Branched relaxation of electronic excitations in rare-gas crystals with traps of different types

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Abstract. Luminescence excitation spectra are used as a probe of competition between exciton traps of two types: exciton localization centres and centres of exciton trapping followed by transforming to another electronic state. A strong competition between localization and transforming centres takes place only under excitation above the dielectric gap E_g (with energy $E > E_g$). For $E < E_g$ the action of transforming traps is usually suppressed by localization centres. A strong change in excitation spectra near the point E_g is explained by a nontrivial structure of the exciton band formed by the mixing of free excitons with polaronic states—excimer quasi-molecules. The nature and action mechanism of both types of trap are explored. To localize heavy exciton polarons, small lattice defects are sufficient. Transforming traps exist in the form of stable molecular ions, conditioned by large defects capturing light electrons, and impurity centres. The trapping cross sections of the centres of different types are strongly (but in different ways) dependent on the exciton energy.

1. Introduction

It is known that relaxation of electronic excitations in rare-gas solids is accompanied by branching of relaxation paths [1, 2]. In the course of relaxation an exciton can persist in a free state up to the moment of radiative transition to the ground state. But, unlike in the case of a sample of solid Xe with extremely high crystal quality [3–5], the excitons have a predominant probability of being self-trapped or localized on lattice defects (mainly on vacancies or small vacancy clusters) in crystals of usual sample quality. A trapped or self-trapped exciton forms an excimer quasi-molecule R_2^* (R = Ne, Ar, Kr, Xe) which goes to the ground state via emitting photon in the M-band lying in the vacuum-ultraviolet region. (There exist also one-site local centres R^*, but they do not play any noticeable role for argon, krypton, and xenon studied below.) Excimer quasi-molecules R_2^* can be formed also in another way: a free hole R^+ is easily self-trapped, forming a molecular ion R_2^+, and after recombination with an electron it turns into the neutral molecule R_2^*. Irrespective of the manner of their formation, excimer molecules R_2^* go to the ground state via emission in the M-band or, for brevity, M-luminescence.

Recently the authors have shown that molecular ions R_2^+ participate in the relaxation process also in another nontrivial way. If some of the electrons are localized in shallow or deep traps and drop out from the recombination process, the same number of molecular

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ions R_2^+ remain stable in the electrically neutral crystal. The influence of shallow and deep electron traps on a concentration of stable R_2^+-centres was studied by measurement of $1\frac{1}{2}_u - 2\frac{1}{2}_g$ transitions in absorption and laser-induced fluorescence [6–8]. Stable molecular ions capture excitons and go to an excited state with the subsequent light emission in the H-band lying in the near-ultraviolet region (H-luminescence) [9–11].

Thus, relaxation of excitons branches into M- and H-channels, terminating in M- or H-luminescence (emission in the M- or H-band, respectively). An exciton gets to the M-channel via trapping or self-trapping without changing its atomic state [12]. In contrast, the entry to the H-channel is by transfer of the excitation to a molecular ion R_2^+ [9, 10]. To avoid terminological confusion, we shall speak about exciton trapping by a localization centre in the former case and by a transforming centre in the latter. As will be shown below, there exist also other types both of transforming traps and of localization centres which significantly complicates the relaxation process.

The aim of the present paper is to reconstruct the main features of this branched relaxation process. In doing so, allowance will be made for the mixing of free excitons (FE) with excimer quasi-molecular states which fundamentally affects the exciton band structure and relaxation processes [12, 13].

The logic of the exposition is somewhat different from a conventional scheme. Section 3 contains experimental data indicative of new exciton relaxation paths or of nontrivial mechanisms of their competition. These mechanisms are inferred from experimental results after their exposition (section 4) and corroborated or illustrated by additional experiments presented in section 5 and 6.

2. Experimental details

The experiments were performed at the SUPERLUMI 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 [14]. The samples were grown from high-purity Ar (99.999%) and Kr (99.99%) gas in a special cryogenic cell [15] attached to the helium cryostat. Kr gas had an initial impurity of Xe with concentration 0.005 at.%. After condensation the cell was opened and the measurements of photoluminescence and excitation spectra were performed. The number 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^{-1} at $T \approx \frac{2}{3}T_t$ (T_t is the triple-point temperature) 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 one of which is red-shifted due to lattice defects [16]. In this way, bulk, completely clear samples were obtained with a thickness up to a few millimetres. The samples were therefore 'optically thick' throughout the whole range of photon energy of excitation covered in the present paper. Selective photon excitation was performed with $\Delta\lambda = 0.25$ nm. Both in luminescence and excitation spectra, the luminescence was spectrally dispersed with the 0.5 m Pouey monochromator ($\Delta\lambda = 2$ nm) equipped with a solar-blind photomultiplier. In the excitation spectra, the luminescence intensity was measured as a function of the photon energy of the exciting light and then normalized to the intensity of the incident exciting radiation.

