VUV-radiation induced creation of intrinsic neutral and charged centers in rare gas crystals

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Abstract

Formation and radiative relaxation of intrinsic neutral and ionic molecular centers in pure rare gas crystals have been studied by the method of luminescence excitation spectroscopy. Based on a comparison with recent thermoluminescence and cathodoluminescence data, a new analysis of radiation-induced changes in H, M and W luminescence bands permits the distinction of the electron–hole recombination channels in a population of continuum-forming states. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Rare gas crystals constitute a group of insulating materials characterized by the largest electronic band gap energies and their emissions are situated in VUV. Because of a simple crystal and electronic structure with extremely small cohesion energy they are the universally recognized model systems for experimental and theoretical study of different effects in solids including the processes of defect formation, charge separation, desorption etc. [1]. On the other hand rare gas crystals are widely used as inert matrices in matrix isolation spectroscopy and there is a wealth of papers on investigations of neutral and charged centers in rare gas matrices [2].

The usually used scheme of relaxation of energy

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in rare gas crystals includes some stages [3]. Primary excitation by VUV photons or low energy electrons creates electron–hole pairs. Secondary electrons scatter inelastically and create free excitons, which are self-trapped or trapped into atomic or molecular type centers due to a strong exciton–phonon interaction. The electronic structure of molecular trapped excitons is similar to rare gas excimers R_2^* (R = rare gas atom) and radiative decay of these centers produces the most prominent feature in low-temperature VUV-luminescence from solid Ar, Kr and Xe. In addition to these neutral intrinsic trapped centers, the self-trapping of holes due to the hole–lattice interaction results in a formation of intrinsic ionic centers which have electronic structure of dimer ions R_2^+. Radiative relaxation of these centers at excitation above the band-gap energy E_g has been investigated recently [4].

This paper focuses on electron–hole recombination channels in a population of molecular-emitting

centers in rare gas crystals studied by selective excitation of luminescence with synchrotron radiation in the excitonic energy range.

2. Experiment

The experiments were performed at the SUPER-LUMI experimental station of the Hamburger Synchrotronstrahlungslabor HASYLAB at DESY. The set-up was designed for time and spectrally resolved luminescence under selective photon excitation in the vacuum–ultraviolet spectral range and was described recently in detail [5]. The samples were grown from high purity vapor phase in a special cryogenic cell under isobaric ($P = 80$ Pa) conditions with the constant rate of cooling of 0.1 K/s. Selective photon excitation was carried out with $\Delta\lambda = 0.25$ nm. The excitation spectra of spectrally selected luminescence bands, shown in this paper, were measured by different detectors. They are not corrected for the sensitivity of corresponding detecting channels. Therefore, it is not possible to compare absolute intensity of excitation spectra at the given photon energy.

3. Results and discussion

The molecular luminescence spectra of solid Ar, Kr, and Xe, which were measured at photon excitation energies $E = E_g$, are shown in Fig. 1. The most intensive feature in luminescence spectra is the so-called M-band which is formed by the $^{1,3}\Sigma_u^+ \rightarrow {}^1\Sigma_g^+$ transitions in molecular type self-trapped excitons R_2^*. These neutral trapped centers are formed mainly during exciton self-trapping by overcoming of the adiabatic barrier [1,3]. Recent measurements of thermoluminescence in the spectrally selected range of the M-band show the existence of a very weak contribution of the electron–hole recombination channel to the population of the M-band forming states [6]. Radiative 'hot' transitions from vibrationally excited states of molecular trapped excitons shape wings of the M-bands [7].

