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**Self-Quenching Effects of Excitons in CaWO_4
under High Density XUV Free Electron Laser Excitation¹**

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Abstract—Using free electron laser excitation in the XUV range, CaWO_4 samples were exposed to ultrashort intense photon pulses (photon energy, 89.84 eV; average pulse energy, 10 μJ ; pulse length, 25 fs), and their luminescence was studied with time-resolved spectroscopy. In the decay curves measured in the temperature range 8–300 K, a nonexponential emission decay with shortening of the lifetimes over the first few microseconds was observed, depending on the excitation density. Using a model for dipole–dipole interaction of excitons under nonuniform excitation densities, the structure of the decay curves can be reproduced in good agreement with the experimental data, and parameters for the initial exciton interaction can be calculated.

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1. INTRODUCTION

In the past few years, new sources for highly intense, ultrashort laser pulses with photon energies in the vacuum and extreme ultraviolet (VUV and XUV) ranges, based on free electron lasers (FEL), have been developed. The first FEL of this kind to provide a beam for interested scientists is the FLASH facility of DESY in Hamburg [1]. In addition, several other FELs operating at photon energies ranging from VUV to soft x-ray energies are in the planning phase or under construction elsewhere. Also, a joint European x-ray FEL source, which will provide intense coherent x-ray pulses of femtosecond duration, will be built at DESY, and it is scheduled to be operational in 2013.

With the development of these new sources, new challenges also appear in the field of material science. The photon densities of an XUV FEL are close to the expected damage thresholds of the materials used as optical elements for the FEL radiation, and extensive research has been directed in the past years to investigate their durability under these conditions [2, 3]. Aside from the problem of radiation-induced damage of the optical components, the performance and stability of materials used for the detection of radiation requires investigation. Scintillators are already now widely used to monitor and tune the performance of the FEL at FLASH [4], and future experiments at the XFEL may rely strongly on the performance of scintillators and visualization screens under the intense x-ray excitation.

First experiments were carried out during the test phase for the currently operating FLASH FEL for various samples using pulses with 13.9-eV photon energy, and a distinct change in the decay behavior was observed [5]. Due to time constraints, many questions raised as a result of the experiments remain open. With the FLASH laser now in operation, we had a chance of investigating various scintillator materials in more detail.

In this work, we focus on luminescence from CaWO_4 crystals. Renewed interest to tungstate crystals as scintillator materials has appeared in the past decades due to their radiation hardness and the occurrence of fast (a few nanoseconds in PbWO_4) intrinsic emission bands [6–8]. The intrinsic nature of these luminescence bands allows the application of a model for self-quenching due to exciton–exciton interaction outlined in [9].

2. EXPERIMENTAL

The measurements were performed at the BL1 beamline of the XUV free electron laser facility FLASH of DESY in Hamburg, Germany. This unique facility provides ultrashort laser pulses (25 fs), and the photon energy used in experiments was 89.84 eV. An illuminated circular spot on our samples was about 150 μm in diameter. The pulse energy of the FEL varies statistically from pulse to pulse due to the stochastic process of self-amplification by spontaneous emission [1]. In addition to this inherent distribution of pulse

¹ The text was submitted by the authors in English.

energies, a N_2 gas attenuator in the beamline with controllable pressure was used to reduce the average FEL beam intensities over a range from 10 to 100% compared to the unattenuated beam. The maximum values for the peak energies were about 25 μJ , which corresponds to 1.7×10^{12} photons per pulse for the given photon energy. A polished single-crystal sample of CaWO_4 was glued on the cold finger of a He cryostat prior to mounting in an UHV experimental chamber. Measurements were performed at $T = 8$ and 300 K.

When studying the decay spectra, luminescence was detected using an XP2020Q photomultiplier in combination with suitable bandpass filters to select the desired emission range. Decay curves were recorded as single-shot measurements for each FEL pulse using a fast digital oscilloscope. A reference signal from a microchannel plate detector in the beamline monitoring the FEL intensity for each pulse was recorded simultaneously with the decay to allow precise comparison of the measured data. The values for the pulse energies used throughout this work were obtained through linear regression from the pulse energies recorded in the database of FLASH and the measured beamline detector signals. To reduce the noise level of the recorded single-shot decay curves, decay curves were sorted according to the measured pulse intensities and averaged over 10% intervals of the full pulse energy range.

In addition to the decay measurements, luminescence spectra for the samples were also recorded using an ARC SP308i UV/visible spectrograph equipped with a Princeton Instrument CCD detector. The emission spectra were averaged over 2000 FEL pulses, and the average intensity was adjusted by changing the transmission of the gas attenuator.