3. Excitation spectra of M- and H-luminescence; spectroscopic evidence for a third relaxation channel

It has already been mentioned that, along with the relaxation channel terminating in exciton luminescence, energy relaxation can occur also through excitation of stable molecular ions R_2^+ followed by their emission in the near-ultraviolet H-band (H-luminescence). As regards the luminescence from excitonic states, a predominant part of its intensity is emitted (except in the case of neon) from two-site quasi-molecular states (M-luminescence). As an example, the M- and H-bands of argon luminescence are shown in the inset of figure 1(a). For brevity, the relaxation paths, terminating in M- or H-luminescence, will be called M- and H-channels.
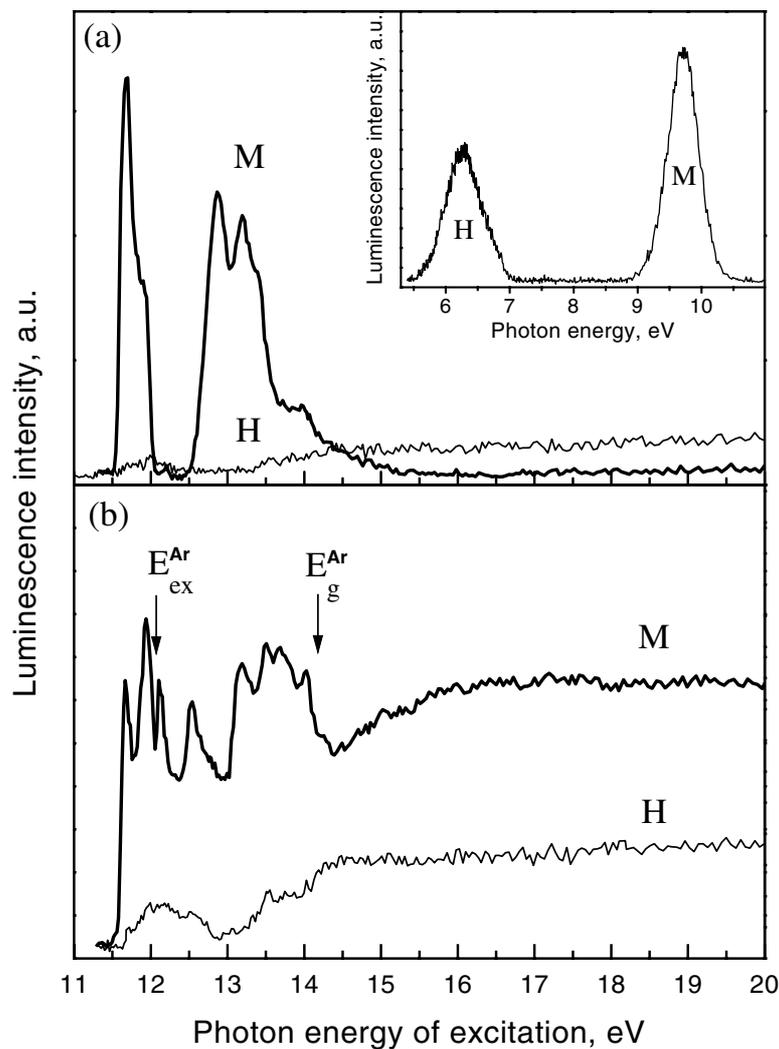
Figure 1. Luminescence excitation spectra of the M-band (thick line) and the H-band (thin line) of solid Ar recorded at $T = 5$ K: (a) before irradiation; (b) after 15 min of irradiation of the sample by zero-order light from the primary monochromator. Inset in (a): the luminescence spectrum of solid Ar recorded with photon excitation energy $E_g = 14.16$ eV at $T = 5$ K.

The spectroscopic data given below provide evidence that, along with the M- and H-channels, there exists also a strong third relaxation channel which terminates neither in M- nor in H-luminescence.

Figure 1(a) shows the excitation spectra of the M- and H-luminescence for a good argon crystal. It can be seen from the figure that for excitation photon energy E below the dielectric gap ($E_g^{Ar} = 14.16$ eV), M-luminescence strongly exceeds H-luminescence in intensity. But as the excitation energy increases above E_g, the M-luminescence intensity falls by more than an order of magnitude whereas the H-luminescence grows only by a factor of two or three. The total luminescence intensity within the M- and H-bands in the excitation energy region below E_g differs by roughly a factor of four from that in the excitation energy region above E_g.

