Secondary Electron Cascade Dynamics in KI and CsI

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We present a study of the characteristics of secondary electron cascades in two photocathode materials, KI and CsI. To do so, we have employed a model that enables us to explicitly follow the electron trajectories once the dielectric properties have been derived semiempirically from the energy loss function. Furthermore, we introduce a modification to the model by which the energy loss function is calculated in a first-principle manner using the GW approximation for the self-energy of the electrons. We find good agreement between the two approaches. Our results show comparable saturation times and secondary electron yields for the cascades in the two materials, and a narrower electron energy distribution (51%) for KI compared to that for CsI.

1. Introduction

The new linear accelerator-based X-ray free electron lasers (XFELs) will produce X-ray pulses with durations of below 100 fs,^{1–3} corresponding to the time scale of atomic vibrations in solids and molecules and of chemical reactions. The pulses produced will have intensities up to 10 orders of magnitude higher than those of the laser-based high harmonics sources available today.^{4,5} These new X-ray sources will not only provide new windows to the studies of phenomena of ultrafast nature, but will also revolutionize structural science by allowing for the diffraction of nanometer sized objects without the need for crystalline periodicity of the sample.^{6–10}

Ultrafast phenomena are typically studied using pump–probe techniques where the dynamics are initiated by a pump laser and probed using X-rays after some time delay. An XFEL will provide only one pulse, therefore most pump–probe experiments will rely on the second pulse to be produced by an external source. Since time jittering between the pump and the probe will affect the temporal resolution, the synchronization between the two is of primary concern.^{11–13} In alternative experimental setups where the same pulse is used as both pump and probe, as in recent holography experiments at the FLASH source in Hamburg, Germany,¹⁴ time jittering is not an issue.

One way to deal with the problem of jitter between the pulses of an XFEL is by the so-called electro-optic sampling technique, developed at the Sub-Picosecond Pulse Source at the Stanford Linear-Accelerator Center by Cavalieri et al.¹¹ By measuring the arrival time for each high-energy electron bunch, a timing resolution higher than 60 fs rms was demonstrated between the X-ray pulses and an external pump laser pulse.

Another more well-established way to measure the jitter between the pump and the probe, and to characterize the pulses, is by use of a streak camera.¹⁵ In a streak camera, photoelectrons are emitted after the cathode is bombarded with X-rays, after which Auger electron decays follow. Inside the photocathode,

either elastic scattering, where the electron momentum changes direction, or inelastic scattering, where secondary electrons (SEs) may be excited from the valence band or energy may be lost to the system, can take place. The inelastic scattering is determined by the dielectric properties of the crystal, which are mediated through three major channels:^{16,17} (i) promotion of band transitions, (ii) plasmon excitations, and (iii) phonon excitations. If the X-ray penetration depth and the incidence geometry favor the escape of SEs from the cathode, these are accelerated through an extraction field and projected into an anode so that their arrival position can be timed back to the originating X-ray pulse. The streak camera's resolution and efficiency is thus determined by the total electron yield and its spread in energy.^{18–20}

Kane²¹ presented a first derivation for the rate of inelastic scattering of electrons by considering the production of electron–hole pairs in silicon. Henke et al.²² performed further investigations for semiconductors and insulators as compared to gold, both theoretically and experimentally, with respect to the electrons' total yield and their distribution in energy. In their model they accounted for both electron and phonon scattering, but worked under a free-electron band description and thus did not fully treat the bound nature of the collective excitations. They found strong structural features for the alkali halide SE energy distributions and suggested these to arise from single-electron promotions from the valence band due to plasmon de-excitations. Fraser^{23,24} examined the total yield and pulsed quantum efficiency with respect to photon incidence angle and energy, and presented a model describing the dynamics in terms of averaged parameters for the SE creation energy and their inelastic mean free path. Boutoul et al.^{25–27} introduced a model in which a more rigorous treatment of the electron–phonon scattering was implemented for CsI, but obtained an energy spread for the SE deviating from Henke's experiments. This discrepancy was claimed to arise from the lack of treatment of plasmons in their model.²⁸ A recent investigation on the efficiency of CsI as a photocathode in a streak camera with grating incidence geometry was presented by Lowney et al.,²⁰ where the unit quantum efficiency between SEs generated inside

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the material and the number of escaping electrons was demonstrated for photon energies between 100 eV and 1 keV.