3. RESULTS AND DISCUSSION

Luminescence spectra for CaWO_4 under 89.84-eV FEL excitation are shown in Fig. 1 for temperatures of 8 and 300 K and different attenuation levels of the FEL. The average pulse energy of the unattenuated radiation is approximately 12 μJ for both temperatures. In the spectra, two well-known emission structures are observed. The strong luminescence band peaking at approximately 450 nm is ascribed to excited WO_4^{2-} centers forming molecular self-trapped excitons (STE) [10], whereas the broader and weaker emission bands at longer wavelengths above ~ 550 nm originate from impurity/defect centers in the crystal. In both low- and room-temperature spectra, this long wavelength tail is suppressed for higher photon fluences. Two different mechanisms can be responsible for this behavior: (i) a higher probability of electron-hole recombination and exciton formation at increased intensities, reducing the probability of energy transport to defect centers by free carriers, and (ii) saturation of the impurity/defect centers, which limits the possible luminescence yield for this type of emission.

Decay spectra of CaWO_4 for different averaged FEL pulse energies are shown in Fig. 2 for sample temperatures of 8 and 300 K. In the initial part of the decay spectra, a strong nonexponential behavior is observed, whereas for decay times larger than ~ 5 ns the decay can be approximated by a single-exponential curve with a radiative lifetime τ_r , comparable to those obtained with low-density excitation [6, 10]. The initial nonexponential decay becomes more pronounced with increasing pulse energies, indicating a direct influence of the excitation density on the radiative lifetime of the STE states in the crystal.

To understand this effect in more detail, we analyzed the data using the model of bimolecular self-quenching of STE under nonuniform excitation densities, which considers energy transfer between two STEs situated at a small distance R due to dipole-dipole interaction. One exciton recombines (non-radiatively or under emission of a virtual photon), and its energy is transferred to the second STE, which becomes excited or ionized to form a free electron-hole pair. Since exciton formation is the prevalent mechanism for relaxation from these excited states, we can assume that, after a relaxation process within some picoseconds, the result of the energy transfer is a single STE. For this process of the type $\text{STE} + \text{STE} \rightarrow \text{STE}$, we can formulate a rate equation for the spatial exciton density $n(\mathbf{r}, t)$ in the form

$$\frac{\partial n(\mathbf{r}, t)}{\partial t} = -\frac{n(\mathbf{r}, t)}{\tau_r} - \gamma(t, \mathbf{r})n^2(\mathbf{r}, t), \quad (1)$$

with a bimolecular rate of reaction $\gamma(t, \mathbf{r})$. In the simplest form, this rate can be expressed as

$$\gamma(t, \mathbf{r}) \equiv \gamma(t) = \frac{q_{d-d} R_{d-d}^3}{2 \sqrt{t \tau_r}}, \quad q_{d-d} = \frac{4\pi^{3/2}}{3} = 7.42, \quad (2)$$

where we use the dipole-dipole transfer radius R_{d-d} [9]. Note that Eq. (2) does not depend on $\mathbf{r}$, because we can expect that any spatial correlation of excitons due to initial creation or diffusion during their lifetime τ_r occurs on a much larger scale than the transfer radius R_{d-d} .

The initial concentration of the excitons due to absorption of a FEL pulse in the crystal can be approximated by a Gaussian radial distribution in the plane of the sample surface and an exponential decrease along the crystal depth z with the absorption coefficient α . Thus, we write the initial STE density as

$$n(\rho, z, 0) = I_0 \frac{\alpha \sigma}{\pi a^2} e^{-\rho^2/a^2 - \alpha z}, \quad (3)$$

where ρ is the radial coordinate on the surface, a is the FEL spot radius, I_0 is the total number of photons in a pulse, and σ is the excitation yield (number of excitons created per incident photon). With this initial condition

Fig. 1. Luminescence spectra of a CaWO₄ crystal at (a) 8 and (b) 300 K, excited with 89.84-eV photons for different attenuation levels (0, 50, and 75%) of the FEL beam.

$n(\mathbf{r}, 0)$, we can solve the rate equation (1) to obtain the decay intensity in the form

$$I_{\text{lum}}(t) = \frac{\sigma I_0}{\tau_r} e^{-t/\tau_r} \times \frac{-\text{Li}_2(-2\pi^2 N_0^{\text{max}} R_{\text{d-d}}^3 \text{erf}(\sqrt{t/\tau_r})/3)}{2\pi^2 N_0^{\text{max}} R_{\text{d-d}}^3 \text{erf}(\sqrt{t/\tau_r})/3}. \quad (4)$$

Here, $N_0^{\text{max}} = I_0 \alpha \sigma / \pi a^2$ is the maximum STE concentration at $\rho = z = 0$, $\text{Li}_2(x)$ is the dilogarithmic function defined as $\text{Li}_2(x) = \int_0^x s^{-1} \ln(1-s) ds$, and $\text{erf}(x)$ is the error function.

Using Eq. (4), model curves were fitted to the data sets of the decays curves at 8 and 300 K shown in

Fig. 2. Measured (circles) and modeled (lines) decay curves for CaWO_4 at (a) 8 and (b) 300 K under excitation with 86.84-eV FEL pulses of different pulse energies.