In connection with this, two questions arise. First, a strong change of the M-band excitation efficiency, observed at the excitation energy $E = E_g$, seems to be incomprehensible. Excitation of the crystal with energy $E < E_g$ creates an exciton which, with a predominant probability, is self-trapped and turns into a quasi-molecule R_2^*. Excitation with energy $E > E_g$ results in the formation of an electron–hole pair which turns either into the same excimer quasi-molecule or into a FE which is subsequently self-trapped as in the former case. The difference between the former and latter cases is at first sight negligible. The question arises of why the M-band excitation efficiency is drastically different in these two cases. This question will be answered in section 4.

Second, in the excitation energy region $E > E_g$ a predominant part of the exciting photon energy is transformed by a route passing by the M- and H-channels. Let us call this unknown relaxation path the third relaxation channel and investigate the question of its nature.

Some conclusions regarding the latter question can be drawn from spectroscopic data. First of all, the third channel does not originate directly from lattice defects. This follows from a well established experimental finding: the more perfect the crystal, the more *strongly* the third channel manifests itself. This statement is illustrated in figure 1 where the excitation M- and H-luminescence spectra are presented for the same argon sample before (figure 1(a)) and after (figure 1(b)) a strong irradiation which created a large number of lattice defects. (The irradiation was produced by the zero-order light of the primary monochromator—about 10^{18} photons cm^{-2} in the range 5–20 eV.) As seen from figure 1(b), in the case of such an imperfect crystal the total intensity emitted in the M- and H-bands is generally higher than that in the case of a good crystal (figure 1(a)) and, unlike that in the latter case, does not diminish as the excitation energy increases above E_g.

Thus, lattice defects do not promote and can even strongly suppress the manifestation of the third relaxation channel. If one simply makes allowance for the competition between the third and H-channels, this is easily explained by there being an increased number of stable R_2^+-centres, equal to the number of electron traps. But figure 1 shows that the presence of photoproduced lattice defects also enhances the M-luminescence, and to an even larger degree than the H-luminescence.

The latter fact means that the localization of electronic excitations on lattice defects impedes their involvement in relaxation through the third channel (this inference will be confirmed spectroscopically in section 6). The only realistic way to explain such a result is to associate the third channel with exciton trapping by uncontrollable impurities which come from the source gas or from residual gases of the set-up. These impurities are inevitably present even in highly pure gases and in high-vacuum chambers [3], and, despite a very low concentration, distinctly manifest themselves in the luminescence [17, 18].

To all appearances, impurities, acting as transforming traps, are responsible for the suppression of M- and H-luminescence in a good crystal (figure 1(a)). After irradiation (figure 1(b)), the crystal contains the same number of impurities but a much greater number

of localization centres (enhancing the M-luminescence) and electron traps (promoting the H-luminescence). Thus, after irradiation the third channel (active mainly above E_g) was suppressed, so the total luminescence intensity, concentrated mainly in the M- and H-bands, became almost independent of the energy (figure 1(b)).

Below, the presumption of a third relaxation channel will be found to be an indispensable element of the relaxation scheme and corroborated by additional experiments.

4. Why is M-luminescence highly sensitive to excitation energy?

At first sight, a change in the excitation efficiency at the excitation energy point $E = E_g$ might be thought to be associated with the population of electron traps: it seems obvious that only at $E > E_g$ can they be filled and can R_2^+-centres be created. However, the possibility of such a mechanism should be discounted since conduction electrons are generated, although with a lower efficiency, also at $E < E_g$ (free excitons are subject to the Poole–Frenkel ionization in electric fields of surface charges produced by irradiation [19]). At low temperature, regardless of the excitation energy and population rate, all of the electron traps are filled during a time short compared to the duration of the experiment (otherwise excitation spectra would exhibit a hysteresis, which was never observed).

4.1. Mixing of free excitons with excimer quasi-molecular states

Thus, the drastic change in the M-luminescence excitation efficiency at the excitation energy point $E = E_g$ should be explained in another nontrivial way.

To that end, it is necessary to take into account the mixing of free excitons with excimer quasi-molecular states conditioned by their common resonance nature [12, 13]. This mixing is shown schematically on the left-hand side of figure 2 where horizontal lines represent the vibrational spectrum of a quasi-molecule intersected by the FE dispersion branch. In the upper part of the exciton band this intersection does not distort the energy spectrum due to a negligibly weak mixing. But in the lower part of the band a noticeable mixing entails the corresponding spectrum distortion shown in the figure.

First let us recall [12, 13] how this mixing influences the relaxation process in the simplest case where only shallow exciton traps are taken into account as localization centres (transforming traps such as molecular ions R_2^+ or impurity centres are absent). In this case two relaxation channels act simultaneously. The usual thermal relaxation channel through the free-exciton dispersion curve persists despite its discontinuities, which do not exceed the Debye frequency. This relaxation path (for short, the F-channel) terminates in free-exciton states near the band bottom (indicated as E_{ex} in figure 2).

