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PHOTON YIELD FROM SOLID KRYPTON AND XENON AT THE EDGE OF EXCITON ABSORPTION

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The spectra of photon yield from solid Xe and Kr were measured in the energy range of absorption of $\Gamma(3/2)$ $n = 1$ excitons. Using combination of time-resolved spectroscopy with selective photoexcitation by synchrotron radiation, the creation of free excitons was experimentally separated from direct population of molecular emitting centers. For the first time the threshold of photon absorption by molecular trapped centers is observed in excitation spectra of free exciton luminescence.

1. Introduction

VUV luminescence spectroscopy is a powerful tool for investigating the final step of the relaxation of electronic excitations in rare gas solids (RGS) — the radiative decay of the emitting centers.[1] The photon excitation spectra of various luminescence bands provide us with information about the interplay of different channels in the course of relaxation of electronic excitations and formation of the emitting centers. It made it possible to investigate recently the effects of exciton mixing in RGS and branched relaxation of electronic excitations.[2–5]

But the measurement of excitation efficiency of free exciton luminescence within the absorption band of the lowest $\Gamma(3/2)$ $n = 1$ excitons itself is attended by inevitable coincidence of the wavelength of exciting and emitting photons and usually it was not carried out in the experimental works. At the same time spatial and temporal fluctuation of the lattice potential caused by phonons and deformability of the lattice induce the broadening and existence of the low-energy tail of the excitonic absorption spectra and dressing of excitons by phonons, which leads to self-trapping of excitons.[6] The absorption spectra of excitons in RGS exhibit the pronounced low-energy tails[7] and photon yield from the samples at selective excitation in the region of the absorption edge carries the information about the interplay of the processes of photon absorption, reflection, scattering and emission in the course of interaction of incident photons with the sample.

Time-resolved fluorescence spectroscopy under selective photoexcitation by synchrotron radiation in the VUV is a unique tool which allows one to study in real time scale the creation of electronic excitations and their relaxation. In the present study the combination of the time-resolved spectroscopy with spectroscopy under selective photoexcitation has been used to study the photon yield from solid Xe and Kr over the energy range of absorption of the $\Gamma(3/2)$ $n = 1$ excitons.

2. Experiment

The experiments were performed at the SUPERLUMI experimental station at HASYLAB, DESY, Hamburg. The samples were grown *in situ* from a high purity (99.996%) vapor phase under near thermodynamic equilibrium conditions at $T = 108$ K (Xe) and 82 K (Kr). The thickness of the sample was

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≈ 0.5 mm. During measurements, the pressure in the sample chamber was in the low 10^{-9} mbar range. All measurements were performed at $T = 7$ K.

Selective photon excitation in the VUV range was performed using a primary 3 m near-normal incidence VUV monochromator with a resolution $\Delta\lambda = 2.5$ Å. The luminescence spectra were measured with a secondary 1 m near-normal incidence monochromator ($\Delta\lambda = 2$ Å) equipped with a position-sensitive detector. The photon yield spectra from the samples were measured with a 0.5 Pouey high-flux VUV monochromator ($\Delta\lambda = 18$ Å) equipped with a multisphere plate detector.

The basis of time resolution is the pulsed nature of synchrotron radiation. The convolution of the temporal behavior of the excitation pulse of photons from the storage ring, the response of the detector, and the electronic used was 0.4 ns. The photon yield spectra from the samples were recorded like the luminescence excitation spectra, fixing the wavelength of the secondary monochromator and scanning the primary monochromator. The photon yield was measured as a function of the energy of the exciting light and then normalized to the intensity of the incident exciting radiation.

To discriminate the signal from the scattered light of excitation beam, the spectra of photon yield were measured within a time window (length Δt) correlated with the excitation pulses (delayed by δt). Three different time windows were set simultaneously: (1) window W1 ($\Delta t = 1.5$ ns, $\delta t = 0$ ns), (2) window W2 ($\Delta t = 2$ ns, $\delta t = 1$ ns) and (3) window W3 ($\Delta t = 32$ ns, $\delta t = 5$ ns).

