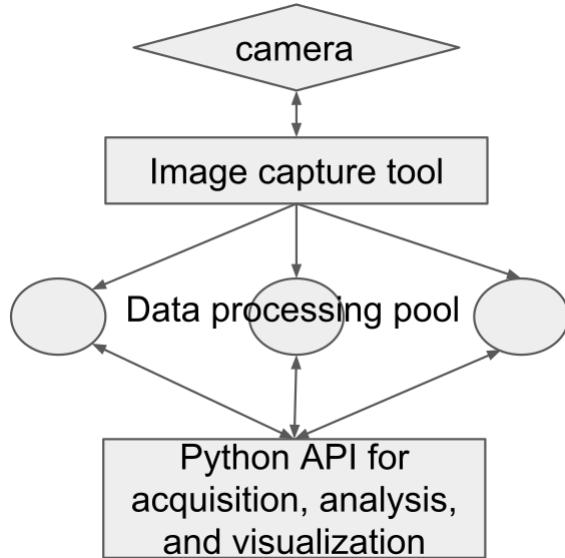
Electronics). This was done to more easily allow sensor replacement if radiation damage occurred. Second, the sensor itself has been modified by removal of the glass cover (Pacific X-Ray). A photo of the resulting camera is shown in Fig. 1. The yellow plastic part holding down the sensor is a simple clamp used to press the sensor against the socket contact pads.

### *8.2.2 II.B. Software*

Charge separation generated by an x-ray photon absorbed in the active layer of a sensor pixel results in a signal with expectation value proportional to the photon's energy. In the simplest case, wherein the entire charge cloud from an x-ray absorption event is concentrated in a single pixel, the detecting pixel has intrinsic sensitivity to the energy of the incident x-ray photon. In the majority of events, however, the charge cloud spreads over a cluster of several adjacent pixels.[187, 188] We have found that, in order to optimize the camera's quantum efficiency (QE) and spectroscopic sensitivity, it is essential to use this prior information to recover the energy and position of each detected photon on an event-by-event basis. To do this we perform a “breadth-first” search [189] of every frame to identify sets of connected pixels with ADC values above a user-specified signal threshold For each cluster thus identified,

the signal is summed over all member pixels and the event's position is inferred from the cluster's center of mass. This technique is similar to event-reconstruction algorithms used for the same purpose in prior literature, with the difference that we place no constraint on the size and shape of signal clusters.[180] The sensor's low noise floor (under 1 e<sup>-</sup> per pixel) allows the use of an aggressively low threshold level, resulting in a high level of signal.[190]

Figure 8.2: Diagram of camera data processing pipeline.



To implement the above analysis while avoiding the prohibitively large quantity of disk storage that offline processing demands, we developed a real-time data processing pipeline; the general framework for this pipeline is shown in Fig. 2. It consists of a collection of several software components communicating with one another over ZeroMQ sockets. First, a customized version of the open source image capture program oaCapture controls the camera's readout,[191] allowing the user to configure the camera's gain and per-frame exposure time. Event reconstruction, which requires the computational throughput of multiple CPU cores, is done by a pool of worker processes collecting frames from the capture application in round-robin fashion. The resulting filtered frames from this parallel pipeline are aggregated on a sink node that communicates with an API component that, in turn, provides users with

high-level functions for acquiring and visualizing pre-processed camera data.