2. Method

We perform studies of SE cascades initiated by impact electrons in two different alkali iodide materials, KI and CsI. We use a model developed by Tanuma, Powell, and Penn (TPP),^{29–35} which derives the dielectric properties of a material from its energy loss function (ELF). This work is a continuation of the approach used for diamond by Ziaja et al.^{36–38} and for water by Timneanu et al.³⁹ This approach enables us to explicitly follow the electron trajectories once the dielectric properties have been derived semiempirically, given the experimental determination of the ELF.⁴⁰ Additionally, we introduce a modification to this model by which the ELF is calculated in a first-principle manner from the screened Coulomb potential of the electrons using the GW approximation for the self-energy of the electrons.⁴¹ In previous publications, an alternative model to the TPP model by Ashley^{42,43} was also employed, but was found to underestimate the number of generated electrons;³⁸ therefore we have chosen not to use it here. Previous results for water have shown good agreement with radiolysis data from experiments, despite the fact that the measurements were performed on longer time scales.⁴⁴

2.1. Band Structures. The GW approximation provides a more accurate description of the band structures of semiconductors than that given by the local density approximation (LDA) of the density functional theory,⁴⁵ and, although it does not explicitly account for the presence of excitons, that is, coupled electron–hole pairs, it provides a better treatment of the dielectric properties from first-principles. The correlation between electrons is dealt with through the inclusion of a self-energy correction to the Hamiltonian,

$$\Sigma = iGW \quad (2.1)$$

where G denotes a Green's function, and W is the screened Coulomb potential. W embodies the dielectric response of the electron gas, ϵ , as

$$W = \epsilon^{-1}v \quad (2.2)$$

where v denotes the bare Coulomb interaction. An extracted ELF from such calculations

$$\text{ELF} = \text{Im}[-\epsilon(\mathbf{q}, \omega)^{-1}] \quad (2.3)$$

accounts for interband transitions and plasmon excitations but leaves out phonon interactions, which significantly contribute to the thermalization of electrons at low energies.

2.2. Cross Sections. The elastic cross section is calculated with the Barbieri/van Hove Phase Shift package using a partial wave expansion technique^{46,47} and is given as

$$\sigma_{\text{elastic}}(E) = \frac{2\pi\hbar^2}{Em_e} \sum_l (2l+1) \sin^2 \delta_l \quad (2.4)$$

where δ_l is the calculated phase shift for each partial wave l . The elastic cross section has limited impact on the final characteristics of the generated cascades. For further details on these calculations, see refs 36–39.

The inelastic cross sections are derived from the ELF as^{16,36}

$$\sigma_{\text{inelastic}}(E) \sim \frac{1}{E} \int_0^\infty d\omega \int_{q^-}^{q^+} \frac{dq}{q} \text{Im}[-\epsilon(q, \omega)^{-1}] \quad (2.5)$$

where

$$q_{\pm} = \frac{\sqrt{2m_e}}{\hbar} (\sqrt{E} \pm \sqrt{E - \hbar\omega}) \quad (2.6)$$

sets the limits for the momentum transfer. The q dependence in eq 2.5 is modeled by the TPP model.³¹

2.3. Electron Trajectories. Classical simulations of the electron trajectories were performed where Newton's equations of motion are solved using a leapfrog integration scheme.³⁹ The energy dependent probabilities for each event, $P(E)$, are given as

$$P(E) = \frac{\rho N_{\text{av}}}{m} \sigma(E) |v_e(E)| \Delta t \quad (2.7)$$

where ρ is the density of the material, N_{av} is Avogadro's number, m is the mass of the molecule, and v_e is the velocity of the electron. The time step $\Delta t = 10^{-2}$ fs was chosen to ensure that $P \ll 1$ in all cases. At each time step in the simulation, the following algorithm is applied to an electron with kinetic energy E_k :

1. If $P(E_k)$ is smaller than a random number, $0 \leq r < 1$, no scattering occurs, the velocity remains unchanged, and the electron position is integrated.
2. If the electron scatters elastically, it changes its momentum randomly.
3. If the electron scatters inelastically, it changes its momentum orientation randomly and loses energy E_{lost} to the system. If $E_{\text{lost}} > E_{\text{gap}}$, an electron is liberated from the valence band with energy $E_k = E_{\text{lost}} - E_{\text{gap}}$; otherwise, E_{lost} is lost to the lattice.

After saturation of the cascades, at around 100 fs, the energy from the initial impact electron dissipates into the system through the creation of SEs and losses to the lattice.

3. Results and Discussion

We perform band structure calculations for the two crystals on a [12 12 12]-point grid in reciprocal space, with an ideal face-centered cubic structure with lattice parameter $a = 7.064$ Å for KI,⁴⁸ a simple cubic structure with lattice parameter $a = 4.562$ Å for CsI,⁴⁸ and an initial valence electron configuration as K:[4s1 3p6], Cs:[6s1 5p6], I:[5p5]. We used an implementation of the GW model by Kotani et al., where W is calculated under the random phase approximation,⁴⁹ and present the obtained electronic structure results for KI and CsI in Figures 1 and 2, respectively.