Simultaneously, energy relaxation can occur also via consecutive thermal transitions between the quasi-molecule vibration levels (represented in the figure by horizontal lines). Translation motion of an excimer two-site excitation turns these levels into narrow polaronic bands. At low temperature, heavy polarons are localized even on shallow traps, present in a real crystal, and turn into vibrationally excited quasi-molecules attached to a fixed site. This form of exciton relaxation between local states (the M-channel) terminates in the lowest vibrational state of a quasi-molecule—that is, in the self-trapped state understood as having its conventional meaning.

Within the upper part of the exciton band, F- and M-channels act independently due to the negligibly weak mixing. But in the lower part of the band, there is a noticeable polaronic admixture with the free excitons, so they can be found in polaronic states and localized on shallow traps. At low temperature the exchange of excitons between the F- and M-channels is of
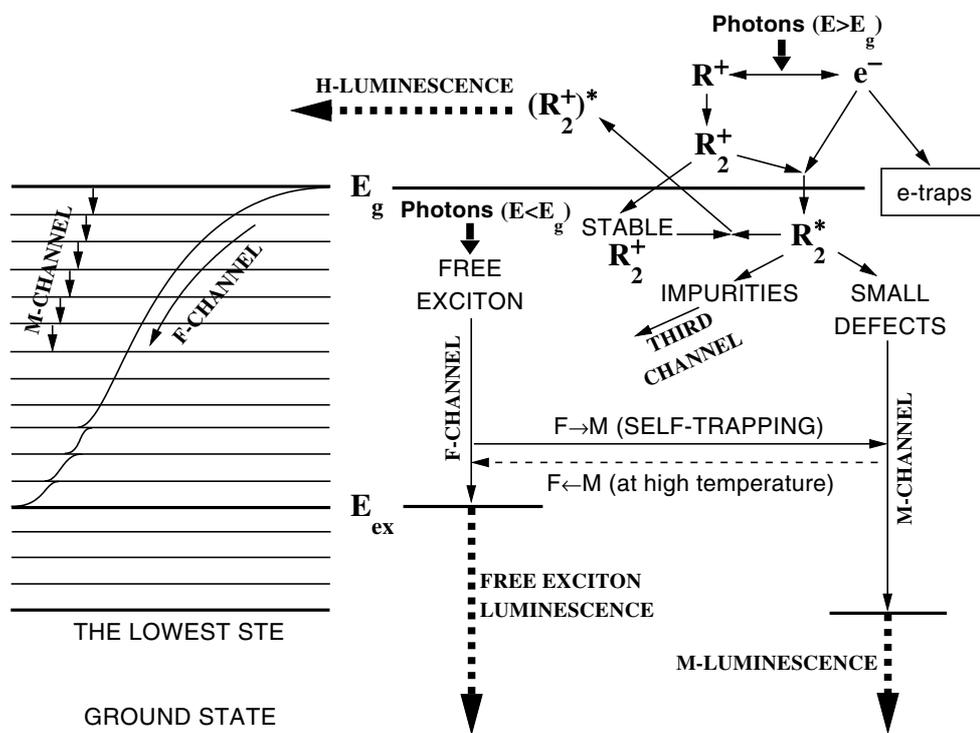
Figure 2. The energy relaxation scheme. Left: a schematic representation of the energy spectrum containing the free-exciton dispersion curve and polaronic subbands (quasi-molecule vibration levels). Right: competing relaxation channels of free excitons (generated at $E < E_g$) and two-site excitons R_2^* (generated at $E > E_g$). Thick solid arrows indicate photon excitation; thick dashed arrows denote luminescence.

one-sided character since trapped polarons cannot go to a free state. Thus, polaronic admixture with FE states permits them to be localized on shallow traps incapable of trapping light free excitons where there is no polaronic admixture [12, 13]. This entails suppression of the F-channel by the M-channel commensurate with the number of small lattice defects and explains the high structure sensitivity of the FE luminescence yield Y_F observed experimentally [3, 20]. Note that at high temperature the exciton polarons may escape from shallow traps [12, 13].

4.2. Competition of the M-channel with other relaxation paths and the crucial role of excitation energy

Let us now extend the outlined relaxation scheme as applied to the competition of the M-channel with other relaxation paths through exciton trapping by transforming centres—molecular ions (the H-channel) and uncontrollable impurities (the third channel).