The nature of near-ultraviolet H-bands is the subject of active current investigations [8–11]. These bands correspond to the third continua in rare gas
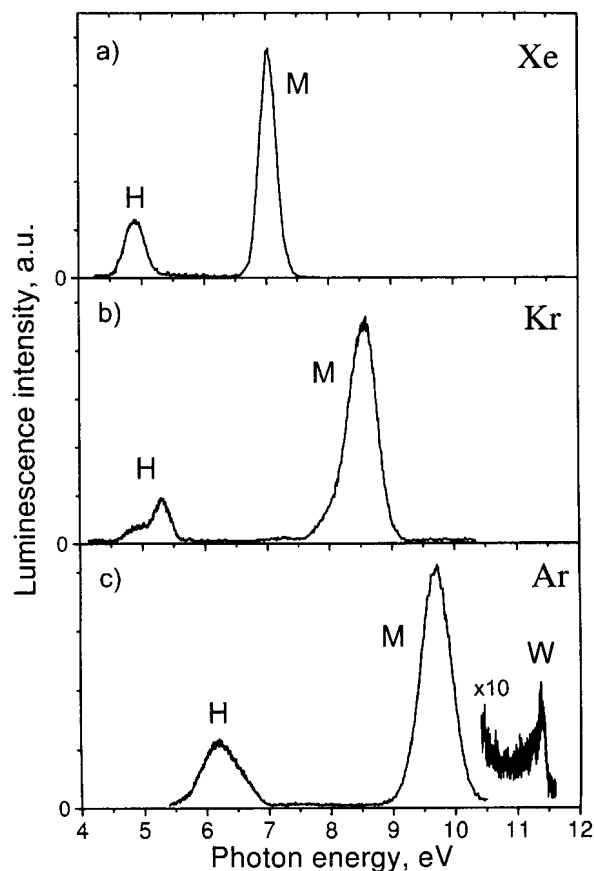

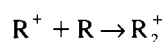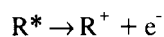Fig. 1. Molecular luminescence spectra of rare gas crystals.

emission, which are formed by transitions in molecular ions [12] from $(R_2^+)^*$ states (corresponding asymptotically to the ground state of an R^+ ion and an excited state of a $R^*({}^3P_{1,2})$ atom) to R_2^+ states (corresponding asymptotically to the ground states of an R^+ ion and an R atom). Comparison of cathodoluminescence [8] and thermoluminescence data [13] with results of analysis of photoelectron scattering [4] and pump–probe experiments [11] shows that, as in the gas phase case, the H-bands originate from the radiative decay of intrinsic excited molecular ionic centers $(R_2^+)^*$ — excited self-trapped holes. These bands require primary creation of free electron–hole pairs and have a clear threshold in excitation spectra at photon energy for the formation of secondary electron–hole pairs: $E_{th} = E_g + E_g(1 + m_e/m_h)$. With literature values [1] of the effective masses of electrons and holes, threshold energies are: $E_{th}^{Xe} =$

20.2 eV, $E_{th}^{Kr} = 25.5$ eV, $E_{th}^{Ar} = 29.6$ eV. The stability of self-trapped holes is defined by electron–hole recombination dynamics and temperature dependence of the H-band shows pronounced correlation with the glow curve of thermoluminescence [8].

Among the rare gas crystals, solid Ar exhibits an additional molecular band (W-band in Fig. 1(c)), which is formed by 'hot' $^{1,3}\Sigma_u^{+(v)} \rightarrow {}^1\Sigma_g^+$ transitions in desorbed vibrationally excited dimers [14]. The temperature behavior of this band is governed by dissociative recombination of self-trapped holes with electrons near the crystal-vacuum interface [15]. Hence, the W- and H-bands show strong dependence on the presence in crystal of charged trapped centers — self-trapped holes and electrons, whereas the M-band forming states populate mainly through neutral excitonic channel. Comparison of the excitation spectra of the H-, M- and W-bands supports this statement.

Fig. 2 shows the photoabsorption spectrum of solid Ar [16] (Fig. 2(a)) and excitation spectra of H-band (Fig. 2(b)), M-band (Fig. 2(c)) and W-band (Fig. 2(d)), which were recorded between 11.3 and 14.5 eV at maxima of corresponding bands. General behavior of excitation spectra of H- and W-bands reproduces all surface (S) and bulk (transverse $n =$ 1,2,3 and longitudinal L) features of photoabsorption. The opposite behavior of the M-band underlines the branching among competing channels of population neutral and charged trapped centers.

