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Radiative relaxation of optically generated intrinsic charged centers in solid Ar

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Abstract

Formation and radiative relaxation of intrinsic ionic centers in solid Ar have been studied by selective excitation with synchrotron radiation. Analysis of the excitation spectrum of the near-UV emission band reveals pronounced thresholds near the band-gap energy E_g and $2E_g$ associated with the creation of initial free electron–hole pairs and secondary ones via inelastic electron–electron scattering. The key role of self-trapped holes in population of the emission forming states is inferred. The hole–exciton interaction is discussed and an interpretation of the relaxation path of electronic excitation is proposed.

Keywords: Self-trapped holes; Photoluminescence; Excitation spectra; Solid Ar

1. Introduction

Generation of electron–hole pairs in rare-gas solids (RGS) gives rise to a variety of dynamic processes including charge transfer, electron–phonon and electron–electron scattering, charge-carrier trapping, etc. It is predicted theoretically that the holes in RGS are self-trapped into molecular type centers [1]. These centers are stable in the lattice as long as electrons are captured in some traps that prevents recombination of charge carriers. The self-trapped holes were revealed in thermoluminescence of solid Ar [2] as a recombination emission at the wavelength of molecular self-trapped excitons (the so-called M-band). It was suggested that excitation and even ionization of self-trapped holes can result in a population of states emitting wide near-ultraviolet (UV) H-band [3]. Up to now, however, no detailed direct study has been done to elucidate the primary stages of emitting states population and dynamic processes involving these states in solid Ar.

The paper presents the results of the first analysis of the near-UV luminescence (the so-called third continuum) of nominally pure solid Ar following primary selective excitation by synchrotron radiation [4].

2. Experiment

The experiments have been performed at the SUPERLUMI experimental station of HASYLAB [5] in an ultra high vacuum environment (a basic pressure in the experimental chamber did not

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exceed 10^{-10} mbar). The samples were grown from a Ar gas (99.999%) in a special cell attached to the helium cryostat. After condensation, the cell was opened and the measurement of photoluminescence and excitation spectra were performed. The amount of structural defects in the samples was changed by varying the condensation conditions: temperature, pressure and deposition rate. Growing the samples under isobaric (P = 80 Pa) conditions with the constant cooling rate of 0.1 K/s in the temperature range 60–50 K resulted in highly transmitting samples with a small quantity of initial defects of structure. The sample quality was controlled by the ratio of luminescence intensities of two subbands (M_1 and M_2) assigned to trapped and self-trapped excitons [6]. Selective photon excitation was carried out with $\Delta\lambda$ = 0.25 nm.

3. Results and discussion

The typical luminescence spectrum of nominally pure solid Ar under photon excitation at the band-gap energy E_g = 14.16 eV is shown in Fig. 1. It consists of a variety of spectral features [7] related in their origin to the bulk of sample (the M-band at 9.72 eV, the c-band at 11.54 eV), its surface (the W-band near 11.38 eV, the b-line at 11.62 eV) and the near-UV band in question H at 6.2 eV with FWHM = 0.7 eV. The well-known M-band stems from radiative decay of self-trapped excitons (subband M_2) and excitons trapped on initial and electronically induced defects of structure (subband M_1) [8,6]. The c-band is due to atomic-type trapped excitons [9]. The b-line and the W-band originate from desorbing atoms and molecules [10, 11].

The measurements of excitation spectra were performed to clear up the primary processes of population of the states emitting the H-band. It is found that this band cannot be excited below the range of intrinsic absorption. Moreover, the band in question can be only slightly excited in the excitonic range of energies $E_1 < E < E_g$ and its behavior is in contrast with that of the M-band (Fig. 2).