First the following circumstance, related to relaxation of photoproduced electron–hole pairs, should be recalled. Since the rate of hole self-trapping far exceeds that of electron–hole recombination (including recombination of hot electrons with holes), electrons mainly recombine with self-trapped holes—molecular ions R_2^+—resulting in the formation of self-trapped excitons R_2^*. Thus, photons with $E > E_g$ create mainly self-trapped excitons. Free excitons are created with a lower probability via recombination of electrons with free holes or in the course of decomposition of molecular ions R_2^+ [21, 22].

To simplify the relaxation scheme (which is rather complicated as seen from figure 2), we shall assume that absorption of photons with energy $E > E_g$ is followed by formation of self-trapped excitons and not of free ones. This simplification does not significantly affect the yield of M-luminescence which is the main object of our consideration. On the other hand, free excitons, created by photons with $E > E_g$, distinctly manifest themselves in the FE luminescence kinetics, providing important information on relaxation processes [4, 5, 21–23]. Most of these are beyond the scope of the present consideration.

We shall consider (figure 2) the simultaneous trapping of exciton polarons by localization centres (small lattice defects) and by transforming traps (R_2^+-centres and impurity centres). The former relaxation path terminates in M-luminescence. Let us show that the latter relaxation path, competing with the M-channel, is essentially suppressed as the initial energy of the exciton polaron decreases, starting from E_g, within the exciton band.

Just below E_g a molecular ion R_2^+ (or a charged impurity) has a very large cross section, σ_i, for exciton trapping. Indeed, a charged trapping centre attracts heavy exciton polarons over the distance r defined by the equation (written in atomic units)

$$\frac{\alpha}{2r^4} = T \tag{1}$$

with T the temperature (expressed in energy units) and the exciton polarizability $\alpha \cong (4/9)\rho^4$ mainly formed by the exciton state of radius ρ [12]. It follows that the exciton trapping cross section of a charged centre (in atomic units) is

$$\sigma_i = \pi r^2 \cong \frac{1.5\rho^2}{\sqrt{T}}. \tag{2}$$

The value of (2) essentially depends on the exciton energy—that is, on the number, n, of the excited shell: for $n = 1$ (the lowest excitation) $\rho \cong 5$ au and for $n = 3$ (near to E_g) $\rho \cong 40$ au [12]. Hence, at $T = 10$ K, σ_i achieves about 4×10^5 au $\cong 10^5$ Å^2 near to E_g and diminishes by two orders of magnitude with a decrease of exciton energy.

Of similar character is the energy dependence of the cross section for exciton trapping by impurity molecules. A charged molecule (of donor or acceptor type) has the same trapping cross section (2) as an R_2^+-centre. A neutral impurity molecule has a smaller trapping cross section but it also grows as the excitation energy nears E_g. Indeed, a neutral molecule attracts an exciton by the van der Waals law, the attraction potential being of the form [12]

$$U = -\frac{\Delta\alpha\,\rho^2}{r^6} \tag{3}$$

where ρ is the exciton-state radius and $\Delta\alpha$ is the difference between the polarizabilities of the impurity molecule and the host atom (this difference is usually positive due to the low polarizability of rare-gas atoms). As the excitation energy nears E_g, the trapping cross section grows proportionally to $\rho^{2/3}$. A similar energy dependence of the cross section for exciton trapping by impurities was recently observed in reference [24].

As regards exciton trapping by localization centres (small lattice defects), its energy dependence is of opposite character: the trapping cross section *increases* with decreasing energy starting from E_g. Indeed, near E_g the size of a high-energy exciton state far exceeds that of a small defect, and the localization depth is correspondingly small; it grows with decrease of the exciton energy and its state radius.

Thus, the M-channel is drastically enhanced at the expense of the H-channels and third channels as the exciton energy lowers starting from E_g.

Keeping this in mind, let us analyse how the relaxation process depends on the exciting photon energy E. For $E > E_g$, a generated hole, after self-trapping and recombination with

an electron, turns into an exciton polaron (a quasi-molecule R_2^*). Its relaxation occurs through the consecutive transitions between the vibrational levels (polaronic subbands). In the upper part of the exciton band, as shown on the left-hand side of figure 2, this relaxation path is not interfered with by the FE dispersion curve and, on the other hand, exciton polarons are trapped with a high probability by transforming centres—molecular ions R_2^+ and impurity molecules. This explains the low yield of M-luminescence under excitation by photons with energy $E > E_g$.