### *8.2.3 II.C. X-ray Measurements*

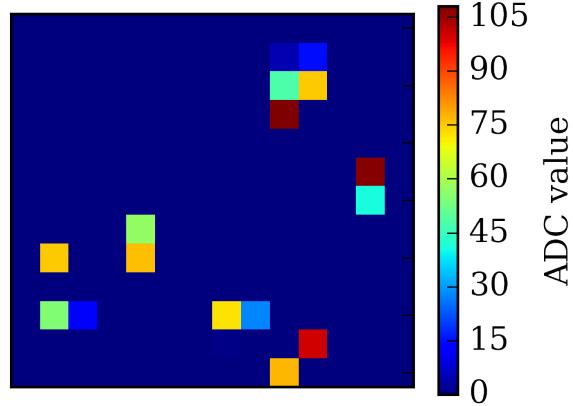
X-ray measurements for direct characterization of the camera performance used a low-powered Rh-anode x-ray tube (Moxtek). For quantum efficiency (QE) determination at different energies, the x-ray tube illuminated appropriate reference targets that generated elemental fluorescence at desired energies. The camera and a commercial SDD (Amptek XR-100SDD) were alternated behind a pinhole that ensured equal illumination on each sensor. The ratio of detection rates, corrected for the SDD's QE, then allows determination of the camera QE. Saturation rate measurements involved direct illumination of the camera by the full broadband output of the x-ray tube, displaced several tens of cm away from the sensor to allow for a useful tube-current range before saturation. Results from the miniature wavelength-dispersive spectrometer follow from methods described in Holden, et al. [188]

## **8.3 III. Results and Discussion**

In this section we address four aspects of the camera operation and performance: the cluster algorithm, energy dispersive operation, quantum efficiency, and finally single-photon counting mode for spectroscopically-constrained imaging. First, a magnified view of a small region of a captured image is presented in Fig. 3, where single-photon signal clusters are readily identifiable. The distribution of cluster sizes is strongly skewed; the largest clusters contain more than 10 pixels, while the mean number is 2.1.

Second, when operated as a spectroscopic sensor, the camera's user-visible output is a histogram, summed over all frames, of number of events binned by per-event signal. This is demonstrated in Fig. 4 (top panel), which shows the direct-illumination spectrum of a laboratory x-ray tube source. The dominant components of the signal are the tube's continuous bremsstrahlung spectrum and Rh L-shell emission from the anode. Two detector artifacts are also visible. First, a peak at the energy of Si K is generated by Si fluorescence photons emitted in the sensor that propagate far enough from their originating interaction

Figure 8.3: Representative cropped region of a camera frame during direct illumination by a Rh anode x-ray tube source operating at 6 kV bias voltage. The total illumination results in detection of  $2 \cdot 10^6$  photons/s using an 80 Hz frame rate.



sites to be registered as separate events. Second, the escape of Si fluorescence from the absorption sites of Rh L photons creates echos of the Rh L peaks (termed escape peaks) that are downshifted by 1.74 keV, the energy of Si K. We find that the camera's energy resolution at the energy of P K is 150 eV (Fig. 4 bottom panel), somewhat inferior to SDD's at this energy but still sufficient for many applications.

Figure 8.4: Energy dispersive spectrum from direct illumination of the camera by a Rh anode x-ray tube source operating at 6 kV bias voltage. The ADC channel at the peak of the Rh L emission contains  $3.2 \times 10^4$  counts. See the text for discussion.

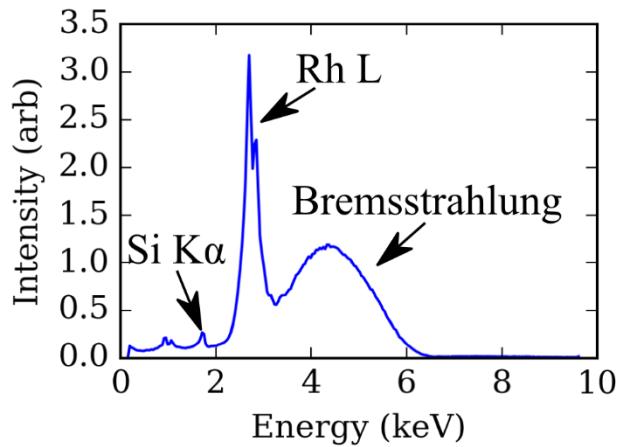


Figure 8.5: The camera's quantum efficiency (QE) as a function of x-ray photon energy, as established by comparison with a commercial Si drift detector (SDD), and under the assumption that the SDD's QE is equal to the x-ray transmission through its 12.7  $\mu\text{m}$ -thick Be window.

