Synchrotron–laser interactions in hexagonal boron nitride: an examination of charge trapping dynamics at the boron K-edge

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Abstract. Synchrotron–laser pump-probe (PP) luminescence measurements have been undertaken in hexagonal-phase boron nitride. For non-resonant excitation below the boron K-edge, the dynamics of the transients induced by the application of laser probes at 1.49, 2.33 and 3.07 eV are determined, as well as the signal recovery to equilibrium after the probes are removed. The transients are shown to be entirely related to the presence of trapping states within the material. By varying the synchrotron pump energy, the system dynamics are shown to change significantly, due to alteration in competition between the defect centres. As the synchrotron energy is scanned across the near-edge x-ray absorption (NEXAFS) region of the boron K-edge (190–205 eV), PP NEXAFS can be extracted directly from the trapping rate changes, and this opens the possibilities for directly linking particular charge trapping centres with their chemical environments. This is the first report where such processes have been used to obtain luminescence-based PP x-ray absorption spectra.

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1. Introduction

Laser–laser pump-probe (PP) spectroscopy is a popular lab-based method for investigating transient carrier dynamics in semiconductors [1]; by extending the measurements to 3rd generation synchrotron sources, chemical and structural information is also potentially available via interaction with the core-level states of the constituent atoms. Hitherto, such core-level synchrotron–laser interactions have mainly been studied via photo-electrons emitted from the sample (e.g. [2, 3]); laser induced changes in the x-ray absorption spectra as the synchrotron energy is scanned over the core levels has mainly been undertaken in dilute molecular systems when studying the structure of excited states (e.g. [4]). Although such techniques are still very much in their infancy, the possibilities will be greatly enhanced by proposed 4th generation light sources, such as the UK’s 4GLS (e.g. [5, 6]). Nevertheless, by judicial selection of materials, processes to be probed and photon production systems to be deployed (such as synchrotron wiggler sources, and lasers with suitably matched photon fluxes), synchrotron–laser x-ray absorption PP experiments can be achievable on 2nd generation light sources such as the Daresbury synchrotron. In doing so, valuable insight can be gained on the electronic and structural properties of materials in advance of more sophisticated experiments which fourth generation light sources will permit.

A rapidly developing method of sample analysis at the SRS is that of optical detection of x-ray absorption spectroscopy (ODXAS; e.g. [7, 8]). As the name implies, XAS of luminescent samples (typically semiconductors and insulators, but also metals) is detected directly via the optical photons emitted, and provides a unique method for linking the luminescent properties of a sample with its chemistry and structure: standard EXAFS analysis methods can be applied for determining structural states (e.g. [9]). ODXAS is an extremely sensitive detection method, and necessarily involves XAS being determined via excited states of the luminescent system: it is thus a prime candidate for extension to PP experiments. The feasibility of doing so was first demonstrated at the SRS [10], where the application of laser light was shown to modulate the synchrotron-generated luminescence yield of wide-gap solids containing defect states. Pure quartz, Ca-aluminosilicate and cubic boron nitride (c-BN) were studied, and the laser interaction was shown to either quench or enhance the synchrotron-induced luminescence, depending on the particular interaction with the defect states. Moreover, by using simple lock-in techniques,
phase-selective EXAFS information was readily available from complex systems whose laser-interaction was variable, thereby directly linking a particular defect state with the crystal phase structure in which it resides.

In this paper, the understanding of the underlying mechanisms of PP-ODXAS is significantly enhanced, by specifically examining the trapping dynamics of charge released in the lattice of homogeneous luminescent material. The work represents an important advance on the previous proof-of-principle study [10] in two respects. Firstly, lock-in amplification methods (as used in previously) are useful for extracting changes in x-ray induced luminescence intensity caused by application of the laser, but provide virtually no useful information on the system dynamics. The latter is crucial for gaining access to details concerning the recombination pathways and trapping competition between radiative and non-radiative defect states. In the present work, full analysis of the luminescence dynamics is provided, both when the laser probe is applied to the sample, and after it is removed (during return to equilibrium). The second advance concerns the material system chosen for these studies, that of hexagonal boron nitride (h-BN). This material is one of the most promising in the field of UV optoelectronics, and has a very high quantum emission efficiency; specific information concerning charge competition in luminescence recombination is therefore of direct relevance to the development of the material for commercial exploitation. This work represents the first comprehensive investigation of the material using PP techniques. (The much more weakly emitting counterpart c-BN was used during the original exploratory studies using lock-in methods [10]. However, the relationship between the crystal structures of h-BN and c-BN are the equivalent of the carbon materials graphite and diamond, and the two materials necessarily need to be considered separately.)