3. Results and Discussion

Among other RGS, VUV luminescence spectra of solid Xe and Kr are similar and consist of two bands: the strong line of free excitons (FE) originating from thermalized excitons, and the broad, Stokes shifted molecular emission band (M) originating from molecular-type self-trapped excitons. The relative intensities of these bands strongly depend on the sample quality.[8] The similarity of the luminescence spectra of Xe and Kr is a result of the similarity of structure and dynamics of their electronic excitations.[9] Coexistence of states of free and self-trapped excitons is provided by existence of a self-trapping adiabatic barrier H between them.[10] The height of the barriers in Xe and Kr are $H^{\mathrm{Xe}} = 20$ meV, $H^{\mathrm{Kr}} = 14$ meV.[10] At low temperatures $T < T_c$ the self-trapping of free excitons is determined by quantum-mechanical tunneling through the barrier. But in the case of heavy RGS the barriers are not transparent.[11] The thermal activation of the self-trapping,[11] which dominates above the critical temperature T_c ($T_c \approx 25$ K for Xe and Kr[10]), will not be discussed in the present paper.

Figure 1 shows luminescence spectra (curves 1) of solid Xe [Fig. 1(a)] and Kr [Fig. 1(b)] and conventional excitation spectra of M-bands (curves 2) recorded at luminescence energies E_M of band maxima. In addition reflection spectra of solid Kr[12] and Xe[13] are presented. Note that the luminescence, excitation and reflection spectra were measured by

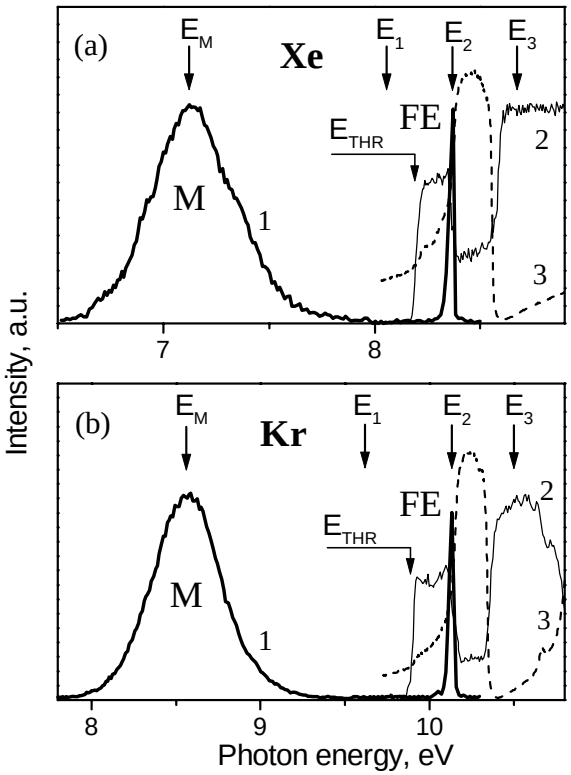

Fig. 1. Spectra of solid Xe (a) and Kr (b). Curves 1 — luminescence spectra under selective photoexcitation with $h\nu = 8.86$ eV (Xe) and $h\nu = 10.61$ eV (Kr). Curves 2 — excitation spectra of M-bands measured at energies E_M. Curves 3 — reflection spectra from Refs. 12 and 13. All spectra were measured at $T = 7$ K. Energies E_1, E_2 and E_3 denote the detection energies at which photon yield spectra in Figs. 2, 3 and 4 were measured.