Fig. 2. For this procedure, values of $\alpha = 10^5 \text{ cm}^{-1}$ and $a = 75 \text{ }\mu\text{m}$ were used. The fitting was performed for a set of 9 decay curves at a sample temperature of 8 K, and a set of 10 curves at 300 K. In this routine, the parameters R_{d-d} and τ_r were fitted using the full data sets and the number of photons I_0 was optimized for each individual decay curve. The value of σ was disregarded, as it always appears as a factor to I_0 in Eq. (4) and no experimental data exist to give a good estimate for its value. From energy conservation, it follows that the number of electron-hole pairs that can be created is $n_{e-h} = E_{ph}/\beta E_g$ (E_{ph} is the energy of incident photon; E_g is the energy gap; β is the conversion efficiency, with its typical values being 2–3), as discussed in [11]. Taking into account the values ~ 7.0 and 4.7 eV required for creating free electron-hole pairs and free excitons in CaWO_4 , respectively, [12], the excitation by 89.84-eV photons could result in up to 19 unrelaxed excitons. However, considering the above formula, the actual conversion is significantly less effective. Still, the value 6 of σ is realistic for the given photon energy.

The resulting decay curves from the fitting procedure are given in Fig. 2 for four different FEL pulse energies at 8 and 300 K. The shared parameters R_{d-d} and τ_r were calculated as $R_{d-d} = 4.34$ (at 8 K) and 2.93 nm

(300 K), as well as $\tau_r = 59.8$ (at 8 K) and $9.1 \text{ }\mu\text{s}$ (300 K). Decay times of $360 \text{ }\mu\text{s}$ were reported in [13] for STE emission in CaWO_4 at 8 K under photoexcitation into the excitonic band. The obtained values for σI_0 are displayed in Fig. 3b as a function of the pulse energy. For comparison, the peak values of the measured decay curves are shown in Fig. 3a.

The overall agreement between the simulated and measured decays as shown in Fig. 2 is rather good, especially if we consider that the fit curves for each temperature only differ in the parameter σI_0 for the number of initial excitons. Comparing this number with the measured maxima of the decay curves (Fig. 3) shows again good agreement regarding the general dependence on pulse energy. More problematic is the comparison of the results for the number of excitons I_0 and the number of photons $I_{0, \text{exp}}$ calculated from the experimental pulse energy (dotted line in Fig. 3b). Considering our previously estimated value for σ of ~ 6 , the fitted values for I_0 are about one order of magnitude lower than the measured ones. A comprehensive explanation for this discrepancy cannot be given at the moment, but several factors should be considered. First, the Gaussian distribution of the beam intensity might be incorrect for the FEL, and the values used for a and α are also estimates. In addition, the first initial nano-

Fig. 3. (a) Measured peak values for the decay curves of CaWO_4 as a function of FEL pulse energy, taken at temperatures of 8 and 300 K. (b) Calculated number of photons per pulse as fitted to the experimental decay curves for various pulse energies and sample temperatures of 8 and 300 K. The dotted line shows the number of STEs for a quantum yield of 1 based on the number of photons per pulse calculated from the pulse energy ($I_{0, \text{exp}}$).

seconds of the decays are not resolved in the spectra, which might influence the accuracy of the calculations. Some influences not covered by the model should also be taken into account. Notably, possible triple correlations of excitations may play a role in the initial phase of the decay, and also the role of various nonradiative processes (e.g., trapping of $e-h$ pairs at impurities) is not considered at all.

The values for τ_r that were produced in the model agree well with the experimentally observed decay behavior at longer decay times, as well as with literature data. It should be noted here that the decay times for the STE luminescence depend strongly on the temperature in the range below ~ 40 K [10]. The difference between the values for R_{d-d} obtained for the two temperatures is probably still within the error margin that is to be expected for this fitting procedure; so, we should consider a single value for R_{d-d} between 3 and 4 nm. This value corresponds well to the results obtained for CdWO_4 under high-order harmonic generation (HHG) laser excitation as reported in [9].

4. CONCLUSIONS

The investigation of CaWO_4 crystals under XUV free electron laser (FEL) radiation with high intensity has given new insight into the exciton interaction under high STE concentrations. The nonexponential deviations in the decay curves could be satisfactorily reproduced within the framework of the excitonic self-quenching model. This process can also explain the nonlinear luminescence yield observed for pulse energies $> 5 \mu\text{J}$ (Fig. 3). The analysis shows clearly that the photon densities achieved in the experiment lie above the threshold where excitations can be considered interaction-free and, thus, nonlinear effects come into play when luminescence is considered. In the CaWO_4 sample, as well as in other crystals, no major changes in emission spectra have been found that could indicate radiation damage. However, in visual inspection of the samples after the irradiation, pitting of the crystal surfaces due to the FEL radiation was observed on a macroscopic scale. Hopefully, measurements with a more collimated beam with a reduced spot size are possible in the future to test our model under more extreme conditions. Aside from FEL-based research, excitation with powerful HHG has provided us with complementary data for CdWO_4 [9, 14].

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