But excitation with energy $E < E_g$ generates free excitons which relax in quite another way. If E is near to E_g, then the created exciton relaxes along the FE dispersion curve which in the upper part of the exciton band is not distorted by intersection with vibrational levels. In the course of such relaxation the exciton persists in a pure free state and there is no polaronic admixture, necessary for capture by any traps, until it gets to the lower part of the band. Here the FE dispersion curve interferes with polaronic subbands, so there is polaronic admixture with the excitons which enables them to be trapped by localization centres. In this part of the exciton band, as was already stated, the competition of transforming traps is suppressed. An exciton is trapped in the same way by a localization centre if it is generated by a photon of a lower energy immediately in the lower part of the exciton band. Thus, the relaxation path, terminating in M-luminescence, predominates under excitation with energy $E < E_g$, no matter what the separation from E_g. This explains why in the case of a good crystal the M-luminescence yield is much greater under excitation with energy $E < E_g$ than for $E > E_g$.

In the case of an imperfect crystal with a high concentration of defects, serving as localization centres, they suppress transforming traps even under excitation with energy $E > E_g$, so the difference between the M-luminescence yields for $E < E_g$ and $E > E_g$ disappears (figure 1(b)).

Note that the difference between the modes of relaxation under excitation with energy $E < E_g$ and with $E > E_g$ manifests itself also in the corresponding difference in relaxation time. It is significantly less under direct generation of excitons by photons with energy $E < E_g$ than in the case of $E > E_g$ where excitons arise after recombination of molecular ions with electrons [23].

4.3. The effect of photoproduced lattice defects on excitation spectra below E_g

Under excitation with photons with energy $E < E_g$, as seen from figure 1, H-luminescence is enhanced by irradiation due to an increase in the number of R_2^+-centres (quite similarly to the case for $E > E_g$). But in the region $E < E_g$ (except the 0.5 eV wide interval just above E_{ex}), photoproduced defects do not exert a strong influence on the M-luminescence intensity. This means that even without irradiation the number of localization centres (small defects) is sufficient to impart a predominant character to the M-channel.

However, as seen from figure 1, M-luminescence is very sensitive to irradiation when excited in the 0.7 eV wide interval just above E_{ex} (coinciding with the energy extent of the lowest exciton band). This fact is naturally explained by a quite other mechanism which is as follows. In the region $E_{ex} < E < E_g$, except the vicinities of the bottoms of the exciton bands, the absorption of exciting light in a perfect crystal is very much weakened, because the quasi-momentum conservation law can be observed only by phonons being simultaneously generated. Such falls in absorption are most pronounced for the lowest band whose bottom has the most separation from the next band bottom (for higher bands there is no significant fall in absorption due to the smaller values of these separations, and for another reason considered below).

Vacancy clusters perturb the free-exciton motion, especially those with trapped charges (see sections 4.2 and 5), which entails the violation of the quasi-momentum conservation law

and a corresponding enhancement of the absorption. This effect is most pronounced for higher excitonic bands since the attraction of an exciton to a charged defect is proportional to the excited-state polarizability (see section 4.2).

Before irradiation, the concentration of charged defects can be high enough to provide a sufficient absorption for higher bands but not for the lowest band. After irradiation, absorption is enhanced for all the bands in proportion to the increased number of defects, but for the above reason this is more noticeable for the lowest band.

5. The double role of lattice defects: large defects as electron traps and small defects as traps for exciton polarons

In the above-described relaxation scheme, lattice defects play a double role:

(i) large defects, capturing light electrons, give rise to stable molecular ions R_2^+—transforming traps responsible for H-luminescence; and

(ii) small defects, capable of trapping only heavy exciton polarons, act as exciton localization centres responsible for M-luminescence.

The role of shallow traps—exciton localization centres—can be played by any lattice defects, in particular by separate vacancies. But a conduction band electron with a small effective mass (near to 0.75 au [12]) can be trapped only by a large defect, e.g. a comparatively big vacancy cluster. The number of such large defects in a crystal is obviously much less than the number of small defects—centres of localization of heavy exciton polarons.

This inference can be verified spectroscopically: the numbers of small and large defects, traced through the M- and H-luminescence intensities, must change in different ways when annealing and irradiating the crystal.

The results of such an experiment are shown in figure 3. An argon sample was sequentially examined in three states:

(1) The initial state, where the sample was of imperfect quality and contained many defects of both types.

(2) The intermediate state after annealing at 23 K, which made the lattice more perfect and diminished the number of defects of both types.

(3) The final state after a weak irradiation (with about 10^{17} photons cm^{-2}), sufficient to enhance the number of lattice defects nearly to the initial level.

Figure 3 displays the M- and H-luminescence excitation spectra of this sample in the sequential stages of its treatment. Attention should be drawn to the excitation energy region $E > E_g$ where lattice defects strongly influence the luminescence excitation efficiency. As could be expected, the excitation efficiency both for M- and for H-luminescence grows or decreases together with the degree of lattice imperfection. But for M-luminescence excitation the efficiency is greater in the final state (3) than in the initial state (1), and for H-luminescence the final excitation efficiency is less than the initial one.