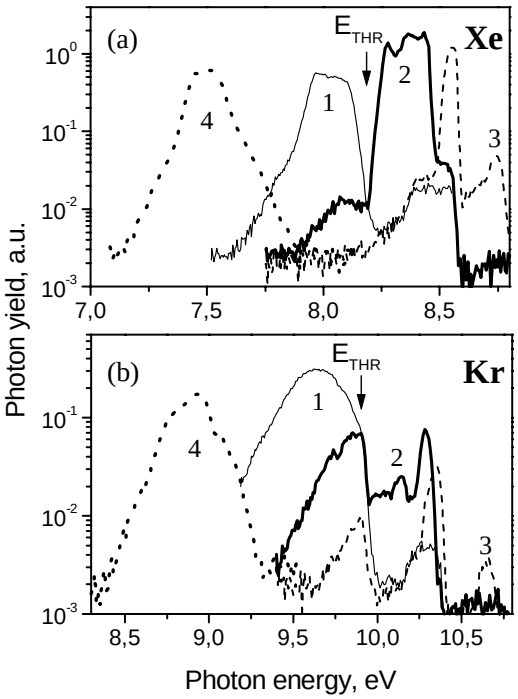

Fig. 2. Photon yield spectra of solid Xe (a) and Kr (b) measured in time window W1 at $T = 7$ K at photon energies E_1 (curves 1) E_2 (curves 2), E_3 (curves 3) and E_4 (curves 4), listed in Table 1 and indicated in Fig. 1 by arrows.

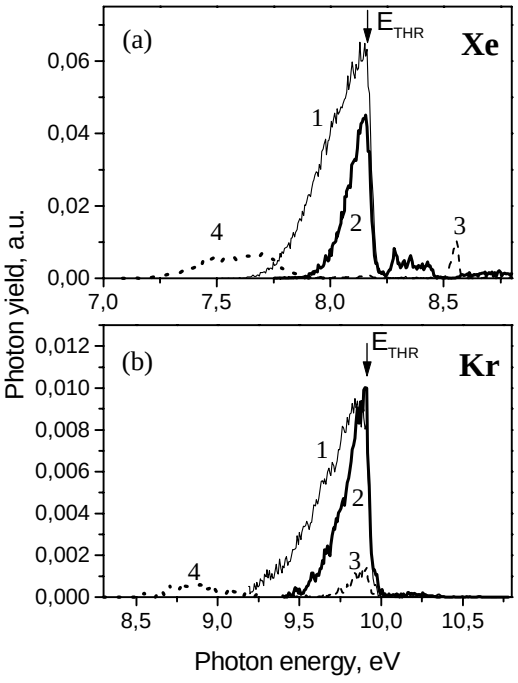

Fig. 3. Same as Fig. 2, for time window W2.

different detectors, and thus direct quantitative comparison of the intensities of these spectra is not possible. Excitation spectra of M-bands exhibit distinct thresholds at photon energies E_{THR} above which direct population of molecular centers trapped at lattice defects occurs.[5]

Figures 2, 3 and 4(a) show photon yield spectra of solid Xe and Kr measured below (curves 1), above (curves 3) and within (curves 2) the absorption band of $\Gamma(3/2)$ $n = 1$ excitons[7] at photon energies E_1, E_3 and E_2 correspondingly in time windows W1 (Fig. 2), W2 (Fig. 3), and W3 [Fig. 4(a)]. The photon energies E_1, E_2 and E_3 are indicated in Fig. 1 by arrows. Energies E_2 were chosen at peak maxima of FE bands and, therefore, only curves 2 are the conventional excitation spectra of free exciton luminescence.

For comparison, the spectra of the photon flux from the samples measured in correspondent time windows at energies E_4 in the transparency ranges