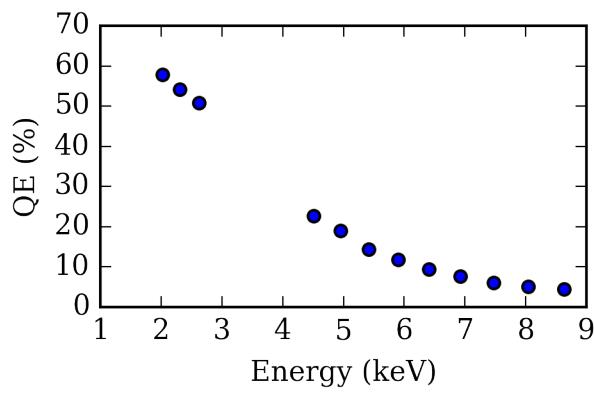
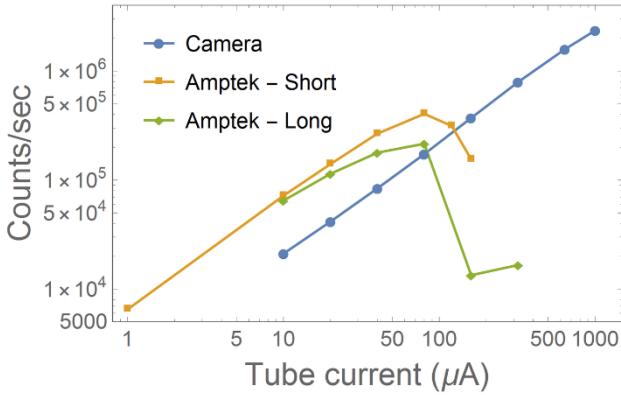
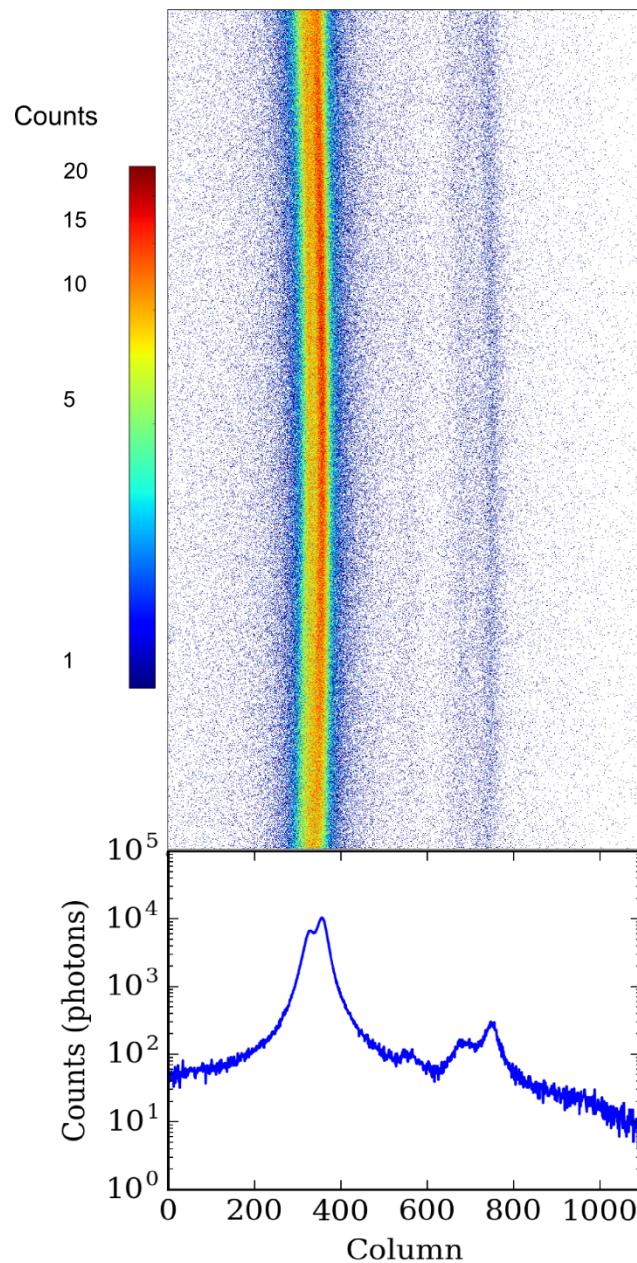