The work concentrates on analysing the changes in the charge trapping dynamics as the synchrotron pump energies are scanned over the boron K-edge; the simple structure of h-BN is regarded as being an ideal for such studies. These processes will also be of direct relevance to understanding the complexities encountered in solid state luminescence radiation dosimetry, where the energy of the radiation being absorbed is close to the fundamental atomic absorption edges of the constituent atoms of the material.

2. Experimental

All experiments were carried out on multipole-wiggler beamline MPW6.1 at Daresbury SRS; this provides high photon fluxes in the XUV range 40–450 eV [11] and is an ideal source to act as a pseudo-CW synchrotron pump for boron nitride material at both the boron and nitrogen K-edges (~190 and 400 eV respectively). Experiments were undertaken at 8 K using the MoLES end-station [12], which is specifically designed to perform ODXAS on multiple synchrotron beamlines, detecting luminescence emission in the range 1.4–6.5 eV. The system was adapted to allow simultaneous synchrotron and laser excitation, using three laser sources acting as the probes: 1.494 eV (830 nm), 100 mW; 2.331 eV (532 nm), 40 mW and 3.069 eV (404 nm), 5 mW. The 1.494 and 3.069 eV lasers are diodes, with modulation in the frequency range CW-20 MHz, whilst the 2.331 eV laser is a frequency doubled YAG, modulating in the range CW-20 kHz. The synchrotron beamspot was adjusted to be ~1 mm × 0.2 mm at the sample, and the laser-probe optics arranged so that the laser spot overfilled the synchrotron-pump beam footprint. The PP luminescence was detected using a multi-alkali photomultiplier tube (Hamamatsu R2949; 2 ns rise time) within a single narrow band at 3.65 eV (0.11 eV FWHM) defined using interference
filters, in combination with a Schott UG11 colour glass filter to effectively remove laser breakthrough at all probe energies. The timing experiments were controlled and recorded using Becker and Hickl delay/gate boards DDG-200 and PMS-400A which, when combined, allow measurements to be undertaken in the range 10 ns to 100 s or more. During the PP experiments, the lasers were continuously modulated with variable on/off timing periods (but mostly as a square wave).

Samples of high purity single-phase h-BN were provided by Element 6 Pty, in the form of powder (sub-micron particle size) hard pressed into a pellet. As mounted on the cryostat cold finger, the sample was of bulk dimension \( \sim 3 \text{ mm} \times 3 \text{ mm} \times 0.1 \text{ mm} \). Powdered samples prepared in this manner have no preferred direction; as a consequence, any potential orientation dependences of either the laser or synchrotron interaction (both of which are linearly polarized) with individual crystallites cannot be analysed in this experiment: the results presented are thus averaged for interactions over all directions.

The choice of excitation and detection windows deployed in the experiment is important. The arrangement is such that luminescence detection occurs at lower energies than the synchrotron pump-beam, but at higher energies than the laser probes: this ensures that the laser probes can only interact with charge that has been generated by the synchrotron pump. If the detection window had been at a lower energy than both the pump and probe light, the possibilities exist to observe luminescence generated by the laser alone (e.g. by charge cycling from the ground to an excited state of a defect) and this is not of interest in the present study.

3. Results and discussion

3.1. h-BN x-ray excited optical luminescence (XEOL) and its context

The XEOL emission spectrum of the h-BN is shown in figure 1(a) when exciting at 190 eV (i.e. just below the boron K-edge). This consists of a number of bands, which can be grouped into two sets: broad-band deep-centre emission, and narrower-band recombination closer to the bandgap energy, which is taken to be that of either excitons, or shallow donor–acceptor pairs. The former consist of two dominant overlapping features found to peak, after deconvolution, at 3.07 and 3.82 eV (0.86 and 1.11 eV FWHM respectively) whilst the latter is made up of three partly resolved bands, peaking at 5.32, 5.49 and 5.63 eV (0.22, 0.16, 0.23 eV FWHM respectively). Figure 1(b) shows these emissions set schematically in context of the excitation and charge capture processes to be described in the following sections: non-resonant XUV photon interaction with the lattice leads to multiple electron-hole excitation events due to scattering and band-to-band excitation etc; the excited particles thermalize within the conduction/valence bands, and then contribute to the luminescence. In contrast, excitation resonant with a core-level can result in the stimulation of just a single free electron that can be emitted from the sample if at the surface or, within the bulk, may contribute to recombination luminescence via the conduction band. The core-hole is filled from electrons in the valence band, resulting in a cascade of electron–hole pairs that subsequently contribute to the luminescence.