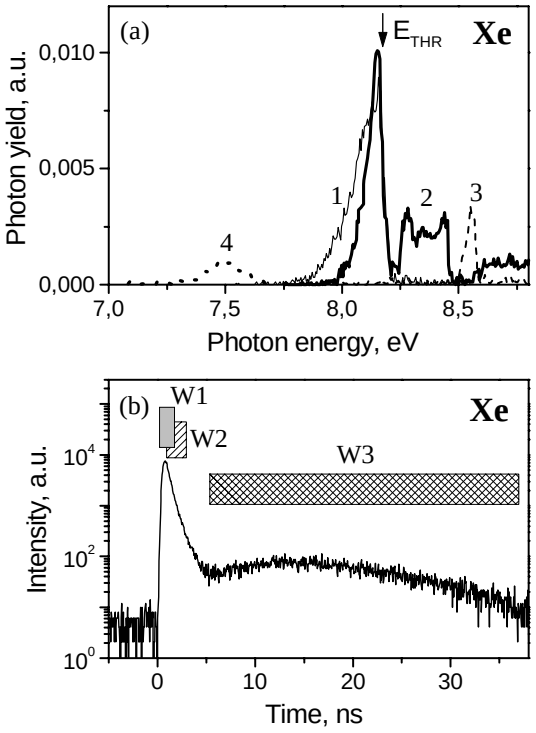

Fig. 4. Part (a) — same as Fig. 2(a), for time window W3. Part (b) — decay curve of FE band of solid Xe at $T = 7$ K, measured at excitation energy $h\nu = 8.86$ eV. W1, W2 and W3 indicate the time windows at which photon yield spectra in Figs. 2, 3 and 4(a) were measured.

Table 1. Photon energies E_1, E_2, E_3, E_4, at which photon yield spectra were recorded, and threshold energy E_{THR} for M-band excitation. All data in eV.

	E_1	E_2	E_3	E_4	E_{THR}
Xe	8,05	8,36	8,67	7,51	8,18
Kr	9,61	10,16	10,5	8,86	9,90

of solid Xe and Kr are presented in Figs. 2, 3 and 4(a) (curves 4). These spectra are the scattered light of synchrotron radiation; they represent the energy distribution in the exciting beam after the primary monochromator (not fully monochromatized). Numerical values of energies E_1, E_2, E_3, E_4 and E_{THR} for Xe and Kr are collected in Table 1.

Figure 4(b) shows the decay curve of free exciton luminescence of solid Xe following primary excitation with $h\nu = 8.86$ eV. Detailed study of the excitonic decays has been made recently.[8,13,14]

Three time windows W1, W2 and W3 are indicated in Fig. 4(b) by rectangles. Time window W1 includes the primary excitation synchrotron pulse (FWHM = 0.4 ns). Time window W2 excludes the excitation pulse and cowers the time interval where the fast intrinsic decay of excitons dominates. At longer times (long-time window W3) the FE decay curve exhibits cascade-type behavior governed by exciton–polariton trapping and nonradiative loss processes.[8] The intensity and the shape of this long-time decay wing strongly depend on the sample quality and it grows with the time of photon irradiation[12] as a result of point defect formation induced by trapping of excitons.[1] One of the possible mechanisms of formation of cascade-type long-time wing is a sequential chain of the processes of exciton ionization[15] on the defects followed by geminate recombination of electrons and holes. The cascade-type behavior of decay curves of free excitons created in the course of electron–hole recombination has been studied recently.[14]

The intensities and the shape of photon yield curves 1, 2 and 3 in Figs. 2–4 strongly differ from correspondent scattered-light curves 4. Curves 1, 2 and 3 exhibit strong interplay of various absorption processes and variation in reflection of the samples. The high-energy parts of excitonic absorption bands overlap with the region of the longitudinal-transverse splitting where excitation efficiency is diminished by a strong reflection (Fig. 1).

During the recording of the photon yield spectra, the crossing of the primary and secondary monochromators occurs (excitation resonant with detection). Therefore, in the case of time window W1 (Fig. 2) the effect of excitonic absorption on the shape of the curves is comparatively weak and usually it is barely visible at a background of the strong stray light of excitation pulses. To set off the effect, the data in Fig. 2 are presented in semilogarithmic plot. Crossing of the monochromators results in overloading of the single photon counting technique and the flat top of the spectra in Fig.2 (a) is a result of such saturation of the electronics. Nevertheless the spectra in Fig. 2 show the features both at energies E_{THR} and at energies of steep decrease of the reflection (8.58 eV for Xe and 10.4 eV for Kr). Above the latter energies the transmission of the samples increases, the depth of excitation grows and the creation of excitons is accompanied by their self-trapping and Stokes shifted emission of M-bands (Fig. 1).