Figure 8.6: Camera count rate as a function of incident photon intensity, controlled via current provided to an x-ray tube source directly illuminating the camera with a broadband spectrum (see Fig. 4). We compare to the same curves for a commercial SDD with pulse shaping times optimized for count rate (short shaping time) or for energy resolution (long shaping time). The low efficiency of the camera is due to the large flux at higher photon energies where its QE is poor, see Figures 4 and 5. Illumination at lower photon energies will retain the high saturation rates but give the improved QE of Fig. 5.



Third, the quantum efficiency (QE) of the detector is presented in Fig. 5. We note a maximum QE of 60% at the energy of P K, a more than two-fold improvement over our previous camera. [187] Under uniform illumination at 6 kV accelerating potential, the observed count rates have only minimal deviations from linearity at count rates up to  $2 \times 10^6$  photons per second 80 Hz frame rate (see Fig. 6) – an impressive performance that is higher than the typical saturation rate of commercial silicon drift detectors. The exposure sub-region shown in Fig. 3 comes from this exposure rate. Note that the photon clusters are still largely disconnected, so that pile-up is infrequent. The lower count rates for the CMOS camera compared to the SDD are a consequence of the camera’s lower quantum efficiency at higher photon energies. The camera should retain the observed high saturation rate performance when illuminated with more monochromatic, lower-energy sources where its QE is higher.

Figure 8.7: Image of the sensor's output when serving as the position-sensitive area detector in miniature wavelength-dispersive spectrometer (Holden, et al., 2017). [188] The signal shown is a S K spectrum. In order to reduce the background level, the camera was configured to reject all events with photon energies outside of a spectral region of interest centered at S K. [188]



Finally, the camera's combination of high saturation count rates and small pixel dimension makes it a strong fit as a position-sensitive detector in compact dispersive x-ray emission spectrometer designs. In such an application the camera's spectroscopic sensitivity may be employed for background rejection (i.e., for rejection of photons with energies outside a pre-specified range), thus minimizing the need for shielding from stray scatter. Holden et al. have demonstrated this advantage in a novel compact wavelength-dispersive spectrometer design with a 10-cm Rowland circle that incorporates the camera as its position-sensitive detector.[188] In Figure 7, we show a representative camera exposure and the resulting processed spectrum. An energy region-of-interest has been set around the nominal S K photon energy so as to strongly reject stray scatter in the spectrometer. This simplified spectrometer design by greatly reducing the need for internal shielding. The spectrometer's small dimensions, which are enabled in part by the camera's fine spatial resolution, give it a large collection efficiency which results in count rates in laboratory studies (using low-power x-ray tube sources) comparable to those at a third-generation synchrotron insertion device. The instrument has thus far been demonstrated in the university-scale laboratory and at the synchrotron. Its potential use at the Linac Coherent Light Source (LCLS) is currently being investigated, especially as the sensor frame rate can likely be matched to the 120 Hz repetition rate of that XFEL.

#### **8.4 IV. Conclusions and Future Directions**

In conclusion, we have reported the development of a spectroscopic x-ray camera based on a mass-produced consumer product. The observed performance suggests a range of potential applications as a high-speed spectroscopic detector with fine spatial resolution and adequate quantum efficiency in the 2 - 6 keV photon energy range. Among these applications, we have demonstrated effective use of the camera as an energy-selective position-sensitive detector in a high-performance compact dispersive spectrometer.