Excitation of the H-band below E_g reflects the intrinsic process of exciton ionization. It was found recently that after excitation of bulk and surface excitons the rare gas crystals exhibit photoconductivity as a result of Poole–Frenkel ionization of free excitons in the electrical fields produced by surface charges generated during the irradiation [17]. Moreover, such an electric field influences the desorption from rare-gas crystals and about 45% of total desorption processes start from ionization events [18]. Therefore free exciton ionization followed by charge trapping:

$$R^* \rightarrow R^+ + e^-$$

$$R^+ + R \rightarrow R_2^+$$

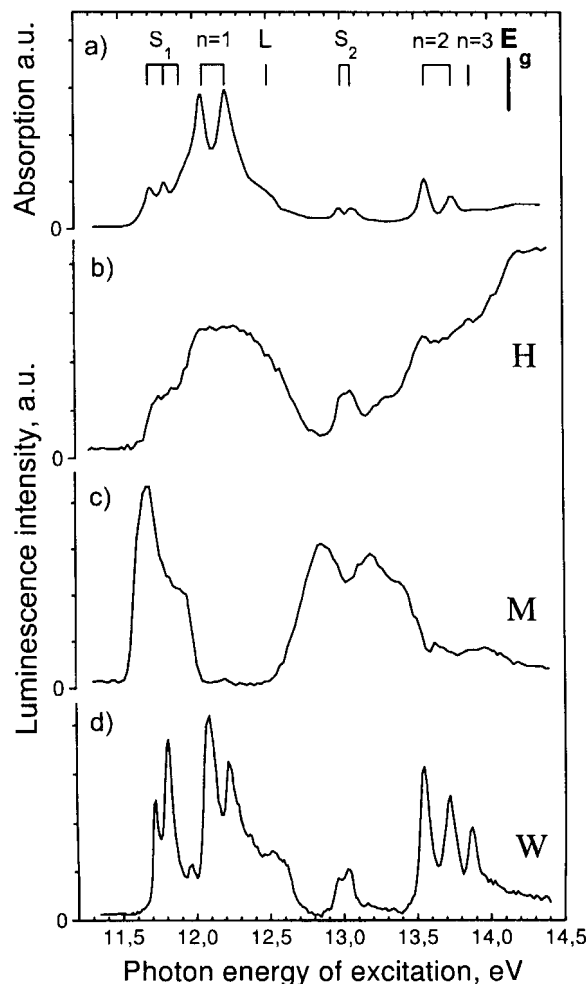is the starting point of the evolution of charged

Fig. 2. Excitation spectra of solid Ar molecular luminescence bands: (a) The absorption spectrum of solid Ar from Ref. [16]; (b) H-band; (c) M-band; (d) W-band.

trapped centers at photon energies of excitation $E <$ E_g. Formation of the emitting $(R_2^+)^*$ center occurs by 'dressing' of the trapped hole by the exciton with subsequent H-band emission:

$$R_2^+ + exciton \rightarrow (R_2^+)^* \rightarrow R^+ + R + h\nu(H\text{-band})$$
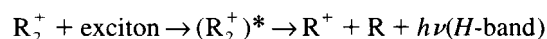
Fig. 3 shows the scheme of continuum-forming states population during energy relaxation. The discussed channels of population are plotted by dashed arrows. The charge separation and trapping are indispensable to producing the stable molecular emitting states via the recombination channel. In rare
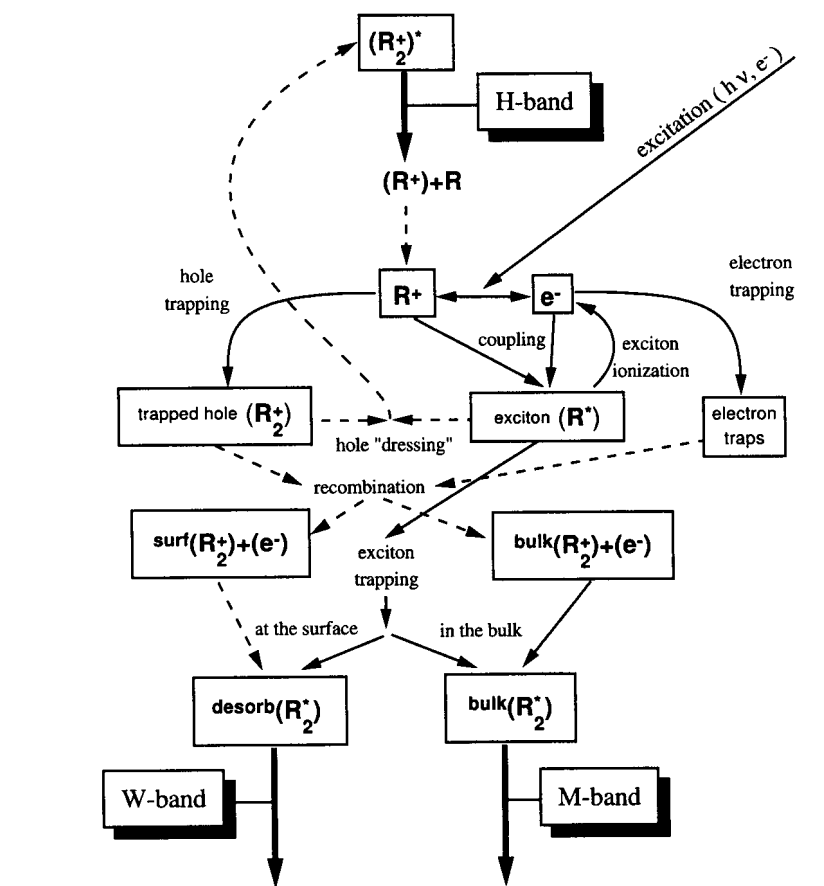
Fig. 3. Scheme of the population of molecular continuum-forming intrinsic neutral and charged trapped centers in rare gas crystals.

gas crystals, in addition to traps for electrons and holes, which were created during crystal growth, charge traps can be formed under irradiation by photons with sub-gap energies during intrinsic processes of exciton self-trapping. Energy release during relaxation of the molecular self-trapped excitons by relaxation jumps and an explosion-like emission of phonons [7] induces the lability of the lattice. The stable Frenkel pair is formed by displacement of the excited molecular center from a centrosymmetric position in the direction $\langle 110 \rangle$ and reorientation of the molecular axis to $\langle 100 \rangle$ direction [19]. The vacancy and interstitial atom can act further as traps for electron and hole [13].

At excitation above E_g direct creation of electron–hole pairs occurs (see Fig. 3). Then charge carriers are trapped or form free exciton. At excitation below

E_g direct creation of excitons occurs. Exciton ionization populates the states of self-trapped holes and trapped electrons. Neutral excitonic channel of population of W- and M-band forming states proceeds via exciton trapping at the surface and in the bulk of the crystal. Additional electron–hole recombination channel also populates these states. Bulk recombination of trapped holes with electrons populates the bulk R_2^* states with subsequent M-band emission [6]:

$$^{\text{bulk}}R_2^+ + e^- \to {}^{\text{bulk}}(R_2^*) \to R + R + h\nu(M\text{-band})$$
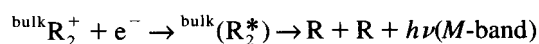
After surface recombination of trapped holes with electrons the excited dimers R_2^* desorb from the surface of the crystal with subsequent W-band emission [15]:

$$^{\text{surf}}R_2^+ + e^- \to {}^{\text{desorb}}(R_2^*) \to R + R + h\nu(W\text{-band})$$
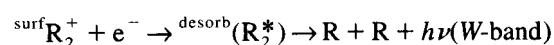
The optical data on the electronic transitions between the ground state and the lowest excited states of intrinsic ionic centers Xe_2^+ were obtained recently in experiments on absorption and laser-induced fluorescence from nominally pure solid Xe [20]. In the samples grown from discharge the correlation of population of charge traps with intensity of absorption and emission bands of ionic molecular centers was found.