In figure 1(b), the bandgap energy \( E_g \) is represented as 5.9 eV; previous measurements of \( E_g \) in h-BN have provided a wide range of estimates, from 4 eV [13], 5.5 eV [14] to 5.9 eV [15]. It is clear that, since defect or exciton related emission is observed up to 5.9 eV, this is probably the minimum energy for \( E_g \) in the material studied here.
Figure 1. (a) The luminescence emission spectrum of the h-BN sample used, excited at 190 eV (8 K). The de-convoluted emission bands are shown, together with an indication of the band edge in the material, the luminescence detection window used in the PP experiments, and the laser probe energies. (b) Schematic of the excitation and relaxation processes in the material involving both the synchrotron pump, and laser probes. In the latter, two processes are possible: photo-eviction from charge located at non-radiative deep centres (designated ‘laser probe (1)’ in the figure), or direct excitation of valence-band electrons to holes located at luminescent recombination centres (‘laser probe (2)’). (c) Theoretical calculation of the penetration depth of pump-photons, as a function of their energy.
The common defect structures in h-BN have been considered by a number of previously reported studies using luminescence excitation and emission spectroscopy, thermoluminescence, electron spin resonance and by theoretical calculations (e.g. [14], [16]–[18]). Although the identity of the defects present is not of direct concern for the present work, it is crucial to appreciate from these studies that a range of non-radiative trapping states are known to commonly occur in the material $\leq 1$ eV below the conduction band edge (one- and three-boron defects), and useful to note that similar deep-centre emissions have previously been observed, potentially arising from nitrogen vacancies and carbon defects.

Finally, figure 1(c) shows the calculated penetration depth of XUV photons in BN, over the boron K-edge; this is shown to drop from 600 nm just below the edge, to 100 nm just above it. As the sample is essentially bulk (thickness $\sim 100 \mu$m) then irrespective of whether excitation is below or above the edge, the full photon energy is thus deposited within the material. The following sections represent a consideration of how this energy becomes dissipated and trapped. In this context, it is relevant to note that, whilst the XUV photons penetrate only some of the sample depth, the lasers probe all of it with effectively a uniform field in the PP interaction region.

3.2. Non-resonant synchrotron–laser interaction: basic processes

The changes induced in the steady-state XEOL signal (at 3.65 eV) are shown in figure 2((a) (i–iii)), when probing the sample with each of the three lasers during pumping with 190 eV photons. The probes all induce transient positive luminescence signals that decay to a constant level whilst the probe remains active; in some cases this is below the original CW-XEOL signal (most clearly seen here with the 2.33 eV laser). Removal of the probes induces a transient in which the emission is further quenched, with the signal recovering in time to the CW-XEOL level.

We seek to demonstrate that these effects result from the competitive interaction of both radiative and non-radiative trapping states in the material. The time-decaying transient PP signal is typical of optically stimulated luminescence (OSL) that result from the laser-induced transfer of charge from deep-lying electron traps, to holes located at luminescence centres. OSL is commonly used in radiation dosimetry of wide bandgap materials (both for geological dating applications and evaluation of artificial radiation doses) where, post-irradiation, the quantity of charge trapped in the material is determined by the intensity of the laser-induced OSL signal (e.g. [19]). In the PP case described here, such trapping processes can be inferred by altering the mark-space ratio between the PP (mark-time) and pump-only space time. This is shown in figures 3(a) and (b) where (with the PP mark-time fixed) the transient signal intensity increases as the laser-off time is incremented, effectively allowing the trapped charge population to build up.