## Chapter 9

### REAL-TIME ANALYSIS TOOLS FOR THE LCLS

A significant drawback of current XFELs, compared to synchrotron light sources, is that they are capable of providing photons to only one endstation at a time. As a result they are vastly oversubscribed, and beamtime is granted in small allocations through highly competitive selection processes. Experimental teams therefore have strong incentives to make the most efficient possible use of beam time. Focusing on the specific case of the LCLS, the high power of the XFEL source (and its 120 Hz repetition rate) facilitates rapid completion of experiments by making very high data collection rates possible . However, fully taking advantage of high data throughput is a problem unto itself, as experiments cannot be fully scripted in advance; it is in practice necessary to make rapid evaluations based on measurement of beam conditions (which, in two-color mode, can be strongly variable), the statistical quality of incoming data, and tentative physical interpretations in the incoming data. This feedback often guides important decisions, such as beam tuning and the motion of samples and detectors.

With the goal of addressing this problem we have developed a software package for real-time analysis and visualization of data in XFEL experiments at the LCLS. The software is implemented using Photon Science Analysis (psana), the internal data analysis framework at the LCLS, and can be run in distributed fashion over hundreds of cores. [168] It attempts to enable a more effective analysis workflow than currently available to LCLS users, excluding those doing specialized experiments of with well-established protocols for which there already exist tailored software packages (such as Cheetah for serial femtosecond crystallography). [192]

This chapter describes a Python API that provides high-level analysis and visu-

alization functions that directly implement common analysis operations, and can serve as a building block for creating more complex custom ones. The API is optimized for use through Jupyter Notebook, and it leverages the rich interactive plotting features available in that environment.

Though it will not be discussed in detail, we note the existence of a second interface to the same analysis framework, consisting of a web application that provides a more user-friendly graphical interface (in exchange for reduced flexibility). This interface was independently developed by Ryan Valenza from the Seidler group.

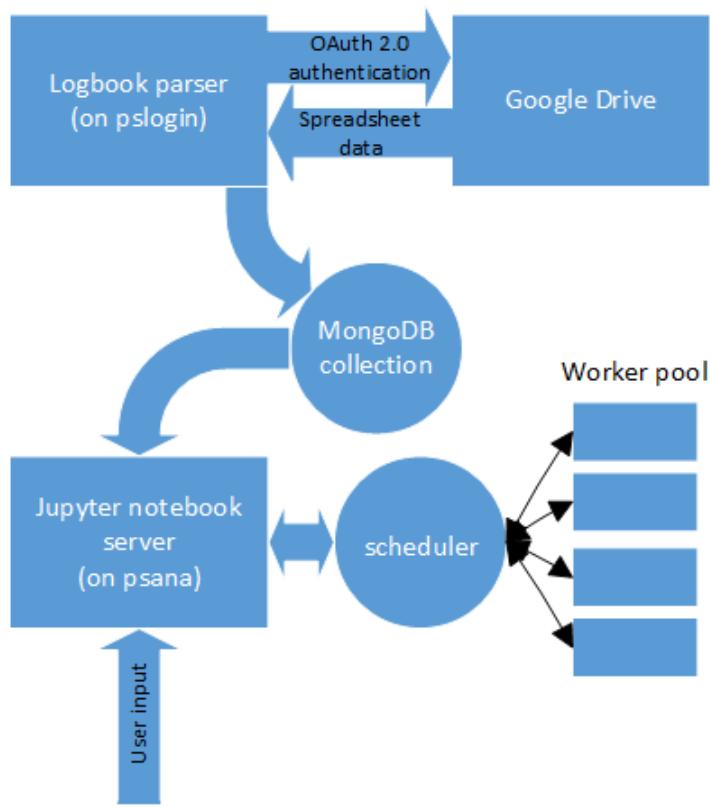
### ***9.1 Integration of Logging and Analysis***

The psana API associates every LCLS pulse (referred to as an event) with two integers, a run number and event number. [168] A run contains a consecutive sequence of events; the maximum number of events in a run is determined by a 17 bit 360 Hz ‘fiducial’ counter that the LCLS timing system distributes to each detector. The association of run/event number combinations to LCLS pulses is in practice further constrained by endstation-specific software and instrumental details: for example, experimental modes that require interruptions in data collections require the run number to be frequently incremented.