The tests provide support of the intrinsic nature of the H-band in nominally pure solid Ar. The excitation spectrum of the H-band yields a pronounced threshold E_1^{thr} at the band-gap energy E_g of solid Ar at 14.16 eV and a second threshold E_2^{thr} in the vicinity of $2E_g$. The second threshold defines the energy needed for additional free electron–hole pairs formation. Simple estimation of E_2^{thr} uses the approximation of parabolic valence and conduction bands [12]: $E_2^{thr} = E_g(2 + m_e/m_h)$ yields the value E_2^{thr} = 29.6 eV with the use of the literature values [1] of the effective mass of electron $m_e = 0.48m_0$ and that of hole $m_h = 5.3m_0$ (m_0 is the free-electron mass). The measured threshold E_2^{thr} agrees closely with the expected value. The manifestation of these thresholds testifies that the

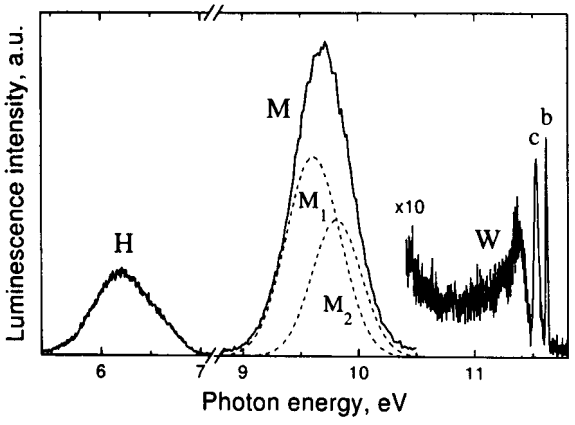

Fig. 1. Luminescence spectrum of solid Ar recorded with photon excitation energy E_g = 14.16 eV at T = 15 K.

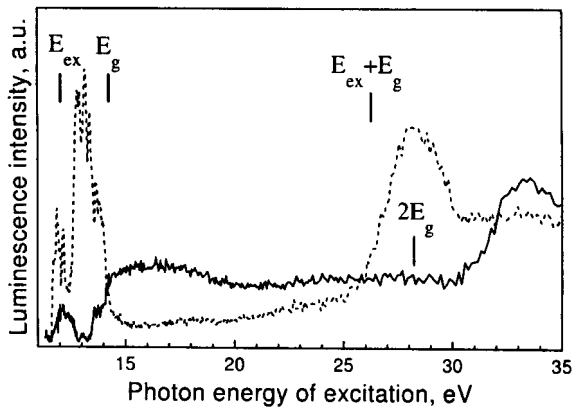

Fig. 2. Luminescence excitation spectra of the H-band (solid curve) and the M-band (dashed curve) recorded at T = 5 K.

creation of free electron–hole pairs is the primary process of population of the continuum forming states. The weak features observed in the excitonic range do not violate this inference and can be explained by the impurity-induced ionization of excitons taking into account the photoelectron emission spectroscopy data [13]. It should be noted that a similar behavior of the third continuum excitation spectra was observed in solid Xe [14] and Kr [15].

The H-band cannot be ascribed to the direct recombination of free electrons and holes, as evident from its energy position. The most likely precursors of the continuum forming states are thought to be the states of self-trapped holes. The stability of these intrinsic ionic centers is defined by recombination dynamics. To put this another way, it depends on how many electrons are captured by different kind of traps, on conditions of electrons release (such as temperature for shallow traps) and on mobility of charge carriers. A special 'pump-probe' experiment was performed to reveal the effect of self-trapped holes accumulation on the H-band behavior. The sample was irradiated for 15 min by the zero-order light of the primary monochromator to increase the number of self-trapped holes due to increase of electron trapping on radiative induced defects of structure [8,16]. Strong enhancement of the H-band emission from irradiated sample was observed at excitation in the energy range above E_g as seen from Fig. 3. It should be noted that the intensity of the band remained constant at excitation via excitonic states. The experiments on the samples with different content of initial structural defects which served as electron traps demonstrated an enhancement of the H-band in presence of those. In Fig. 4 the excitation spectrum recorded for the 'defect' sample is shown (curve 1). The annealing of the sample up to 40 K resulted in suppression of the H-band (curve 2). Following 15 min irradiation of the annealed sample nearly completely restored the excitation spectrum (curve 3). A similar enhancement of the H-band was observed in the presence of deep electron traps (in the samples with oxygen-containing impurities) [3]. The key role of the self-trapped holes in the formation of near-UV emission from nominally pure solid Ar is evident from the ob-