The signal-recovery after the laser probe is removed can be appreciated in this model by the change in competition between pump-induced electrons recombining at the luminescence centres (yielding XEOL) and those becoming trapped at the deep-level (non-radiative) OSL electron traps. For example, just after the laser is removed, the OSL traps are largely empty, meaning that their strong competition yields a suppressed XEOL signal; as the traps become

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5 Calculated from the sum of uncoordinated atom absorption, assembled from tables provided by the Lawrence Berkeley National Laboratory, Centre for X-ray Optics, http://www-cxro.lbl.gov.
3.3. Non-resonant synchrotron–laser interaction: understanding the kinetics

In order to appreciate the subtleties of the charge trapping and de-trapping processes described in subsection 3.2, curve fitting of the PP signals has been undertaken to extract the relevant details. In the most basic model where charge is transferred by the laser from a single donor to a single acceptor centre, and there is no re-trapping of the free electron, OSL decays exponentially with time as the charge in the traps becomes depleted. However, even in the simplest OSL dosimetry systems this rarely occurs, due to the presence of competitive recombination processes and strong re-trapping at the original defect centres etc (e.g. [20]). As the emission of figure 1(a) implies, there are several competitive recombination centres active in the h-BN studied here, and the luminescence is also being monitored during the simultaneous application of both pump and

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Figure 2. (a) Summary of the change induced by pulsed laser probes on the CW luminescence generated using pre-edge pump excitation at 190 eV. Curves (i, ii and iii) are for the 1.49, 3.07 and 2.33 eV lasers respectively. (b) The luminescence transient decay induced by the laser can be fitted extremely well (solid lines) by equation (1) given in the text. This also highlight the fact that the lasers simultaneously can cause quenching of the luminescence, as the zero-level of the transient ($I_0$) can fall below that of the laser-off equilibrium. (c) The recovery to equilibrium of the luminescence, once the laser probe has been removed, can also be effectively modelled, using equation (4) given in the text (shown as the solid line).

filled, the competition reduces and the XEOL intensity recovers to its pump-only equilibrium level.
probe light. Thus, simple exponential decays of trapped charge are not anticipated. However, as the de-trapping by the probe is significantly faster than the trapping caused by the synchrotron light (at the OSL centres), a good first approximation to the dynamics of the OSL de-trapping can be obtained by deploying a general-order decay analysis (e.g. [21]), where the luminescence signal at time \( t \) is given as:

\[
I(t) = \frac{\alpha}{(1 + \beta t)^\gamma}.
\]  

(1)

Here, \( \alpha \) is the OSL intensity on application of the laser at \( t = 0 \) and \( \gamma \) is a constant that defines the decay kinetics: where re-trapping and luminescent recombination probabilities are equal, as in the case for bimolecular kinetics, \( \gamma = 2 \). \( \beta \) represents the probability of electron eviction from an OSL trap for a particular stimulation intensity. Normally, this is of the form [21]:

\[
\beta \propto \frac{n_0 \phi \sigma}{N} \frac{P_T}{P_R}. 
\]  

(2)

Here \( \phi \) is the incident flux, \( \sigma \) is the photoionization cross-section of the OSL defect, \( P_T \) and \( P_R \) are the relative probabilities of a conduction band electron becoming trapped (T) at the OSL

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**Figure 3.** (a) Changing the mark-space \((t_1, t_2)\) timing ratio between the laser-off and laser-on periods of the pulsed PP experiment (3.07 eV laser), causes significant changes in the size of the laser-on induced transient, but not in laser-off recovery to equilibrium. (b) The laser-on transient follows a saturating exponential as a function of the laser-off period. (c) Changing the synchrotron pump-power has a significant effect on the dynamics of both the laser-on transient, and the laser-off recovery rate (shown here for low and high pump powers, normalized to the CW luminescence levels). (d) Whilst the XEOL linearly increases in intensity with pump power, the size of the laser-induced transient is non linear, shown here going into saturation.
defect, or recombining (R) at the luminescence centre. \( n_0 \) and \( N \) are the original trapped charge population in the OSL defects, and the total number of traps respectively.

The most likely reason for the probe photon-energy dependence of the probe-on equilibrium level reducing significantly below the probe-off equilibrium would be direct laser-stimulation of electrons from the valence band, to holes located at the recombination sites that have originally been generated by the synchrotron pump. This will directly result in a reduction in the XEOL luminescence efficiency. Although there will be a time-dependence on this effect, it must be significantly faster than the trapping competition dynamics caused by laser-induced changes in the population of the OSL centres. Faster PP studies planned for the future will elucidate this process, but here the effect can be considered as instantaneous, and folded into the general PP equation, so that the laser-on PP signal changes as:

\[
I(t) = (I_{\text{XEOL,CW}} - I_{\text{Quench}}) \left[ 1 + \frac{\alpha}{(1 + \beta t)^\gamma} \right].
\]

Here, \( I_{\text{XEOL,CW}} \) is the pump-only equilibrium level, and \( I_{\text{Quench}} \) the CW change in this level induced by the laser by direct stimulation of the recombination centres.