Because the LCLS DAQ system does not allow the association of events with user-provided metadata, LCLS users must maintain separate experimental logs in which, for each run number and range of event numbers, they record information related to sample type, beam conditions, and other relevant experimental parameters. In the vast majority of cases, users’ analysis scripts directly expose psana’s data access API, requiring them to explicitly specify datasets in terms of lists of run numbers. To do this the user must manually look up and transcribe information from the experimental logbook, an operation that becomes time-consuming (and potentially error-prone) when frequently repeated, as it usually must be.

In response, we’ve made a step to unify the workflows for experimental logging and analysis. We’ve defined a simple query language with which the user can construct datasets

Figure 9.1: Diagram summarizing the analysis software's architecture.



defined by matches to metadata attributes recorded in the experimental logbook. The implementation is described in Fig. 9.1; briefly, it consists of a daemon (i.e. application component) that accesses data from standard-formatted Google Drive spreadsheets tied to users' personal Google accounts. This daemon parses spreadsheet data into a graph structure associating run numbers with metadata column values and constructs datasets (i.e., sets of run numbers) corresponding to user-provided queries on those column values. Our Python analysis API in turn provides high-level analysis and visualization functions that operate on

these user-defined datasets.

## ***9.2 Interactive Distributed Computing***

A second feature of the software is the simplified fashion in which it leverages the LCLS computing cluster. To do real-time analysis during beam runs it is typically necessary to scale one's workload over tens or hundreds of CPU cores. This is typically done with a batch processing workflow, where command lines for launching parallel analysis scripts are submitted to the LCLS's Platform Load Sharing Facility (LSF), which schedules them for execution on nodes of the cluster. Once a batch job is complete, users typically run a second (non-distributed) program to load and visualize the output data. The time that elapses between submission of a batch job and when it begins running is typically on the order 10 seconds or more, assuming an empty job queue. The separation between the steps of submitting an analysis batch job and loading and viewing its results introduces a delay as well, because the user must manually intervene at two points in the analysis pipeline. These two factors give a batch-processing-based workflow significant overhead.

Our software package offers a significant improvement in this respect: the backend of the analysis API distributes calculations over the LCLS cluster transparently, with no need for the user to submit batch jobs or otherwise steer the parallel computation in any way. Distributed computation is implemented using the parallel computing utility `pathos`, which allows scatter-gather style computation using the same API as Python's multiprocessing module, but with more flexible serialization capability implemented by the module `dill`.

## ***9.3 API features***

The last component of our package is a library of API functions for analyzing and visualizing data. These are in part tailored to MEC, the location of both our LCLS beam runs, but are for the most part generally applicable to other endstations. The API heavily leverages features of the browser-based Jupyter notebook, including interactive Javascript-based plots.

The API provides standard analysis routines for spectroscopy and X-ray powder diffraction. Miscellaneous diagnostic tools are included for, e.g., viewing the readout of area detectors (per-event or averaged over all events in a dataset) and generating histograms or scatter plots of event-by-event signal incident on arbitrary detectors. Most of these functions adopt a general functional programming style that allows the user to alter their behavior, using them as building blocks in more complex, customized applications. For instance, all analysis API calls accept, as optional arguments, user-defined functions for event rejection that take a detector datum as input and return a boolean. A more specialized example of the functions-as-arguments pattern is the histogram API call. In its most basic usage, this function takes an area detector identifier and one or more datasets as arguments, and returns an interactive figure containing histograms of per-event integrated signal on the detector. In a more sophisticated usage, the user could pass in a keyword parameter consisting of a function that, for example, integrates signal over a subregion of the area detector’s 2D data array, instead of its entirety.