We explicitly follow the electron trajectories in SE cascades derived from both experimental (taken from Creuzburg⁴⁰) and first-principle ELF's. The elastic cross sections are shown in Figure 3. At energies below 100 eV, CsI shows a higher elastic cross section due to its higher density ($\rho_{\text{CsI}}/\rho_{\text{KI}} \approx 1.45$). As numerical divergences occur for the calculation of ELF's at zero momentum transfer, we instead perform calculations for the smallest reciprocal vector available in the first Brillouin zone, that is, $\mathbf{q}_{\text{KI}} = (1/12, 1/12, 1/12)(2\pi/a)$ and $\mathbf{q}_{\text{CsI}} = (1/12, 0, 0)(2\pi/a)$. For a discussion on the effects of plasmon dispersions along a direction in reciprocal space, see ref 50 and the references therein.

The collected results presented in Table 1 show that good agreement is obtained between the calculated and experimental band-gaps for both KI and CsI, and we find that the calculated plasmon peak energies increase with atomic number when going from KI to CsI in the alkali iodide series, in contrast to the experimental data. We encounter large discrepancies between first-principle and experimental ELF's for energies above

Figure 1. Upper: LDA band structures (lines) and GW corrections at high symmetry points (circles); the LDA gap is opened from 3.54 to 6.41 eV (6.31 eV experimental value⁵⁹). The Fermi energy relative to the lower valence band is 17.65 eV. Lower: Calculated ELF (line) for the smallest available vector in the first Brillouin zone, $(1/12, 1/12, 1/12)(2\pi/a)$ along with experimental data⁴⁰ ($\times$). The calculations are carried out with the 3p states of K in the core because of numerical complications as band crossing occurs with the 5s state of I. Plasmon peaks are encountered at 8.52 and 13.67 eV.

Figure 2. Upper: LDA band structures (lines) and GW corrections at high symmetry points (circles); the LDA gap is opened from 3.56 to 6.33 eV (6.37 eV experimental value⁵⁹). The Fermi energy relative to the lowest valence band is 15.07 eV. Lower: Calculated ELF (line) for the smallest available vector in the first Brillouin zone, $(1/12, 0, 0)(2\pi/a)$ along with experimental data⁴⁰ ($\times$). Plasmon peaks are encountered at 9.96 and 21.03 eV.

15 eV (see Figures 1 and 2), and these are particularly large in the case of KI, likely because of the K_{3p} states missing in our calculations. The discrepancies between the ELF are reflected in the inelastic cross sections, where results calculated from “first-principles” have larger values than those originating from experimental ELFs, as given by eq 2.5. Figure 4 shows the inelastic cross section calculated from both first-principle and experimental ELFs. In both cases, CsI gives a cross section larger than KI, but the difference between the two is smaller when calculated from experimental ELFs. This is due to the fact that the discrepancy between the two calculated ELFs is

Figure 3. Elastic cross sections for KI (full) and CsI (dashed) obtained from partial wave expansions. The differences between the two crystal structures reduce significantly as the kinetic energy of the electrons increases.

TABLE 1. First-Principle Results for the Band Gap Energy, E_{gap} , Valence Bandwidth, E_{vbw} , and Plasmon Energy, E_{pl} , Listed Next to Experimental Data^a

	KI _{calc}	KI _{exp}	CsI _{calc}	CsI _{exp}
E_{gap}	6.41 eV	6.31 eV ^b	6.33 eV	6.37 eV ^b
E_{vbw}	1.39 eV	1.8 eV ^b	1.63 eV	1.65 eV ^b
E_{pl}	8.52 eV	11.8 eV ^c	9.96 eV	10.3 eV ^c
N_{SE}	19.84		20.18	
E_{ch}	25.67 eV		24.78 eV	
$E_{\text{ch}}/E_{\text{gap}}$	4.0	~3	3.91	~3
$E_{\text{pl}}/E_{\text{gap}}$	1.32	1.87	1.57	1.62

^a The average number of SEs generated by a 500 eV initiating electron, N_{SE} , is given along with the average electron–hole pair creation energy, E_{ch} . When compared to the band gap, $E_{\text{ch}}/E_{\text{gap}}$ and $E_{\text{pl}}/E_{\text{gap}}$ provide a phenomenological measure for the ranking of the semiconductor as an SE emitter. ^b Reference 59. ^c Reference 40.

Figure 4. Inelastic cross section for KI and CsI obtained from eq 2.5 using the TPP model for calculated and experimental ELFs.

larger than the experimental one, as the ELF and the inelastic cross section relate through eq 2.5.