When considering the XEOL signal recovery after the probe light is removed, the simplest possible situation is where there is just a single type of competitive non-radiative OSL trap within a uniform pump radiation field; this would result in exponential recovery to the equilibrium. If there is more than one competing trap, the recovery would be a sum of exponentials. However, the present situation is expected to be more complex, since the pump radiation field is strongly variable with depth, implying a continuous distribution of trapping rates even for a single-trap model.

Based on the above comments, a stretched exponential function is used to model the XEOL signal recovery after the termination of the laser light, of the form

\[
I(t) = I_{\text{XEOL,CW}} (1 - \eta (\exp \{-\xi t\}^\mu)).
\]

Here, \( \eta \) and \( \xi \) are constants that relate to the trapping parameters of the system (\( \xi \) defining the re-trapping rate and \( \eta \) being a function of the relative number of available competitive traps); \( \mu \) is representative of the distribution of exponentials.

Stretched exponentials are commonly used to describe the dynamics of excited carriers in amorphous materials (e.g. \[22\]), where \( \mu \) represents the geometry of the localized states, but it has also been used to consider OSL decay kinetics in dosimetry systems with complex trapping dynamics \[23\].

The development of a complete theoretical basis for the PP kinetics is beyond the scope of the present investigation, but the verity of the simplified equations used in the signal analysis (3) and (4) can be appreciated by reference to the fitted curves in figures 2(b) and (c) for stimulation with the highest power available from both lasers and synchrotron. The full set of parameters used in the fitting, are provided in table 1. To a first approximation, 100% synchrotron pump power corresponds to \( \sim 10^{12} \) photons s\(^{-1}\) (\( \sim 5 \times 10^{16} \) photons cm\(^{-2}\) s\(^{-1}\)) at 190 eV and the 100% laser powers correspond to \( \sim 4 \times 10^{17} \), \( 10^{17} \), \( 10^{16} \) photons s\(^{-1}\) (\( 10^{21}, 2 \times 10^{20} \) and \( 2 \times 10^{19} \) photons cm\(^{-2}\) s\(^{-1}\)) at 1.49, 2.33 and 3.07 eV respectively. What is particularly striking about the inter-comparison of the parameters is that, whilst the OSL decay kinetics are quite variable (as expected, due to differences in the photon fluxes and photo-ionization cross-sections at the different laser energies), the recovery kinetics are essentially invariant with the preceding
Table 1. System parameters describing the fitted curves shown in figures 2(b) and (c), following the PP, and pump-only recovery kinetic equations (3) and (4) (see text).

| Laser                  | Pump + probe kinetics | Pump-only recovery kinetics |
|------------------------|-----------------------|----------------------------|
|                        | $I_{\text{Quench}}$ (%) | \( \alpha \) | \( \beta \) | \( \gamma \) | \( \eta \) | \( \xi \) | \( \mu \) |
| 1.494 eV (830 nm)      | +1.6                  | 0.63 | 63 | 0.93 | 0.078 | 7.46 | 0.35 |
| 3.07 eV (404 nm)       | −3.6                  | 1.33 | 875 | 0.54 | 0.121 | 5.38 | 0.37 |
| 2.33 eV (532 nm)       | −8.0                  | 1.44 | 487 | 0.92 | 0.155 | 4.65 | 0.43 |

Figure 4. Variation of the PP system dynamics (3.07 eV probe, 190 eV pump energy) as a function of synchrotron pump power. The parameters \( \alpha \), \( \beta \) and \( \gamma \) describe the laser-on dynamics (following equation (1)) and the \( \eta \), \( \xi \) and \( \mu \) parameters describe the system recovery to equilibrium, once the laser is removed (following equation (4)).

laser probe, indicating that the same competition processes are active in each of the three cases.

The quality of the fits in figures 2(b) and (c) enables trends in the PP signal parameters to be followed as other experimental conditions are changed. The most obvious example is shown in figure 3(b), where the increase in the OSL signal with duration of the pump-only period is clearly apparent (following a saturating exponential); this is similarly the case for increasing the pump power (figure 3(d)), although the XEOL itself increments linearly to the first approximation.