This means that in the final state the crystal contained more exciton localization centres (small defects) and fewer electron traps (large defects) than in the initial state. A weak irradiation of the sample, carried out after annealing, produced a number of small defects exceeding the initial number, but was insufficient to increase the number of large defects up to the initial level.
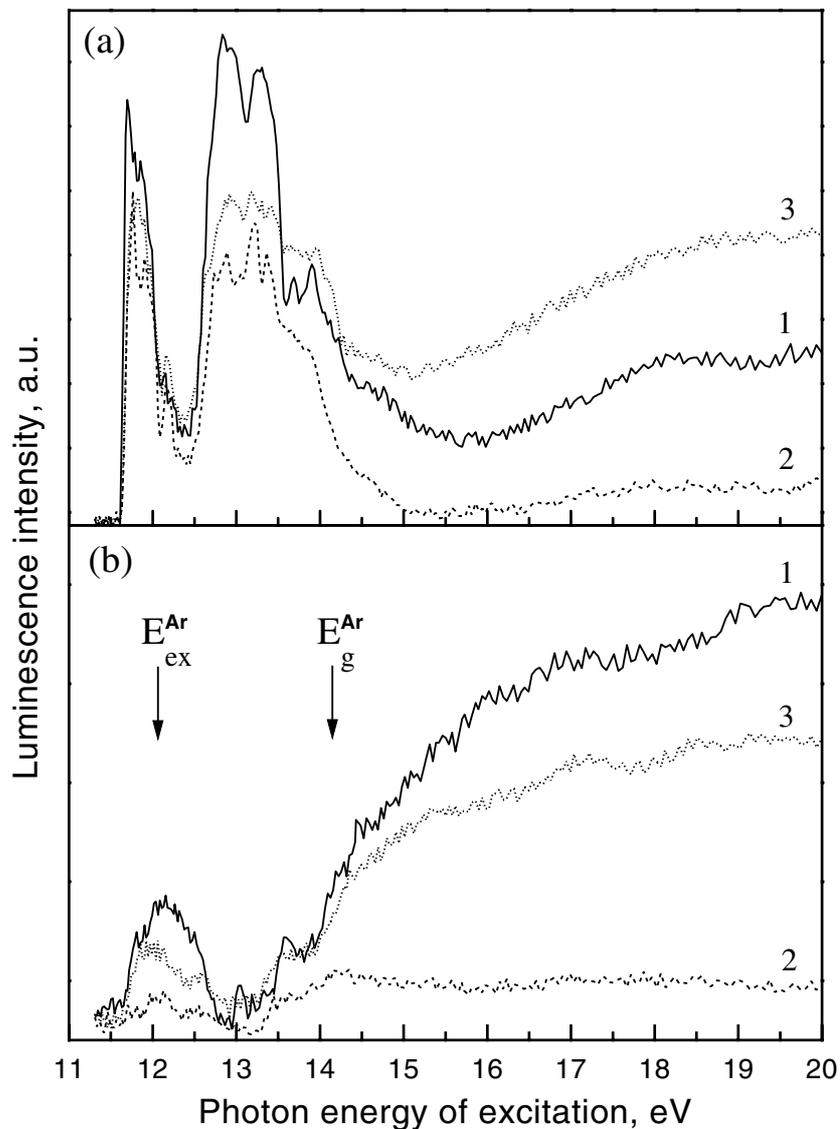
Figure 3. The evolution of the excitation spectra of (a) the M-band and (b) the H-band of an imperfect Ar sample: (1) initial spectrum; (2) after annealing at 23 K; (3) after subsequent photon irradiation.

6. Modelling of exciton traps in a krypton crystal by xenon atoms

It was shown above that lattice defects (mainly small defects present predominantly) enhance M-luminescence through localization of heavy exciton polarons. It is interesting to prove spectroscopically that the role of lattice defects in the enhancement of M-luminescence is indeed reduced to their action as exciton localization centres. If this is true, then exciton localization centres, if realized in a perfect lattice in the form of a proper impurity, must also compete with the same transforming traps and this competition must manifest itself in a similar character of the M-luminescence excitation spectrum.

The role of such localization centres can be played by xenon impurity atoms incorporated in the krypton lattice. Such impurity produces a very weak deformation of the crystalline surroundings [12]. On the other hand, a weak atomic xenon impurity in a krypton lattice acts mainly as an exciton localization centre (transfer of excitation from krypton to xenon is weakened due to a significant energy gap [25, 26]). A xenon atom, having almost double the polarizability of the host atom, attracts exciton polarons and is capable of localizing them.