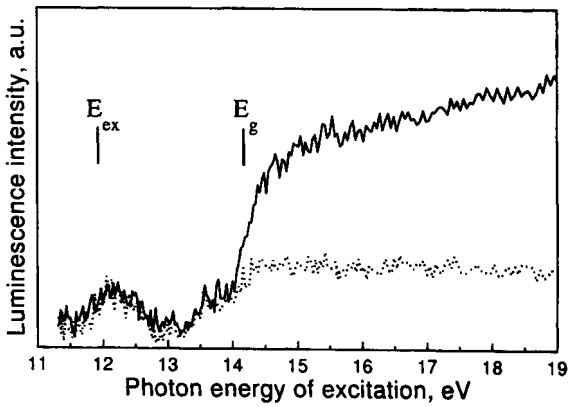

Fig. 3. Excitation spectra of the H-band measured at $T = 5$ K before photon pumping (dotted curve) and after it (solid curve).

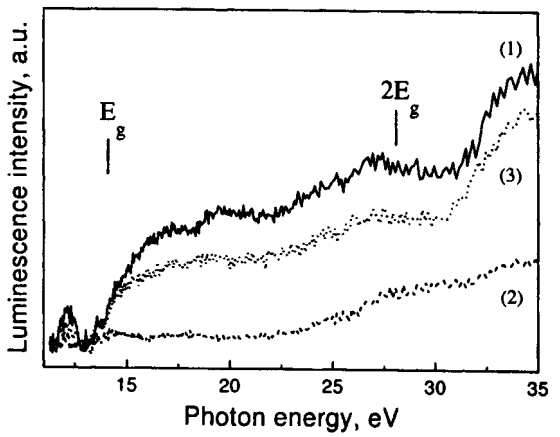

Fig. 4. The evolution of the H-band excitation spectrum of the "defect" sample (curve 1): after annealing (curve 2) and following photon pumping (curve 3).

served features of the excitation spectrum and the temperature behavior of the H-band – quenching with increasing temperature from 19 K, where the release of electrons from their traps occurs [3,17]. A more likely assumption as to the origin of the H-band seems to be the radiative transitions from the excited states of self-trapped holes with configuration of the molecular ion Ar_2^+ to lower-lying repulsive states. According to this assumption the population of the continuum-forming states is a two-step process: (i) self-trapping of holes

followed by (ii) their excitation:

$Ar^+ + Ar \rightarrow Ar_2^+$,

$Ar_2^+ + \text{exciton} \rightarrow (Ar_2^+)^* \rightarrow Ar^+ + Ar + h\nu$.

The theoretical study [18] of the Rydberg excited electronic states correlated with $(Ar^+)^* + Ar^*$ revealed the lowest bound state $(2)^2\Sigma_g^+$ which had a pronounced well at a short internuclear distance close to that of the ground state $(1)^2\Sigma_u^+$ molecular ion potential. The calculated allowed transition $(2)^2\Sigma_g^+ \rightarrow (1)^2\Pi_u$ energy was found to be about 5.8 eV. This value is shifted from 0.4 eV to lower energies with respect to the experimental one. It should be remarked that the calculation was performed for a free ion Ar_2^+ and the transition energies strongly depend on the equilibrium distances of the upper state potentials because of the repulsive character of the lower states at short distances.

Notice that the H-band is of a nonelementary structure and the contribution of other transitions cannot be excluded. Specifically, the contribution of transitions in the Ar_2^{++} center cannot be excluded at excitation above the threshold for the Ar^{2+} formation. The question on the involvement of more complex ionic centers such as Ar_3^+ still remain unsolved. Moreover, the emitting centers are located not only in the bulk of sample but on the surface as shown by the coating experiment [4]. Detailed assignment of emitting states requires further investigation.

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