In order to understand the changes induced in the system when scanning the pump energies over the core-level energy (PP-ODXAS mode), fuller consideration of the system dynamics is required. These are displayed in figure 4 for the \( (\alpha, \beta, \gamma, \eta, \xi, \mu) \) parameter set in the example case of the 3.07 eV (404 nm) laser; equivalent results are achievable with the other two laser...
energies. In the synchrotron pump-power range 20–100%, the parameters ($\eta$, $\mu$) are weakly variable, but with a linear dependence of $\xi$: this is exactly as anticipated within the simple charge trapping-competition model elaborated above. The OSL shows signs of partial saturation in all the ($\alpha$, $\beta$, $\gamma$) responses, in particular ($\alpha$, $\gamma$); the parameter $\beta$, however, which should be proportional to the trapped charge population, appears to be invariant with pump-power for levels >50%. Whilst the information being yielded by the PP and the pump-only dynamics is thus not contradictory, it is clear that more complex second-order trapping effects must be in operation. There are multiple possible mechanisms that could account for these (e.g. preferential association of OSL and recombination centres that are not monitored here), but the data set provided in figure 4 are adequate to follow the signal responses as the pump-energy is scanned in the boron near-edge x-ray absorption fine structure (NEXAFS) region, as described in the following section.

3.4. Boron PP-NEXAFS: changes in the trapping dynamics

The basic (no-laser) OD-NEXAFS spectrum for the h-BN is shown in figure 5(a), for the excitation range 190–205 eV. All the features are as previously measured for this material type [24]–[26], including the strong well-defined 1s-to-$\pi^*$ resonance at 191.7 eV, and the broader peaks >197 eV, corresponding to the 1s-to-$\sigma^*$ transitions. Note that the resonances appear as reductions in the non-resonant luminescence background ($\sim$35% for $\pi^*$) as is typical for samples whose thickness are greater than the penetration depth of the exciting photons: see [27] for a theoretical consideration of this effect.

An overview of the additional transients induced by the application (and removal) of laser probe during the NEXAFS scan can be appreciated from figure 5(b) for the example case of the 3.04 eV laser. The complex PP-decay and pump-only-recovery, considered in subsection 3.3 for the single sub-edge pump excitation energy at 190 eV, are shown to modulate the XEOL signals over the whole NEXAFS scan range. However, the full details of the modulation caused by the lasers can only be appreciated by the dynamic parameters obtainable by fitting the spectra to
Figure 6. By fitting to equations (3) and (4) (see text), changes in the PP dynamics can be followed as a function of the pump energy across the boron NEXAFS region. As for figure 4, the parameters $\alpha$, $\beta$ and $\gamma$ describe the laser-on dynamics and the $\eta$, $\xi$ and $\mu$ parameters describe the system recovery to equilibrium, once the laser is removed. Results for two laser probes are provided. Thick line: 2.33 eV laser. Thin line: 3.07 eV laser.

equations (1), (3) and (4). The results are presented in figures 6 and 7: for clarity, only the 3.04 eV and 2.33 eV laser results are presented, as these show the biggest variation in effects. Note that the parameters obtained relate only to the relative probe-induced change in the CW pump-only XEOL signal at any particular pump excitation energy.

In traversing the boron $K$-edge, the main first-order influence on the PP dynamics is likely to arise from an apparent increase in excitation flux density, as the penetration depth of the pump photons falls by a factor 6 from just below, to just above the edge (figure 1(c)). As anticipated from the analysis presented in figure 4, the parameters that are likely to be weakly variable with photon energy are $\beta$ for the PP transient, and $(\eta, \mu)$ for the pump-only recovery. As shown in figure 6, this appears to be the case; the signals display no significant spectral features, changing only very slowly and monotonically as a function of pump energy. In contrast, the $\alpha$
Figure 7. The simultaneous laser-induced quenching of the XEOL signal ($I_{\text{Quench}}$, equation (3)), obtainable from the curve fitting, is shown to be very different depending on the laser probe energy chosen (shown here as a percentage change in the CW laser-off equilibrium level).