Figure 4 demonstrates the M-luminescence excitation spectrum of a good krypton sample with a trace amount of xenon impurity in the initial state (solid line) and after a long annealing at 40 K (dashed line). As seen from the figure, in this case annealing exerts a strong effect on M-luminescence which is of opposite character as compared to the case of an imperfect crystal (figure 3).
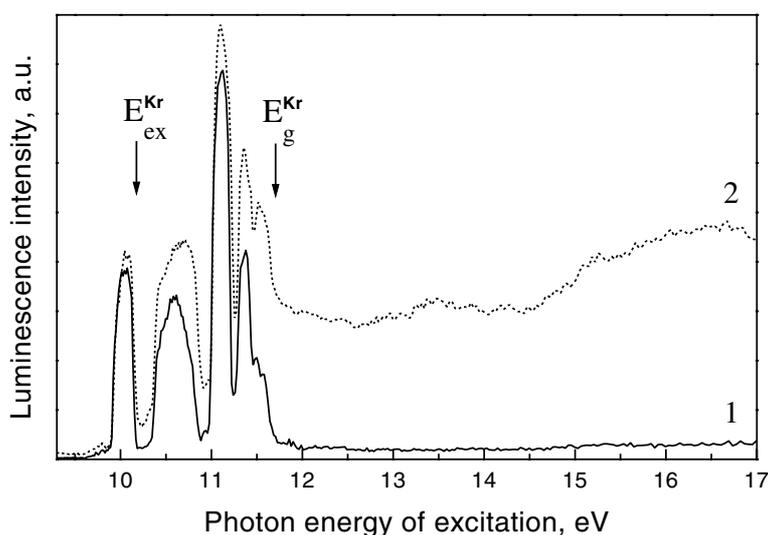
Figure 4. M-luminescence excitation spectra of solid Kr with 0.005% Xe impurity recorded at $T = 5$ K before (curve 1) and after (curve 2) long-time annealing at 40 K.

This striking difference is due to the difference in nature of the exciton localization centres responsible for M-luminescence: in the case of an imperfect crystal, presented in figure 3, localization centres were realized in the form of lattice defects and almost disappeared after annealing; but in the case of a good crystal with localization centres in the form of atomic xenon impurity (figure 4), their number was not influenced by annealing (luminescence spectra provide evidence that the number of Xe_2 molecules, formed due to xenon diffusion, is small compared to the number of xenon atoms). Thus, contrary to the case for an imperfect crystal (figure 3), M-luminescence need not diminish after annealing.

The strong enhancement of M-luminescence due to annealing, demonstrated by figure 4, should be assigned to the suppression of competing channels. Annealing essentially reduces the number of electron traps and, hence, the number of stable R_2^+-centres acting as transforming exciton traps and responsible for H-luminescence (see figure 3(b)). For the reason explained in section 4.2, this effect manifests itself most strongly in the excitation energy region above E_g ($E_g^{Kr} = 11.61$ eV).

It can be assumed that annealing also suppresses the third channel: the thermal diffusion of uncontrollable impurity molecules can result in their coagulation or in exit to the surface. Light small molecules (such as CO, NO, O_2 or N_2) have a much greater diffusion coefficient

than heavy xenon atoms and can coagulate much more strongly.

Thus, xenon impurity atoms act as exciton localization centres, competing with transforming traps, and their influence on M-luminescence (but not the behaviour under annealing) is similar to that of another type of localization centre—lattice defects.

7. Summary

There are exciton traps of two types:

 (1) centres of exciton localization followed by their emission (M-luminescence) from the same electronic state, somewhat modified by two-site self-trapping, and
 (2) centres of exciton trapping followed by transforming to quite another electronic state (in particular, to an excited state of a molecular ion).

A strong competition between localization centres and transforming traps takes place under excitation with energy $E > E_g$. In this case the competition can suppress either localization or transforming centres depending on the set of lattice defects (including stable R_2^+-centres conditioned by electron traps) and impurities.

But under excitation with energy $E < E_g$ the competition is much more favourable to localization centres and M-luminescence, which makes a strong impact on the luminescence excitation spectrum.

Such character of the excitation spectra is explained making allowance for the mixing of FE with polaronic states—excimer quasi-molecules R_2^*. This mixing is of significance only in the lower part of the exciton band. An exciton, if generated by a photon with energy $E < E_g$, relaxes in a free state down to the lower part of the band where there is a polaronic admixture and it can be captured by any traps. But in this part of the exciton band, transforming centres have a small trapping cross section and cannot compete with localization centres. In contrast, under excitation with energy $E > E_g$, an exciton gets to a polaronic state just below E_g where it can be captured either by transforming centres (with a large trapping cross section) or by localization centres—small defects (due to their large numbers).

Thus, luminescence excitation spectra can be used as a probe of competing relaxation channels.

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