Both within short-time W1 and long-time W2 windows the intensities of the photon yield spectra (curves 1, 2 and 3 in Figs. 2 and 3) exceed the intensity of scattered light (curves 4) in several times. Therefore the observed shape of the photon yield spectra is determined by intrinsic processes of exciton creation. At energies $E < E_{\mathrm{THR}}$ the photon absorption at low-energy Lorenzian tails of exciton absorption bands creates excitons directly at the bottom of the excitonic bands. The energy of such excitons is not enough to overcome the barrier between free and self-trapped excitonic states and they give no contribution to excitation spectra of luminescence bands of self-trapped excitons (Fig. 1). Thus, threshold energy E_{THR} separate energy range where free and self-trapped excitons coexist from energy range where only free exciton creation is possible. At the same time, the existence of the low-energy tails in long-time window W3 at times more then 5 ns after excitation pulse demonstrates the importance of trap-controlled cascade-type processes at photon absorption below the excitonic resonance.

4. Conclusions

Time-resolved spectra of photon yield from solid Xe and Kr were measured at the edge of exciton absorption. Using the selective photoexcitation

technique, the threshold energy of population of molecular trapped states in RGS was detected in excitation spectra of free exciton luminescence. To the best of our knowledge this is the first report on experimental separation of the range of photoexcitation where free and self-trapped excitons in RGS coexist from the range where photon absorption creates only free excitons.

References

1. A. N. Ogurtsov, E. V. Savchenko, M. Kirm, B. Steeg and G. Zimmerer, *J. Electron Spectrosc. Relat. Phenom.* **101–103**, 479 (1999).
2. A. N. Ogurtsov, A. M. Ratner, E. V. Savchenko, V. Kisand and S. Vielhauer, *J. Phys.*: *Cond. Matter* **12**, 2769 (2000).
3. A. M. Ratner, *Phys. Lett.* **A265**, 411 (2000).
4. E. Gminder, M. Kirm, V. Kisand, B. Steeg, S. Vielhauer and G. Zimmerer, *J. Luminesc.* **87–89**, 555 (2000).
5. A. N. Ogurtsov and E. V. Savchenko, *J. Low Temp. Phys.* **122**, 233 (2001).
6. M. Ueta, H. Kanzaki, K. Kobayashi, Y. Toyozawa and E. Hanamura, *Excitonic Processes in Solids*, Springer Series in Solid-State Sciences, Vol. 60 (Springer-Verlag, Berlin, 1986).
7. B. Sonntag, in *Rare Gas Solids*, Vol. 2, eds. M. L. Klein and J. A. Venables (Academic, London, 1977).
8. D. Varging, I. Reimand and G. Zimmerer, *Phys. Stat. Sol. (b)* **185**, 301 (1994).
9. K. S. Song and R. T. Williams, *Self-Trapped Excitons*, 2nd ed. (Springer-Verlag, Berlin, 1996).
10. I. Ya. Fugol, *Adv. Phys.* **37**, 1 (1988).
11. E. I. Rashba, in *Excitons*, eds. E. I. Rashba and M. D. Sturge, (North-Holland, Amsterdam, 1982).
12. V. Kisand, dissertation (Universität Hamburg, Hamburg, 2001).
13. G. Zimmerer, *J. Low Temp. Phys.* **111**, 629 (1998).
14. I. Reimand, E. Gminder, M. Kirm, V. Kisand, B. Steeg, D. Varding and G. Zimmerer, *Phys. Stat. Sol. (b)* **214**, 81 (1999).
15. J. Kraft, A. Schrimpf, B. Schweitzer, K. Ibbeken and H. J. Stockmann, *Europhys. Lett.* **39**, 459 (1997).