4. Conclusion

Electronically induced formation of intrinsic neutral and charged emitting centers in the configuration of rare gas excimers R_2^* and excited molecular ions $(R_2^+)^*$ have been studied by thermoactivated, cathodoluminescence and selective excitation spectroscopy methods. Additional channels of population of molecular continuum forming states through recombination of electrons with self-trapped holes in rare gas crystals are proposed. Selective excitation of molecular luminescent bands underlines the competition between excitonic and recombination channels of energy relaxation.

References

[1] K.S. Song, R.T. Williams, Self-trapped excitons, 2nd ed, Springer Series in Solid-state Sciences, Vol. 105, Springer-Verlag, Berlin, Heidelberg, New York, 1996.

[2] V.E. Bondybey, A.M. Smith, J. Agreiter, Chem. Rev. 96 (1996) 2113.

[3] G. Zimmerer, in: U.M. Grassano, N. Terzi (Eds.), Excited-state Spectroscopy in Solids, North-Holland, Amsterdam, 1987, p. 37.

[4] A.N. Ogurtsov, E.V. Savchenko, J. Becker, M. Runne, G. Zimmerer, Chem. Phys. Lett. 281 (1997) 281.

[5] G. Zimmerer, Nucl. Instr. Meth. Phys. Res. A 308 (1991) 178.

[6] E.V. Savchenko, A.N. Ogurtsov, O.N. Grigorashchenko, S.A. Gubin, Low Temp. Phys. 22 (1996) 926.

[7] V. Hizhnyakov, M. Selg, M. Kink, R. Kink, J. Maksimov, J. Low Temp. Phys. 111 (1998) 709.

[8] O.N. Grigorashchenko, S.A. Gubin, A.N. Ogurtsov, E.V. Savchenko, J. Electron Spectrosc. Relat. Phenom. 79 (1996) 107.

[9] M. Hävecker, M. Runne, G. Zimmerer, J. Electron Spectrosc. Relat. Phenom. 79 (1996) 103.

[10] A.N. Ogurtsov, E.V. Savchenko, J. Becker, M. Runne, G. Zimmerer, Low Temp. Phys. 23 (1997) 851.

[11] A.N. Ogurtsov, E.V. Savchenko, J. Becker, M. Runne, G. Zimmerer, J. Luminesc. 76–77 (1998) 478.

[12] A.M. Boichenko, V.F. Tarasenko, A.V. Fedenev, S.I. Yakovlenko, Quantum Electron. 27 (1997) 679.

[13] A.N. Ogurtsov, E.V. Savchenko, O.N. Grigorashchenko, S.A. Gubin, I.Ya. Fugol, Low Temp. Phys. 22 (1996) 922.

[14] C.T. Reimann, W.L. Brown, D.E. Grosjean, M.J. Nowakowski, W.T. Buller, Phys. Rev. B 45 (1992) 43.

[15] O.N. Grigorashchenko, A.N. Ogurtsov, E.V. Savchenko, J. Becker, M. Runne, G. Zimmerer, Surf. Sci. 390 (1997) 277.

[16] V. Saile, M. Skibowski, W. Steinmann, P. Gürtler, E.E. Koch, A. Kozevnikov, Phys. Rev. Lett. 37 (1976) 305.

[17] J. Kraft, A. Schrimpf, B. Schweitzer, K. Ibbeken, H.-J. Stockmann, Europhys. Lett. 39 (1997) 459.

[18] D.E. Grosjean, R.A. Baragiola, W.L. Brown, Phys. Rev. Lett. 74 (1995) 1474.

[19] E.V. Savchenko, A.N. Ogurtsov, O.N. Grigorashchenko, S.A. Gubin, Chem. Phys. 189 (1994) 415.

[20] E.V. Savchenko, N. Caspary, A. Lammers, V.E. Bondybey, J. Low Temp. Phys. 111 (1998) 693.