This software is under continued development. The primary ongoing effort is an overhaul of the parallel-processing backend to use the distributed computing library Dask. Dask’s valuable features, in our context, include a task scheduler with the ability to dispatch work to a pool of worker processes in intelligent fashion (with awareness of task dependencies and data locality), and with flexibility and fault tolerance—allowing, for example, the dynamic addition and removal of worker processes.

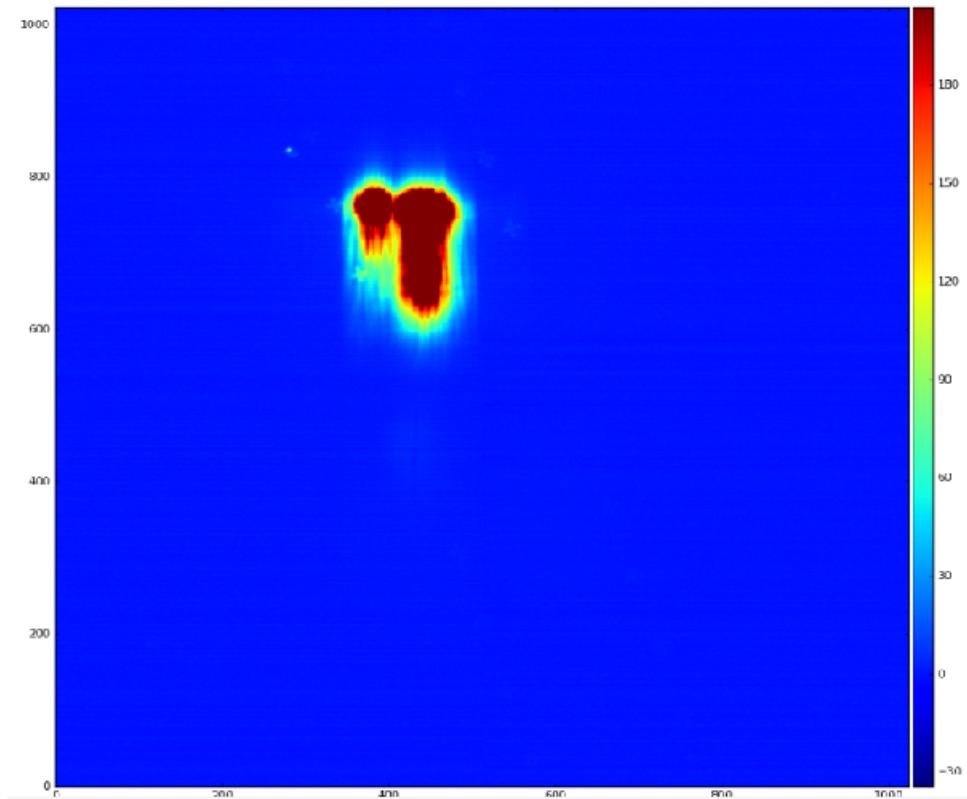
Figure 9.2: Jupyter Notebook screen capture demonstrating a simple example of the API’s usage. First a dataset is defined via a query matching all run numbers between 200 and 210 for which the recorded value for the XFEL transmission is 0.11. Two metadata attributes of the resulting dataset are then printed. In the last line of input, we call the API function `datashow.show`, which takes a list of datasets (in this case containing the single defined dataset) and an area detector identifier (in this case ‘si’, the identifier for a downstream silicon spectrometer monitoring the XFEL spectrum) and displays the average of detector readouts over all events. This data was collected at LCLS beam run LK20.

```
In [13]: from dataaccess.nbfuctions import get_query_dataset as query
from dataaccess.datashow import show

ds = query('runs 200 210 transmission 0.11');
print [(attr, ds.get_attribute(attr)) for attr in ['transmission', 'runs']]

show([ds], 'si');

[('transmission', 0.11), ('runs', [206])]
```



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