The most significant Auger electron decay for KI and for CsI occurs at energies of 293 eV⁵¹ and 724 eV,⁵² respectively, since these energies determine the total number of SE emissions; about 2.5 times more SEs would be expected for CsI than for KI (see argument below). As we wish to make a comparison

Figure 5. Number of generated SEs in KI and CsI with an originating impact electron energy of 500 eV.

Figure 6. Radius of gyration, or the electrons average distance from the electron clouds center of mass as a function of time.

between the two crystals, we initiate the cascades at the same energy (500 eV) and average the results over 500 simulations. Despite the discrepancies between the calculated and experimental ELF, the characteristics of the generated electrons agree well. The number of generated SEs, the radius of gyration (i.e., the average distance of the electrons from the cloud center of mass), the energy loss to the lattice, and the SE distribution in time and energy are used to illustrate the dynamics of the cascades (Figures 5–8, respectively).

The radius of gyration shown in Figure 5 reflects the difference in density between the two crystals, with the electron clouds in KI showing a slightly more localized nature. We find that the number of SE emissions depends linearly on the energy of the originating impact electrons up to 1000 eV (data not shown), in agreement with ref 53. Our calculations show that the generation of SEs in CsI saturates slightly faster than in KI (Figures 6–8) and that the number of generated SEs after saturation is about 20 for both KI and CsI (see Figure 6). Experimentally determined electron yields from a 160 nm-thick CsI film show that a 500 eV electron would generate around 10 SEs.⁵³ This value is comparable to the results presented here, taking the X-ray penetration depth and the exponentially decaying escape rate for SEs when moving toward the surface into account.⁵⁴

Figure 7. The distribution of the initial impact electron's energy between the SEs and the lattice.

Figure 8. The SE distributions in time and energy generated from calculated ELF for KI (upper) and CsI (lower) from an initial impact electron of 500 eV.

In Figure 7 we see how the original impact electron's energy dissipates in the system through the creation of SEs and losses to the lattice. For KI, the energy loss to the lattice after saturation is about 65%; for CsI, it is about 55%. A study on diamond by Ziaja et al.,³⁷ showed that energy losses to the lattice led to a reduction of the total number of generated SEs by a factor of 2, comparable to what is found in the present work.

The energy distribution of the SEs after saturation is 51% narrower for KI than for CsI (9.99 eV and 19.5 eV, respectively). This is illustrated by Figure 8, where the energy profile for the normalized average number of electrons in the cascade is shown for different times. Experimental studies show similar trends for the width of the SE energy distribution, where we find 0.61 eV for KI and 1.6 eV for CsI.²² Impact energies comparable to that of the higher conduction bands (i.e., $E_k \sim 50$ eV) are reached after only a few inelastic collisions in the cascade. At these energies, a free-electron approach is no longer proper since the bound nature of the electrons will have an impact on the

scattering probabilities. In semiconductors and insulators, because of the presence of a band gap, inelastic scattering is mainly mediated by direct and indirect (e.g., plasmon decay) electron–hole pair creation.¹⁶ Our first-principle calculations account for a more detailed band structure, by which a more accurate picture is given for these bound structure effects. Still missing in our approach is a proper treatment of the low-energy regime, where phonon scattering becomes significant for the energy loss of the SEs.^{20,22,26}

Since our main objective is to compare the characteristics of the electron cascades generated in KI and CsI, we have, for the sake of simplicity, not included the treatment of holes. The average electron–hole pair creation energy is given by the ratio between the energy deposited in the system and the total number of SEs generated. Our calculated values listed in Table 1 compare well with the empirical expectation $E_{\text{eh}} \approx 3E_{\text{gap}}$.⁵⁵ For alkali iodides, because of the wide band gap and the comparatively narrow valence band widths, a hole in the valence has low probability for scattering and creating SEs.^{56,57} Thus, the neglect of holes in our treatment is to some extent justified.

4. Conclusions

We present a new approach for calculating SE cascades in solids from first-principle calculations of the ELF. Our results show that the electron cascade spatial and energy dynamics agree well with the conventional approach where calculations are based on an experimental ELF. This article presents the first study emphasizing photocathode materials for streak cameras.

Comparison between the electron cascades for KI and CsI shows that the saturation times are below 100 fs, that the energy loss to the lattice is about 65% for KI and 55% for CsI, and that the distribution in energy for the SEs is 51% narrower in KI. The average electron–hole pair creation energy is comparable between the two materials. These characteristics indicate that, in a streak camera, a KI photocathode would give a higher temporal resolution than a CsI photocathode would. This is, however, a preliminary theoretical investigation, and further work to refine the model is necessary, such as the incorporation of energy losses due to phonon scattering. It would be of interest to replace the TPP modeling of the momentum dependence when calculating the ELF with a model deriving the probabilities for inelastic scattering directly from first-principle band structures, for example, as presented by Silkin et al.⁵⁸

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