parameter, which effectively measures the trapped charge population in the OSL centres, has distinct structure in the pump-energy response, which is directly comparable with the NEXAFS features. For all laser energies, the parameter reduces during resonant x-ray absorption. This is to be expected if the OSL centres are within the saturation regime. The decay rate of the PP transient, as defined by the $\gamma$-parameter, also has the NEXAFS features imprinted on it. What is particularly interesting, however, is that the sign of the rate-change is different, depending on the laser probe chosen. For example, the decay rate increases at resonance, for the 3.07 eV laser, whilst it decreases when probing with 2.33 eV photons. Such rate-changes are also observable in the pump-only recovery dynamics, as provided by the $\xi$-parameter (equation (4)). As for $\gamma$, the post-probe recovery becomes faster at resonance for the 3.07 eV laser, and slower for the 2.33 eV laser. These results provide a clear indication that the two lasers are not necessarily probing exactly the same processes, and this is even more evident when the laser-quenching signal is considered ($I_{\text{Quench}}$, equation (3)). As shown in figure 7, the 2.33 eV laser induced essentially the same relative quenching signal irrespective of pump-energy (changing only from 14 to 12% quenching between 190 and 205 eV), whereas for the 3.07 eV laser, this is highly variable, with the NEXAFS features clearly discernable from the PP curve, and the greatest quenching occurring for pre-edge non-resonant pump excitation.

Some of the basic changes in the PP processes described above can be appreciated in terms of the basic conceptual model provided in figure 1(b), involving the laser interaction with both OSL defects (laser probe 1 process) and recombination centres (laser probe 2).

According to figure 3(d), the XEOL signal is not in the saturation range of the pump-powers available in these experiments, but the OSL defects are (i.e., there must be more recombination centres than OSL trapping sites). Thus, during the NEXAFS scan, a laser that probes the recombination centres (e.g. the 2.33 eV laser) will have an effect directly proportional to the size of the ODXAS signal; such removal of charge will reduce their overall availability for recombination, and thus acts to reduce the rate of decay of both the transient PP signal and the pump-only recovery. As the 2.33 eV laser stimulates both probe 1 and 2 processes, and as the OSL centres are in the saturation regime (whereas the recombination centres are not), the combined

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effect is to cause the NEXAFS spectrum to be imprinted on both the $\gamma$ and $\xi$ parameters as reductions in their value.

By following similar arguments, the fact that the quenching levels (figure 7) reduce at the NEXAFS resonances for the 3.07 eV laser would lead to the observed increases in the $\gamma$ and $\xi$ parameter rates at resonance. However, the simple two-level model of figure 1(b) cannot of itself account for this reduction in quenching. The two most likely explanations are (i) that the laser probes a defect whose concentration with depth is variable or, (ii) there is a second recombination defect that is resonantly probed with the laser, but whose population is significantly smaller than the main luminescence centre, and is thus in a saturation regime. In which case, the effectiveness of the laser to quench the luminescence is reduced at resonance, where the flux density is significantly increased. Bearing in mind that this is a hard-pressed bulk composite of sub-micron particles, the first possibility is highly unlikely: such effects would normally be expected in single crystal bulk samples, containing defect concentration gradients. Consequently, our conclusion is that the PP-NEXAFS features for the 3.07 eV laser arise from competition between charges located at different recombination sites.

4. Summary and future directions

In the first study of its kind, h-BN crystals have been used to understand the dynamics of luminescence-derived synchrotron–laser PP interactions, as the pump energies are scanned across the core level energy of the constituent atoms. The dynamics are shown to be driven by the competitive capture of synchrotron-generated charge at both radiative and non-radiative defect sites within the material. The laser probes act to disturb the pump-induced equilibrium, and the dynamical response is found to be a function of the pump energy. As a consequence, PP NEXAFS signals can be obtained from the interaction dynamics. Three laser energies are used in the work presented (1.5, 2.33 and 3.07 eV), and these are shown to probe different defect sites, resulting in significant modifications in the charge transfer (and hence PP) dynamics.

It is clear that by allowing the probe energies to be continuously tuneable, the full ionization cross-sections of the defect centres can be obtainable from such experiments. As a result, there is obvious potential for directly correlating particular defect sites with the structural and chemical nature of the host in which they reside (via the PP NEXAFS), and this will be of particular relevance to complex materials in which several luminescent phases co-exists. Such probe-tuneable experiments are planned for the future. We also intend to build a full theoretical framework for describing the charge transfer dynamics, provided here experimentally. This will allow extrapolation of the results to experimental systems where higher pump/probe powers and faster timing is available; such studies will be invaluable for anticipating the outcome of experiments on 3rd and 4th generation synchrotron light sources.

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